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Thermochimica Acta 304/305 (1997) 111–119

thermochimica
acta

Principles for the interpretation of temperature-modulated DSC measurements. Part 2: A thermodynamic approach

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Received 8 August 1996; accepted 21 May 1997

Abstract

At evaluation of TM-DSC (temperature-modulated differential scanning calorimetry) curves using linear response theory we obtain a complex heat capacity, which consists of a real and an imaginary part. It can be shown that C'' is connected to the time-dependent processes. It includes information about the internal entropy change. In the case of phase transitions and chemical reactions, this internal entropy change is related to the change in structure.

For a description of time-dependent processes, a new internal parameter ζ (order parameter) is necessary. ζ is a function of time and describes the kinetics of the system. If the thermodynamic behaviour is known, $\zeta(t)$ can be determined. Phenomenological or molecular models for the order parameter $\zeta(t)$ can be used for a description of measured TM-DSC curves. © 1997 Elsevier Science B.V.

Keywords: Heat capacity ; Kinetics; Polymer melting; Temperature-modulated DSC

1. Introduction

In 1992, a temperature-modulated DSC (TM-DSC) method was introduced by Reading et al. [1–3]. In this type of DSC, the conventional temperature program (linear heating, cooling or isothermal conditions) is superposed by a periodic temperature change:

$$T(t) = T_0 + \beta_0 t + T_a \sin\omega_0 t \tag{1}$$

where T_0 is the initial temperature, β_0 the underlying heating rate, T_a the temperature amplitude and ω_0 the angular frequency ($\omega_0 = 2\pi/t_p$; t_p is the period). The measured heat-flow data are separated into an underlying component (related to the conventional DSC signal) and a periodic component:

$$\Phi(t) = \Phi_u(t) + \Phi_p(t) \tag{2}$$

where the linear part of Eq. (1) yields the underlying component Φ_u, and the sinusoidal term the periodic component Φ_p. In practice, different types of periodic signal forms are used [4].

Different methods of separation in underlying and periodic components are possible [5,6]. Prerequisites for the separation are the linear superposition of both components, a linear sample response to the periodic component as well as a linear measuring instrument. The influence of the underlying component on the periodic component is dependent on the experimental conditions. A suitable choice of the underlying heating rate β_0 is important. If the underlying heating rate is too large, crossover effects occur [4,7]. The linearity

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PII S0040-6031(97)00203-7

of the sample response is dependent on the type of the thermal event and the amplitude of the periodic temperature change [4]. The temperature amplitude T_a should be as low as possible.

If the DSC is a linear instrument, there is a linear relationship between the measured signal X_m and the heat-flow rate Φ_s:

$$\Phi_s(t) = \mathbf{A} \circ X_m(t) \tag{3}$$

where **A** is a linear operator. (In the simplest case **A** is a constant calibration factor.)

The linearity of conventional DSC has been demonstrated already [8–11]. The linearity is independent of the type of temperature programme (e.g. isothermal, scanning or modulated). In the case of a first-order phase transition of a pure substance, deviations from linearity occur [12]. However, during a first-order transition, the true temperature amplitude is less than that indicated [13].

If all conditions are optimum, the first harmonic of the periodic heat-flow component reads as follows:

$$\Phi_{p1}(t) = \Phi_a(t)\cos(\omega_0 t - \varphi) \tag{4}$$

where Φ_a is the amplitude of the heat-low rate and φ the phase shift between the heating rate $\beta = \mathrm{d}T/\mathrm{d}t$ and the heat-flow rate Φ_s. Both the phase shift and Φ_a are influenced by the heat transfer [5,14]. After calibration of amplitude and phase [15,16], the complex frequency-dependent heat capacity

$$C(\omega) = C'(\omega) - iC''(\omega) \tag{5}$$

can be calculated from the measured curve. The real part C' describes the component in phase with the heating rate and the imaginary part C'' the component out of phase.

It can be shown that when the imaginary part of the heat capacity (and the phase shift) vanishes, the thermal event can be described in terms of reversible thermodynamics. In this case, the event is time-independent and the system is in equilibrium [17].

If a time-dependent process occurs in the sample then, in general, this causes a non-zero imaginary component of the heat capacity. The fundamental theory for description of such processes is irreversible thermodynamics.

