



ELSEVIER

Thermochemica Acta 282/283 (1996) 143–155

thermochemica
acta

Linearity, steady state, and complex heat capacity in modulated differential scanning calorimetry¹

Bernhard Wunderlich*, Andreas Boller, Iwao Okazaki²,
Stefan Kreitmeier³

Department of Chemistry, The University of Tennessee, Knoxville, TN 37996–1600, and Chemistry and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831–6197, USA

Abstract

Modulated differential scanning calorimetry (MDSC) has recently seen a large growth due to the availability of commercial instrumentation. In this paper it will be shown that MDSC based on heat flow presents a linear system as long as the conditions of measurement are carefully controlled. It will further be proven that for typical MDSC, a steady state can be maintained for heat capacity increases many times the typical increase of heat capacity with temperature. This permits not only measurement of heat capacity with continuous increase of temperature, but also the testing of glass transition regions and shallow endotherms as seen at the beginning of melting for nonreversible components. Finally, it will be shown that it may be possible to use a complex heat capacity for the description of the glass transition, but that the imaginary part of the heat capacity seems not to refer to any meaningful quantity.

Keywords: Calorimetry; Complex heat capacity; Glass transition; Heat flow calorimeter; Instrument lag; Linear equation; MDSC; Modulated calorimetry

1. Introduction

Differential scanning calorimetry (DSC) was developed in the 1960s when it became possible to extract increasingly more quantitative estimates of heats of transitions, and

* Corresponding author.

¹ Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

² On leave from the Toray Industries, Inc., Otsu, Shiga 520, Japan.

³ Present Address: University at Regensburg, Polymerphysik, Regensburg, D-93040, Germany.

finally also heat capacities, from experiments in differential thermal analysis (DTA) [1]. One of the first steps towards calorimetry based on DTA was made by Ozawa [2] through a quantitative discussion of the effect of thermal conductivity, heat capacity, and enthalpy changes on the measured temperature difference ΔT . The argument goes as follows: If there is a temperature difference within a material, heat Q will flow from an area of higher to that of lower temperature according to the following equation (Fourier's law of the flow of heat)

$$\vec{u} = -\kappa \text{grad } T = -\kappa \nabla T \quad (1)$$

with \vec{u} representing the heat flow vector in $\text{Jm}^{-2}\text{s}^{-1}$, κ the thermal conductivity in $\text{Jm}^{-1}\text{K}^{-1}\text{s}^{-1}$, and ∇T the temperature gradient $\partial T/\partial r$. The net rate of flow out of any volume V , bounded by the closed surface S is then given by the integral of the normal component u_n of \vec{u} at the surface over the complete surface S

$$\int u_n dS = \int \text{div } \vec{u} dV \quad (2)$$

with $\text{div } \vec{u}$ representing the scalar product of ∇ with \vec{u} . Such scalar heat flow $\partial Q/\partial t$ per unit volume can also be written in terms of the temperature rise

$$\partial Q/\partial t = \rho c_p \partial T/\partial t \quad (3)$$

where ρ is the density in kgm^{-3} and c_p the specific heat capacity in $\text{JK}^{-1}\text{g}^{-1}$. Eqs. (1)–(3) hold for any region in space and can be combined and integrated to give the Fourier equation

$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho c_p} \text{div grad } T = k \nabla^2 T \quad (4)$$

where k is the thermal diffusivity in m^2s^{-1} and ∇^2 the Laplacian operator. Since the Fourier equation is a linear and homogeneous differential equation, the initial approach in DTA from a nonequilibrium temperature distribution to steady state, and any subsequent transients, can be evaluated independently and then combined for the overall solution of the heat flow problem, *i.e.* the heat flow in a calorimeter is basically linear⁴. Based on Eq. (4) it became possible to describe quantitatively any DTA of simple geometry (usually cylindrical) [3]. Not only was it possible to describe the thermodynamic variables, the kinetics of the glass transition was also quantitatively described, using the simple hole theory derived by Hirai and Eyring [4], which is also based on a linear differential equation, keeping the overall system linear [5].

By introducing the condition of negligible temperature gradient within the sample, the thermal conductivity in the Fourier equation could be assigned to the instrument and made accessible to simple calibration. This permitted direct calorimetry by DTA, now commonly called DSC. Two major classes of instruments were developed commercially, heat-flux-based and power-compensation-based DSCs. For the heat-

⁴ The linked quantities of a linear system are related by linear differential equations. Such equations and, therefore, such systems obey the principle of superposition, namely, the combined effect of a number of causes acting together is the sum of the effects of the causes acting separately.

flux-based calorimeter, the heat-flow equations are again based exclusively on the Fourier equation and the now much simpler mathematical description was developed based on the initial work by Müller and Martin [6]. Even the melting under ideal conditions (one-component, close-to-equilibrium melting) could be shown to be describable by a superposition of heat-flow segments (baseline method), keeping the overall system linear [3]. For the power-compensated DSC as first described by O'Neil and coworkers [7], difficulties arose in keeping the power response on melting linear [8]. As was pointed out recently by Ozawa [9], this does not, however, affect the overall calorimetric response (heat of transition) and special methods to desmear non-linear response curves have been developed [10]. Similarly, in the heat-flow calorimeters, deviations from linearity may come about because of electronic baseline corrections and other non-linear data handling after the initial measurement.

The most recent development added a periodic modulation to DSC. For the heat-flux calorimeter this method was developed by Reading [11]. A transparent mathematical description of this MDSC was published by us earlier [12] with the help of information supplied by the manufacturer [13]. Particularly for the measurement of heat capacity, a quasi-isothermal measurement technique could be developed that can lead to heat capacity measurement by modulation about a constant temperature [14]. As experience on MDSC is accumulating, it becomes obvious that more stringent conditions about the linearity of the calorimeter system exist for MDSC. In addition, the accomplishment of a steady state for easy data evaluation is also of greater importance. Finally, the question arises if, since one is making frequency-dependent measurements, it may not be useful to work with complex⁵ heat capacities. These three basic questions for MDSC will be addressed in this paper. At present there is not enough detailed information on the power-compensated dynamic DSC (DDSC) to analyze this system in the same manner [15]. One must observe, however, that in standard DSC the two types of instruments could be made to behave similarly [16]. With the added feature of modulation, the differences may become more obvious and progress towards better calorimetry may evolve by testing various instrumentation, modulation, and deconvolution methods [17].

2. Linearity of transitions

The main condition of measurement with DSC was stated in the Introduction to be the maintenance of a negligible temperature gradient within the sample. Under such conditions the Fourier equation of heat flow gives a simple description of the heat flow in the calorimeter. If, in addition, steady state is maintained throughout the measurement, the modulation of the calorimeter is a function of the heat capacity only, *i.e.* it is independent of the thermal conductivity (see Eq. (4)). The procedures needed to check

⁵ A complex number $a + ib$ is a pair of real numbers (a, b) with addition and multiplications defined as $(a, b) + (c, d) = (a + c, b + d)$ and $(a, b) \times (c, d) = (ac - bd, ad + bc)$. The real numbers a and b are called the *real* and *imaginary* parts of the complex number (a, b) . The terms real and imaginary are historical accidents since both a and b are real numbers and complex numbers are often useful to describe *real* phenomena. (Since $(0, 1) \times (0, 1) = (-1, 0)$ it is obvious that $i \equiv (-1)^{1/2}$).

these conditions for MDSC experiments was given in Ref. [14]. It was already pointed out in the Introduction that as long as the Fourier heat-flow equation can be used for the description of the experiment, the system is linear. Steady state, however, is not a condition for linearity since, given the necessary parameters (thermal conductivity and geometry), a linear differential equation can be written that describes the system, although this equation may not be easy to solve.

Adding the occurrence of a transition in the sample, there is a further kinetic term to be considered that may or may not be linear. Using classical irreversible thermodynamics for the description of the kinetics of the transition, a linear solution is possible, at least close to equilibrium.

The resulting linear rate equation is based on the assumption that the driving force for transitions is proportional to the change in free enthalpy [18]. The question of the linearity of the transitions is thus one of how far from equilibrium is the sample during the analysis and over how large a range from equilibrium is the first-order approximation applicable.

Many first-order melting and disordering transitions are exceedingly fast, so that their kinetics can be neglected [19]. Equilibrium is attained as soon as thermal conductivity has established the new temperature. The computation is particularly simple if one can assume that the transition leads to a fixed temperature of the sample during the transition. Under these conditions, the solution is linear for the heat flux calorimeter and commonly used under the name “baseline method.” A full description and derivation of the linear equations is given, for example in Section 4.4.2 of Ref. [1]. For more than one component in the sample, broader melting ranges are possible. These must then be treated by superposition of the distribution of melting peaks.