At sufficiently small perturbations, the linear response theory is the tool for a description of the time-dependent sample response [18]. In this case, the behaviour of the sample is described by a generalised compliance. For a frequency-dependent experiment, the generalised compliance is a complex characteristic, as in Eq. (5). The use of the complex heat capacity $C(\omega)$ for a description of thermal processes is common. One of the first application of $C(\omega)$ is the description of the dispersion of ultrasonic waves [19]. The complex heat capacity can be measured by the so-called 3ω-method in a wide frequency range [20–22]. It is shown that the linear response theory is a useful approach for time-dependent thermal processes [23,24]. As an application of this idea, we discuss the thermodynamics of different time-dependent processes measured by TM-DSC in this paper.

Attention is directed to the complex specific heat capacity. In the discussion of the TM-DSC curves, we have to distinguish between different cases which differ relative to their closeness to equilibrium. Here, we will focus on processes close to equilibrium. Nevertheless, an outlook to non-linear effects is given.

The fundamental extension of the thermodynamics for time-dependent processes is done with the introduction of an additional time-dependent internal variable ζ. The influence of this variable on the measured properties is shown elsewhere [25].

2. Thermodynamic basis for description of TM-DSC results

2.1. The complex heat capacity

If the system is not in equilibrium, an additional variable ζ must be introduced to quantify the respective internal degrees of freedom. ζ is a time-dependent function. In this case, the total differential of the entropy for isobaric conditions reads

$$dS = \left(\frac{\partial S}{\partial T}\right)_{p,\zeta} \mathrm{d}T \left(\frac{\partial S}{\partial \zeta}\right)_{p,T} \mathrm{d}\zeta \tag{6}$$

In other words, all other variables are assumed to be constant. Then the generalised isobaric heat capacity can be defined as [17]

$$C(T,\zeta(t)) \equiv T\left(\frac{\mathrm{d}S(T,\zeta)}{\mathrm{d}T}\right) = T\left(\frac{\partial S}{\partial T}\right)_{p,\zeta} + T\left(\frac{\partial S}{\partial \zeta}\right)_{p,T} \frac{\mathrm{d}\zeta(t)}{\mathrm{d}T} \tag{7}$$

The first term represents the static part C_{st}, and the second the dynamic (time-dependent) part $C_{dyn}(t)$ of the heat capacity, respectively:

$$C(t) = C_{st} + C_{dyn}(t) \tag{8}$$

C_{st} is determined by the fast modes of the molecular motions (which are always in equilibrium), and C_{dyn} is due to all internal degrees of freedom with a distinct time dependence during the experiment.

However, if the heat capacity is time dependent, so is the entropy of the sample. The reason for this is an internal 'structural change' of the sample. The sample needs time to absorb the heat needed by all internal degrees of freedom. The characteristic time is dependent on the molecular processes in question. If the time-dependent process is not far from equilibrium, the entropy relaxation can be written in terms of the linear response theory as a convolution product:

$$\Delta S(t) = \frac{C_{st}}{T}\Delta T(t) + \int_{-\infty}^{t} \psi(t-t')\Delta T(t')\mathrm{d}t' \tag{9}$$

where $\Delta T(t)$ is a small, time-dependent, temperature change and $\psi(t)$ the retardation function. Fourier transform yields an equation for a frequency-dependent experiment

$$\Delta S(\omega) = \frac{C_{st}}{T}\Delta T(\omega) + \psi(\omega)\Delta T(\omega) \tag{10}$$

where

$$\psi(\omega) = \int_{0}^{t} \psi(t)\exp(-i\omega t)\mathrm{d}t \tag{11}$$

A comparison of Eq. (10) with Eqs. (6) and (7) shows that $\psi(\omega)$ contains the heat capacity:

$$\psi(\omega) = \frac{C_{dyn}(\omega)}{T} \tag{12a}$$

Eq. (9) yields the correspondence between the time-dependent retardation and the dynamic part of the heat capacity:

$$\psi(t) = \frac{\dot{C}_{dyn}(t)}{T} \tag{12b}$$

Therefore, the entropy change reads as follows:

$$\Delta S(t) = \frac{C_{st}}{T}\Delta T(t) + \int_{-\infty}^{t} \frac{\dot{C}_{dyn}(t-t')}{T}\Delta T(t')\mathrm{d}t' \tag{13}$$

In the sense of this equation C/T is the 'entropy compliance' [26], similar to the permittivity ε in a dielectric experiment. Eq. (13) is only valid if ΔT is not larger than the order of magnitude of the characteristic temperature fluctuation δT of the related modes.