Transitions with low enthalpy gains may even keep steady state throughout the change. In this case the transition can be extracted from an apparent heat capacity by subtracting the appropriate baseline of the known transition-free heat capacity, which is available, for example, through the ATHAS Data Bank [20]. In all these cases linearity is preserved and standard scanning calorimetry can give quantitative information. The conditions must also be kept on introduction of modulation.

A quite different behavior is observed on crystallization, recrystallization, annealing, and crystal perfection. These processes occur usually *via* nonequilibrium paths far from equilibrium and are not linear [19, 21]. If they are sufficiently fast, they may not be modulated at all and are observed as completely nonreversing phenomena. If they can be modulated, they are still most likely nonlinear and a quantitative analysis may not be possible although the total heat effect is always linear, as shown by Ozawa [9]. A typical example is the Avrami description of nucleation and growth under consideration of crystal impingement [21]. The kinetics of this process is described by a double-exponential, nonlinear differential equation. The best solution for the quantitative analysis of such processes is isothermal calorimetry without modulation. Similarly, the melting kinetics of macromolecules may sometimes show superheating [19, 22] and is then sufficiently slow to interfere with the MDSC.

Combining melting with crystallization, recrystallization, etc. presents, naturally, the greatest challenge to modulated DSC. By choosing judiciously the modulation and

underlying heat flow, it is possible, at least qualitatively, to separate equilibrium (or zero-entropy-production) processes from nonequilibrium processes. Of particular use in this case is a modulation that reaches zero heating rate at the minimum or maximum of modulation. The equilibrium process should stop at this point (if a steady state is maintained), and any residual heat effect is indicative of an irreversible exothermic or endothermic process.

The theory of the glass transition is still not fully understood. Its kinetics for thermal analysis by dynamic differential thermal analysis (DDTA) was analyzed earlier and shown to be linear over the complete transition range as long as one stays with the simple “hole model” [5]. It was proven recently that a quantitative point-by-point quasi-isothermal MDSC analysis is also possible [23]. One expects much new insight from such analyses, revealing more details about the complexity of the glass transition.

This rather optimistic analysis of the question of linearity contrasts, to some degree with the more pessimistic assessments of Ozawa [9] and also Schawe [24]. It may well be that their more negative outlook is based on experience with the (almost) power-compensation DSC. In such instruments the linearity must be established by design of the electronic circuitry and a more stringent adherence to a symmetric design between sample and reference calorimeter. At least the early versions of the Perkin-Elmer DSC were not linear in the melting range, as pointed out in the Introduction, and special desmearing techniques had to be applied for quantitative analysis in the melting range. New techniques of this type (or improved power compensation) must be developed to make full use of modulation. Once this is accomplished, a faster response time due to the shorter heat diffusion path may be possible. A more detailed discussion of the linearity of power-compensated DSC was given recently [25]. It must be remarked, however, that ultimately even power-compensation DSC depends on negligible temperature gradient within the sample for ease of data evaluation.

3. Discussion of the steady state

In a previous publication steady state was shown to be the basic condition for all calorimetric heat capacity analyses [14]. A knowledge of the quality of the steady state is particularly important as one goes through heat capacity changes, for example, in the glass transition coupled with a hysteresis peak, or in a broad melting peak with a possibility of exothermic recrystallization. In this section, the extent of deviations from the steady state during measurement will be discussed. In its simplest form, the approach to steady state is expressed by the equation [14].

$$T_s(t) - T_0 - \langle q \rangle t = -\langle q \rangle \frac{C_s}{K} (1 - e^{-Kt/C_s}) + A_{T_s} [\sin(\omega t - \varepsilon) + \sin \varepsilon e^{-Kt/C_s}] \quad (5)$$

where $T_s(t)$ is the sample temperature at time t , T_0 the starting temperature of the experiment, $\langle q \rangle$ the underlying, linear heating rate averaged over one modulation period, C_s the sample calorimeter heat capacity (sample plus pan), K the calibration constant (Newton's law constant in $\text{Js}^{-1}\text{K}^{-1}$), A_{T_s} , the amplitude of the sinusoidal modulation (set to a constant value), ω the modulation frequency, and ε the phase lag

relative to the block temperature of the MDSC. Due to the linearity of the differential equation for modulated heat flow, separate solutions for the steady state can be seen for the underlying heating rate and the modulation.