If $\Delta T(t)$ is a small temperature step at the moment $t_0 = 0$

$$\Delta T(t) = \Delta T\Theta(t-t_0) \tag{14}$$

(where Θ is the step function) and Eq. (13) reads

$$\Delta S(t) = \left(C_{st} + C_{dyn}(t)\right)\frac{\Delta T}{T} \tag{15}$$

Comparing Eqs. (7) and (15) yields:

$$\Delta\zeta(t) = C_{dyn}(t)\frac{\Delta T}{T\left(\frac{\partial T}{\partial \zeta}\right)_{p,T}} \tag{16}$$

The connection between the dynamic part of the heat capacity and ζ is given by

$$\dot{\zeta}(t) \propto \dot{C}_{dyn}(t) \tag{17}$$

In case of TM-DSC measurements, the frequency-dependent heat capacity $C(\omega)$ is measured. Eqs. (12a) and (12b) leads to the connection between $C(\omega)$ and the time-dependent heat capacity $C(t)$:

$$\begin{aligned} C(\omega) &\equiv C_{st} + \int_{0}^{\infty} \dot{C}_{dyn}(t)e^{-i\omega t}\mathrm{d}t = C'(\omega) - iC''(\omega) \\ &= C_{st} + C'_{dyn}(\omega) - iC''_{dyn}(\omega) \end{aligned} \tag{18}$$

In analogy, the frequency dependence of ζ is:

$$\zeta(\omega) = \int_{0}^{\infty} \dot{\zeta}(t)e^{-\omega t}\mathrm{d}t \tag{19}$$

From Eqs. (6),(8) and (13), and subsequent differentiation, it follows:

$$\left(\frac{\partial S}{\partial \zeta}\right)_{p,T}\dot{\zeta}(t)=\frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{\infty}\frac{\dot{C}_{dyn}(t-t')}{T}\Delta T(t')\mathrm{d}t' \tag{20}$$

The Fourier transform of Eq. (20) is given by

$$\left(\frac{\partial S}{\partial \zeta}\right)_{p,T}\zeta(\omega)=C_{dyn}(\omega)\frac{i\omega\Delta T(\omega)}{T} \tag{21}$$

If we, for instance, choose $\Delta T(t)$ as a step function (Eq. (14)), we get the same relationship between ζ and C, as in Eq. (16):

$$\zeta(\omega)=C_{dyn}(\omega)\frac{\Delta T}{T\left(\frac{\partial S}{\partial \zeta}\right)_{p,T}} \tag{22}$$

As a result, the time-dependent function ζ is proportional to the dynamic part of the heat capacity in this linear case.

2.2. *Processes close to equilibrium (e.g. relaxation)*

In analogy to Eq. (6), the total differential of the Gibbs free enthalpy G reads:

$$\mathrm{d}G=\left(\frac{\partial G}{\partial T}\right)_{p,\zeta}\mathrm{d}T+\left(\frac{\partial G}{\partial P}\right)_{T,\zeta}\mathrm{d}p+\left(\frac{\partial G}{\partial \zeta}\right)_{p,T}\mathrm{d}\zeta(t) \tag{23}$$

By using of the definition of G

$$G=H-TS \tag{24}$$

Eq. (23) yields [27]:

$$\mathrm{d}G=S\mathrm{d}T+V\mathrm{d}p-A\mathrm{d}\zeta \tag{25}$$

where A is the affinity, hence

$$\left(\frac{\partial G}{\partial \zeta}\right)_{p,T}=-A \tag{26}$$

The connection between the generalised flow rates and forces is given by dynamic relationships. In this case, the generalised force is A/T and the generalised flow rates $\mathrm{d}\zeta/dt$. The phenomenological kinetic equation reads, in linear approximation [27], as follows:

$$\frac{\mathrm{d}\zeta}{\mathrm{d}t}=\frac{L}{T}A \tag{27}$$

where L is a phenomenological coefficient.