Fig. 1 gives a comparison between MDSC and DSC by a superposition of three standard DSC traces that match the maximum, average (underlying), and minimum heating rates of the MDSC. Not only do the traces match quantitatively, they also show a longer time for reaching steady state on MDSC. The time needed to reach steady state can also be deduced from the Lissajous figures shown in Fig. 2 obtained by plotting the sample temperature *versus* the heat flow (temperature difference). It takes several cycles until the ellipse of steady state is retraced. The Lissajous figure is an important indicator for steady state and plotting it a recommended procedure for any quantitative MDSC experiment.

To get a more quantitative insight into the distance from steady state, the calorimeter with the larger heat capacity is analyzed further. If it reaches a given percentage deviation, set for the present discussion at 5%, steady state is considered either to be gained or lost. The somewhat large error is chosen since for the heat flow HF (or ΔT), both the reference temperature T_r and T_s deviate from steady state and the difference should show a somewhat smaller error. All calculations are carried out with a value of 50 s for C_s/K , a value on the large side for present-day DSC. Typical values for C_s/K may range from 0.1 to 100 s depending on instrument construction and sample heat capacity. The modulation amplitude A_{T_s} is taken to be 1.0 K, and the underlying heating rate $\langle q \rangle = 3.0 \text{ K min}^{-1}$ (0.05 K s^{-1}). Eq. (5) can then be rewritten to express the distance from steady state Λ (in K)

$$\Lambda = T_s(t) - T_0 - \langle q \rangle t + \langle q \rangle \frac{C_s}{K} - A_{T_s} [\sin(\omega t - \varepsilon)] = [\langle q \rangle \frac{C_s}{K} + A_{T_s} \sin \varepsilon] e^{-Kt/C_s} \quad (6)$$

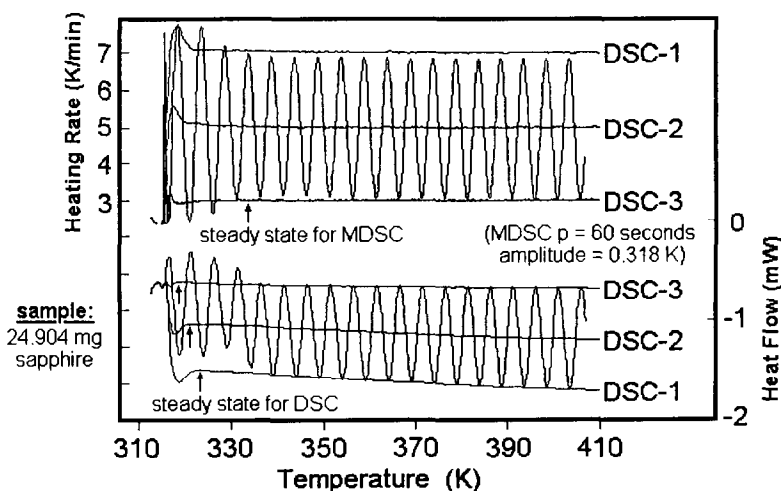


Fig. 1. Comparison of times to attain steady state in DSC and MDSC.

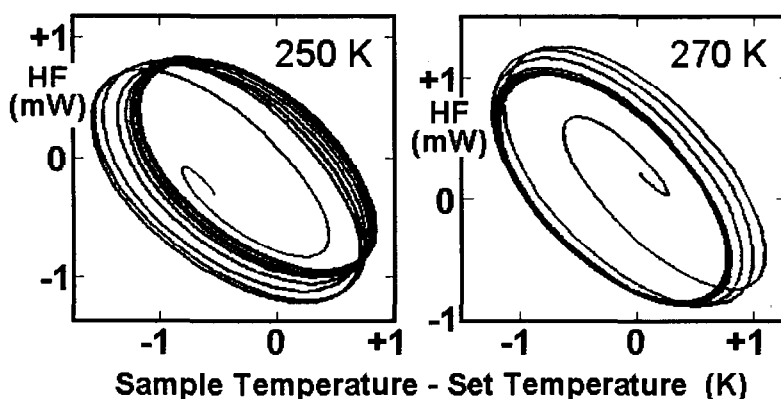


Fig. 2. Analysis of an MDSC run. The heat flow HF is plotted against the modulated sample temperature (24.9 mg of sapphire, period 99 s, modulation amplitude 1.0 K).