In general, the affinity depends on the distance from equilibrium, which may be expressed by a Taylor series around the equilibrium value $\zeta_e=0$:

$$\begin{aligned}A&=\left(\frac{\partial A}{\partial \zeta_e}\right)\zeta+\frac{1}{2}\left(\frac{\partial^2 A}{\partial \zeta^2}\right)_e\zeta^2+\dots\\&=-\left(\frac{\partial^2 G}{\partial^2 \zeta}\right)_e\zeta-\frac{1}{2}\left(\frac{\partial^3 G}{\partial \zeta^3}\right)_e\zeta^2-\dots\end{aligned} \tag{28}$$

At equilibrium, the values of A and ζ are zero. When sufficiently close to equilibrium, we can restrict ourselves to the first non-zero term in Eq. (28) only. Inserting Eq. (28) into Eq. (26) yields:

$$\frac{\mathrm{d}\zeta}{\mathrm{d}t}-\frac{L}{T}\left(\frac{\partial^2 G}{\partial \zeta^2}\right)_e\zeta=0 \tag{29}$$

The solution of this differential equation is:

$$\zeta(t)=\zeta_0 e^{-t/\tau} \tag{30}$$

with the relaxation time τ given by:

$$\tau=\frac{T}{L\left(\frac{\partial^2 G}{\partial \zeta^2}\right)_e} \tag{31}$$

The response of the heat capacity on a temperature step, in this case, is given by:

$$C(t)=\Delta C(1-e^{-t/\tau})+C_{st} \tag{32}$$

The frequency-dependent complex heat capacity for such simple relaxation is

$$C'(\omega)=C_{st}+\frac{\Delta C}{1+\omega^2\tau^2} \tag{33}$$

and

$$C''(\omega)=\Delta C\frac{\omega\tau}{1+\omega^2\tau^2} \tag{34}$$

Within the relaxation region, the real part C' shows a step and the imaginary part C'' a peak as function of frequency. The peak maximum of C'' corresponds to the inflection point of C'. The temperature dependence of $C(\omega)$ is given by temperature dependence of the relaxation time τ.

One example for such a relaxation process is the glass transition. However, for a correct description of a real glass transition, one single relaxation time is not sufficient because the real relaxation process is broader, as follows from Eqs. (33) and (34).

Therefore, a distribution of relaxation times should be used for description. For a detailed description of measured curves in the glass-transition region, see Ref. [28].

2.3. *Affinity and linearity*

From the second law of thermodynamics, we get information about the reversibility or irreversibility of processes:

$$\mathrm{d}S \geq \frac{\delta Q}{T} \tag{35}$$

The right-hand side of this relation is determined by the heat exchanged. The equality sign is true for reversible processes only. In the case of irreversibility, the entropy change is larger than the exchanged heat δQ suggests. The difference is defined as the internal entropy change $\mathrm{d}S_i$ of the system. For irreversible processes Eq. (35) may be written as:

$$\mathrm{d}S = \mathrm{d}S_i + \mathrm{d}S_e \tag{36}$$

Thus, $\mathrm{d}S_e$ denotes the entropy exchanged with heat, and $\mathrm{d}S_i$ the additional entropy change inside the system.

The connection between the internal time dependent variable ζ and the entropy production is [27]:

$$\frac{\mathrm{d}S_i}{\mathrm{d}t} = \frac{A}{T}\frac{\mathrm{d}\zeta}{\mathrm{d}t} \tag{37}$$

The affinity may be expressed as a Taylor series around the starting value A_0 at $t = 0$:

$$A = A_0 + \left(\frac{\partial A}{\partial \zeta}\right)_{t=0} (\zeta - \zeta_0) + \frac{1}{2}\left(\frac{\partial^2 A}{\partial \zeta^2}\right)_{t=0} \times (\zeta - \zeta_0)^2 + \ldots \tag{38}$$

Close to equilibrium, only the constant term A_0 is relevant. A constant affinity is, however, a prerequisite for the validity of the principle of superposition of linear response theory. This is a fundamental condition for all commercially applied evaluation methods of TM-DSC data.

Increasing the distance from equilibrium changes Eq. (37) to:

$$\frac{\mathrm{d}S_\mathrm{i}}{\mathrm{d}t} = \frac{A_0}{T} + \frac{\mathrm{d}\zeta}{\mathrm{d}t} + \left(\frac{\partial A}{\partial \zeta}\right)_{t=0} \frac{\zeta - \zeta_0}{T}\frac{\mathrm{d}\zeta}{\mathrm{d}t} \tag{39}$$

The second term on the right-hand side of Eq. (39) produces higher harmonics in the measured curves. Eq. (35) shows that $\mathrm{d}S_i$ and $\mathrm{d}\zeta$ are proportional in the linear case. If the distance to equilibrium increases, higher harmonics occur and this simple linear relation between $\mathrm{d}S_i$ and $\zeta(t)$ is not valid. In such cases we lose information about the process if we use linear evaluation procedures. For the practice of TM-DSC, the conditions of linearity are dependent on the thermal process in question.