With the parameters just given $\Lambda \approx 3 \exp(-t/50)$, and it takes about 160 s to reach the 5% value when starting the measurement from $T_b = T_s = T_r$ (beginning of the experiment, $t = 0$). The approximate steady-state lag of the temperature due to the underlying heating rate is $\langle q \rangle C_s / K = 2.5$ K, *i.e.* it is the dominating effect under the given conditions. For large modulation amplitudes and small values of C_s / K and/or $\langle q \rangle$, the second term may well be more important.

The modulation amplitude in Fig. 1 is sufficiently small so that it should not cause as large an increase in lag as seen. The likely reason for the late beginning of steady state with modulation must be a control problem connected with the setting of a constant A_{T_s} at the sample position and not at the block and should not be of influence later in the experiment.

Any subsequent change in C_s will cause a new deviation from steady state that can be estimated analogously because of the linearity of the heat flux equation. An instantaneous, step-wise increase in heat capacity causes a loss of steady state Λ that dies off with the exponential given by Eq. (6) (note that C_p also enters into ϵ).

A third case of loss of the steady state may be the occurrence of a glass transition over a limited temperature range. For a severe test, data for (hypothetical) amorphous polyethylene are used with an increase in C_p of $10 \text{ J K}^{-1} \text{ mol}^{-1}$ at the glass transition temperature T_g , and an overall heat capacity of the solid of about $20 \text{ J K}^{-1} \text{ mol}^{-1}$. Assuming, furthermore, the glass transition occurs linearly over a temperature range of about 10 K (5% increase in heat capacity per kelvin of temperature increase), the plot given in Fig. 3 can be calculated by stepwise addition of the appropriate multiple terms derived from Eq. (6). The filled squares represent the increase in heat capacity in a lag-free experiment. The computed T_s shows the observed sample temperature, and the difference is the lag. The lag of 3 K in fixing the glass transition temperature is, perhaps, still acceptable for common determinations of the glass transition, but must be considered in discussing the kinetics of the glass transition [23]. The deviation of the heat capacity by more than 10% between 235 and 243 K is, however, not acceptable.

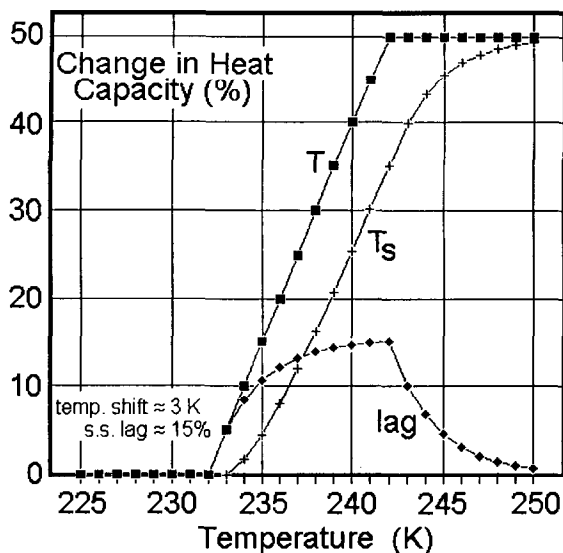


Fig. 3. Lags in MDSC during a simulated glass transition. For parameters and equations, see text.

For the reporting of C_p for the ATHAS Data Bank this error was in the past eliminated by extrapolation of the solid and liquid heat capacities of T_g [20]. For integration of the heat capacities to enthalpy, it was assumed that a vertical increase in ΔC_p occurs at T_g . Comparing the polyethylene case with polystyrene or poly (ethylene terephthalate), two polymers that are often used as standards, one sees changes in heat capacity of 19% and 30% at the glass transition, *i.e.* their lags are closer to the 5% error in heat capacity. Similarly, a reduction in C_s and ε can make heat capacity measurements through the glass transition stay in steady state. For highest precision, two sets of measurement are recommended. One with large C_s for the solid and liquid heat capacities, and one with small C_s in the glass transition region for the study of the kinetics.