3. Heat capacity and internal entropy change

The exchanged entropy is connected to the measured heat

$$\mathrm{d}S_e = \frac{\delta Q}{T} \tag{40}$$

From Eqs. (36),(37) and (40) for the entropy change it follows:

$$\mathrm{d}S = \frac{\delta Q}{T} + \frac{A}{T}\mathrm{d}\zeta \tag{41}$$

The time derivative yields the rate of entropy change as the sum of the entropy flow and the entropy production:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\Phi}{T} + \frac{A}{T}\frac{\mathrm{d}\zeta}{\mathrm{d}t} \tag{42}$$

Let us look at a step experiment (Fig. 1). At the time $t = t_0$, the temperature changes by a small temperature step (Eq. (14)). As response on the ΔT-step the entropy also changes stepwise by ΔS. But only a part of ΔS is entropy exchange ΔS_e. The other is an internal entropy change ΔS_i. The entropy exchange $\Delta S_{e,st}$ at t_0 is determined by C_{st}:

$$\Delta S_e(t_0) \equiv \Delta S_{e,st} = \frac{C_{st}}{T}\Delta T \tag{43}$$

The internal entropy change is maximised at this moment. Because the slow internal processes cannot absorb all energy at this moment, ΔS_e increases and ΔS_i decreases in time. After all, as $t \longrightarrow \infty$, ΔS_i is zero and all entropy is exchanged. The sample is in equilibrium then. During the experiment ΔS is constant. From Eq. (36), it follows that the connection between

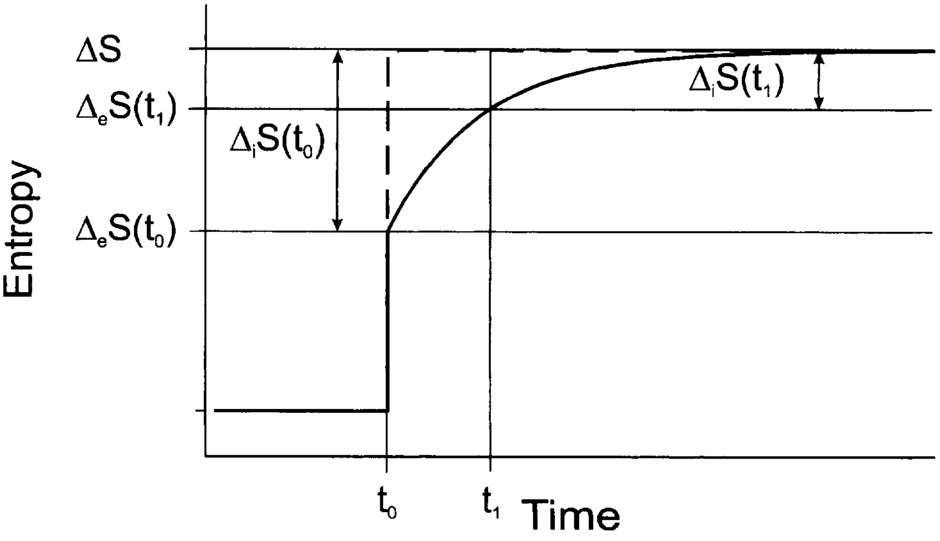

Fig. 1. Scheme of relaxation of the entropy after a temperature step at t_0.

entropy flow and entropy production is given by:

$$\frac{dS_e}{dt} = -\frac{dS_i}{dt} \tag{44}$$

For this quasi-isothermal case, the measured heat-flow rate is

$$\Phi(t) = \dot{C}_{dyn}(t)\Delta T \tag{45}$$

Inserting in Eq. (40), and comparing with Eq. (42) yields

$$\dot{C}_{dyn}(t) = -\frac{A}{\Delta T}\dot{\zeta}(t) \tag{46}$$

or

$$\dot{C}_{dyn}(t) = -\frac{T}{\Delta T}\frac{dS_i}{dt} \tag{47}$$

Both Eqs. (46) and (47) show the connection of the dynamic part of heat capacity with the internal variable ζ and the internal entropy change, respectively. C_{dyn} describes the change of ΔS_i in time, which is due to a temperature step ΔT (i.e. $\Delta S_i(t_0) - \Delta S_i(t)$) but not the absolute amount of it.