A fourth estimate of deviations from steady state is suggested to judge a continuous linear increase in heat capacity with a negligible modulation effect. The deviation from the steady state, Λ , for a continuous increase in heat capacity is given by the integral of the lag equation from time zero to ∞ , with the preexponential factor replaced by the change in C_p (in $\% \text{ K}^{-1}$) $\times \langle q \rangle$ (in K s^{-1})

$$\Lambda = \langle q \rangle \left(\frac{dC_p}{dT} \right) \int_0^{\infty} e^{-kt/C_s} dt = \langle q \rangle \left(\frac{dC_p}{dT} \right) C_s / K \quad (7)$$

From this estimate, one can see that a change in heat capacity of less than $2\% \text{ K}^{-1}$ is within the chosen error limit of 5% ($C_s K = 50 \text{ s}$, $\langle q \rangle = 0.05 \text{ K s}^{-1}$, see also Fig. 3). A typical increase of the heat capacity per kelvin in the solid state is, for example, 0.4% (polystyrene from 200 to 300 K), *i.e.* a considerable amount of premelting or broad transition can be assessed with good accuracy without losing steady state.

Further qualitative interpretation may be possible to levels as high as 25–50% K⁻¹ lag. In addition, a desmearing of the curve shown for the glass transition is possible as long as the condition of negligible temperature gradient within the sample is not violated. Also, one must remember that the heat of transition determined from the total heat flow is correct when using the baseline method [9].

4. Complex heat capacity

The similarity of the description of temperature-modulated DSC and dynamic mechanical analysis (DMA) and also dielectric thermal analysis (DETA) has brought up the question whether a complex heat capacity would be of use in analogy to the modulus (the stress/strain ratio). It was suggested by Schawe that one could write for the complex heat capacity [24]

$$C^* = C' - iC'' = C_0 e^{-i\delta} \quad (8)$$

where C' is the real part or “storage heat capacity,” the instantaneous response to a change in temperature in analogy to the storage modulus, and C'' is the “loss heat capacity” represented by the imaginary, delayed part in analogy to the loss modulus. It follows then that the “modulus of the heat capacity” in analogy to the mechanical modulus (ratio of the peak stress to peak strain) is

$$|C_0| = \sqrt{(C')^2 + (C'')^2} \quad (9)$$

A comparison of the corresponding terms in DMA and DSC is summarized in Fig. 4. In the DMA experiments G is, for example, the shear modulus, σ , the stress, ϵ , the strain, and δ , the phase lag.

The MDSC discussion has established that one must separate two applications of the formalism of complex physical quantities. First, those that represent mainly the *calorimeter response functions*. The complex heat flow is given, for example, by [12]

$$HF_{\cos}(t) = [HF_{\text{mod}}(t) - \langle HF(t) \rangle] \cos \omega t \quad t \leq t_1 \quad [= A_{HF} \sin(\omega t - \delta) \cos \omega t] \quad (10)$$

$$HF_{\sin}(t) = [HF_{\text{mod}}(t) - \langle HF(t) \rangle] \sin \omega t \quad t \leq t_1 \quad [= A_{HF} \sin(\omega t - \delta) \sin \omega t] \quad (11)$$

$$\langle A_{HF}(t_2) \rangle = 2\sqrt{\langle HF_{\sin}(t_2) \rangle^2 + \langle HF_{\cos}(t_2) \rangle^2} \quad (12)$$

where HF indicates the various heat flow amplitudes, $\langle \rangle$ marks averaging of the amplitudes over a full modulation amplitude to separate the modulation effect, and δ is the phase lag of the heat flow. The temperatures are given by analogous equations. The “real” part of the heat flow is the response to the sinusoidal modulation of the block temperature; it is the sinusoidal component of Eq. (11), while the “imaginary” part is

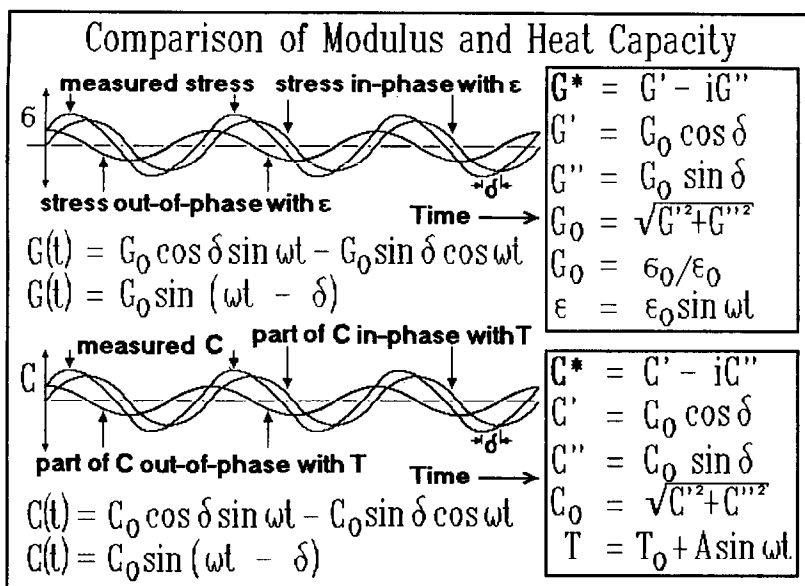


Fig. 4. Comparison of the nomenclature as applied to complex modulus and heat capacity.