In case of TM-DSC periodic signals are used. Let us first discuss the entropy change during one period of modulation of TM-DSC. In order to simplify, we discuss the quasi-isothermal case (underlying heating rate $\beta_0 = 0$). During one period of temperature modulation the sample follows a cyclic process. If the system is in the steady state we come to the same state after each period. The entropy exchange for one period, ΔS_{period}, reads:

$$\Delta S_{period} = \int\limits_{t-t_p/2}^{t+t_p/2} \frac{1}{T(t')}\frac{\delta Q(t')}{dt'}dt' = \int\limits_{t-t_p/2}^{t+t_p/2} \frac{\Phi(t')}{T(t')}dt' \tag{48}$$

where t_p is the period and $\Phi(t)$ the heat-flow rate, respectively.

In the linear case, at a certain ω_0, the heat-flow rate into the sample is [17]:

$$\begin{aligned}\Phi(t) &= \omega_0 T_a |C| \cos(\omega_0 t - \varphi) \\ &= \omega_0 T_a C' \cos\omega_0 t + \omega_0 T_a C'' \sin\omega_0 t\end{aligned} \tag{49}$$

Thus, from Eq. (48), we obtain

$$\begin{aligned}\Delta S_{period} = &\int\limits_{t-t_p/2}^{t+t_p/2} \frac{\omega_0 T_a C' \cos(\omega_0 t')}{T_0 + T_a \sin(\omega_0 t')}dt' \\ &+ \int\limits_{t-t_p/2}^{t+t_p/2} \frac{\omega_0 T_a C'' \sin(\omega_0 t')}{T_0 + T_a \sin(\omega_0 t')}dt' \\ &= 0 + 2\pi C'' - \omega_0 T_0 C''\end{aligned}$$

$$\times \int_{t-t_p/2}^{t+t_p/2} \frac{dt'}{T_0 + T_a \sin(\omega_0 t')}$$

$$= 0 + 2\pi C'' \left(1 - \frac{T_0}{\sqrt{T_0^2 - T_a^2}}\right) \tag{50}$$

The term in brackets may be expressed as a series (because $T_0 \gg T_a$):

$$\frac{T_0}{\sqrt{T_0^2 + T_a^2}} = 1 + \frac{1}{2}\left(\frac{T_a}{T_0}\right)^2 + \frac{3}{8}\left(\frac{T_a}{T_0}\right)^2 + \dots \tag{51}$$

The first term in Eq. (50) (which always is zero) contains the real part of heat capacity and, thus, that part of exchanged heat which is in phase with the temperature change.

The second term in Eq. (50) is connected to the imaginary part C''

$$\Delta S_{period} = 2\pi C'' \left(1 - \frac{T_0}{\sqrt{T_0^2 + T_a^2}}\right) \approx -\pi C'' \left(\frac{T_a}{T_0}\right)^2 \tag{52}$$

The entropy of the surroundings increases by this small value during each period. The sample remains in the same state after one cycle. Therefore, the sample and surroundings exchange the entropy ΔS_{period}.

From this it follows that the measured properties $C_{dyn}(t)$ and $C(\omega)$ describe the linear internal entropy change in the sample during the time-dependent processes. To get the complete information of the linear time-dependent process, a large frequency or time range must be measured. In case of TM-DSC, this frequency range is limited to two decades. This restriction can be expanded particularly by a changing T_0.

4. A simple model for the entropy change during relaxation processes

For relaxation processes, a step change of C' is connected to a small peak in C'' (see Eqs. (33) and (34)). In this section we will present a simple model for interpretation of this C''.

The dynamic response in a sample is determined by the different types of modes of the molecular motions. To every type of mode a characteristic time τ can be assigned. For instance, a simple liquid is characterised by two different classes of molecular motions whose characteristic relaxation times differ by several orders of magnitude. The elemental motions (i.e. vibrations, rotations, etc.) are very fast. In contrast, the cooperative motions (typical for a liquid) are relatively slow.

Within the framework of this model, the sample may be considered to be divided into different subsystems. The energy exchange between the subsystems is small compared to the total content of energy of these subsystems. The cooperative movements should be characterised by only one characteristic time (or frequency f_i). In other words, one subsystem represents the cooperative movement and the rest is considered to be the thermal bath (the surroundings) with respect to this subsystem. This model is shown in Fig. 2. The energy transfer between the subsystem and the thermal bath may be expressed by the time dependence of the internal parameter ζ. The thermal bath represents the static part of the heat capacity C_{st}. The energy transfer between the surroundings and the thermal bath is more rapid compared with the experimental time.

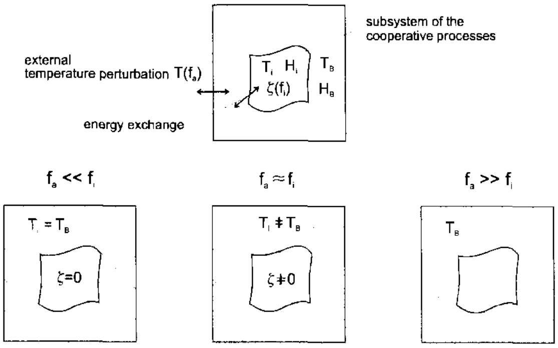

Fig. 2. Illustration of the behaviour of cooperative modes of the molecular motions in a liquid for different external perturbations (f_a – frequency of the external temperature change; f_i – characteristic frequency of the cooperative mode; T – external temperature; T_B – temperature of the thermal bath; T_i – temperature of the subsystem of the cooperative movements; H_B – enthalpy of the thermal bath; and H_i – enthalpy of the subsystem).

If we have an external temperature change with a frequency f_a which is much lower than f_i, the energy transfer between the thermal bath and the related subsystem takes place immediately and this subsystem contributes an 'additional' heat capacity ΔC ($C = C_{st} + \Delta C$) to the system in equilibrium ($\mathrm{d}S_i = 0$).

At the relatively high frequency of the external temperature change ($f_\mathrm{a} \gg f_\mathrm{i}$), an energy exchange between the thermal bath and the corresponding subsystem is impossible, because the time of change in ζ is too large compared with the internal relaxation time. In this case, the system has the same behaviour as a system without this subsystem. For the experimenter, this subsystem seems not to exist in the experiment. The measured heat capacity is lower accordingly ($C = C_{st}$).

If $f_i \approx f_a$, an energy transfer from the thermal bath into the subsystem is possible, but the time is not large enough for the subsystem to obtain the same temperature as the thermal bath. In this case the temperatures of the subsystems differ, and the temperature distribution is not homogeneous within the total system. In this case, the effective heat capacity depends on the energy that this subsystem can absorb, and the internal entropy change $\mathrm{d}S_\mathrm{i}$ is connected to the internal temperature differences.

This simple model describes the heat capacity curves for a glass transition measured by TM-DSC. The relationship between the internal frequencies (determined by the relaxation time of the cooperative modes) and the external frequencies is caused by the temperature dependence of the characteristic time of the subsystem that characterises the cooperative movements. The corresponding internal frequency decreases with decreasing temperature. At relatively high temperatures, the internal frequency decreases with decreasing temperature. At relatively high temperatures, the internal frequency is high and all subsystems contribute to the heat capacity C'. The sample is in equilibrium and C'' disappears. With decreasing temperature the frequencies approach one another. Internal gradients arise and C' decreases. In this range C'' is greater that zero. If the temperature decreases still further, the corresponding subsystem has hardly any influence on the dynamic behaviour of the sample. The cooperativity is frozen, C' characterises only the thermal bath of fast motions, and C'' disappears again.

5. Conclusions

One of the problems of the TM-DSC experiments and its interpretation is the information deduced from the frequency-dependent complex heat capacity $C(\omega)$. It is shown that $C(\omega)$ can be described using a time-dependent variable ζ. $C(\omega)$ corresponds to the internal entropy change of the sample and includes information about the irreversibility of a process.

Since the evaluation method of the measured data is based on a linear theory, non-linear effects cannot be described exactly. This could be the reason that the imaginary component of the heat capacity is smaller than expected, especially in case of a reaction far from equilibrium.

The knowledge of the time-dependent internal variable ζ allows the description of the measured curves. This is shown for polymer melting in Ref. [25].

Acknowledgements

The author gratefully acknowledges discussions with E. Bergmann (IFA GmbH Ulm) and G.W.H. Höhne (Universität Ulm), and the support of the Perkin–Elmer Corporation.

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