given by cosine component of Eq. (10). In the derivation of the basic heat capacity equations, it was shown, furthermore, that using complex notations for heat flow (temperature difference) and temperature simplifies the calculations [12]. In these applications, the definition of complex quantities is mathematically correct and useful, but rather inappropriate when applied to sample properties, since the so-defined quantities are based mainly on instrumental and not materials properties. The storage and loss components are different for every calorimeter and vary even with sample placement. Out of these instrument-specific response functions, the sample-specific averaged and smoothed heat flow and temperature can be derived using Eq. (12) and its analog, *i.e.* only the amplitudes of the phase-shifted quantities have meaning for the calculation of heat capacity (compare to Eq. (9)). This was realized rather early, and although the phase angles have been measured and discussed, they proved for experimental reasons of lesser importance and precision than the phase-shifted amplitudes [11].

The interpretation of a time-dependent heat capacity is different, as seen in the glass transition region [5]. Note, however, that there are only a few other calorimetric effects that are sufficiently reversing in the time scale of the typical present-day calorimeters to be characterized with a complex heat capacity. (None other but the glass transition come to mind on writing this paper!). As pointed out by Schawe [24], it may be advantageous to talk about a complex heat capacity when interpreting the shift in the glass transition with frequency. Before presenting such work, it must first be proven, however, for the calorimeter used (heat-flux or power-compensated) that the instru-

mental response is linear and the lag is within acceptable error limits or has been properly separated from the sample response.

Finally, the meaning of the various heat capacities listed in the figure and the appropriateness of the proposed nomenclature must be scrutinized. First, it must be noted that in order to agree with the prior definition of the temperature lag as a positive number, we write $C' - iC''$ in Eq. (8) instead of the otherwise common $C' + iC''$. The term complex heat capacity for C^* is by its very definition, naturally, appropriate. It must not be confused with the subscript $*$ used in the hole theory to designate equilibrium properties [5]. Modulus, however, is a term strictly taken from the description of mechanical properties as measured, for example, by DMA. It is not appropriate for the description of C_0 in Eq. (9).

For the description of the complex heat capacity in the glass transition region, C_0 is the difference in heat capacity between liquid and glass [5].

$$C_0 = \Delta C_p = C_p(\text{liquid}) - C_{p_0} \quad (13)$$

where $C_p(\text{liquid})$ is the equilibrium heat capacity of the liquid, and C_p the (metastable) equilibrium heat capacity of the solid. The two parts of ΔC_p can be measured in the temperature region of the stable liquid and the metastable glass, respectively, and then extrapolated into the glass transition region. The “apparent heat capacity”, $\Delta C_p^\#$, measured in the glass transition region, is equal to the real part of Eq. (8), $C' = \Delta C_p^\# \cos \delta$, and C'' can be computed ($= \Delta C_p^\# \sin \delta$).

The real and imaginary parts of the heat capacity are linked to “storage” and “loss” enthalpies when integrating the complex heat capacity over the sinusoidally changing temperature of the sample ($T = T_0 + A \sin \omega t$). This is similar to the case of the complex mechanical modulus that can be linked to work W done on and recovered from the sample by integration of the complex stress σ over the sinusoidal strain ε . The energy dissipated over one cycle, $\Delta W''$, is given in the DMA experiment by $-G'' \varepsilon_0^2 \pi$. The integral of $-\Delta C_p^\# \sin \delta \cos \omega t d(A \sin \omega t)$ over one modulation cycle suggests an enthalpy “loss” of $-A \pi \Delta C_p^\# \sin \delta = -A \pi C''$. The in-phase heat capacity gives as much of an increase in enthalpy on heating as a decrease on cooling; thus it corresponds to a “storage” term.

The computation of a loss heat capacity raises the question of where the corresponding amount of heat is seen in calorimetry, *i.e.* how “real” it is. Since heat capacity is not directly measured, but computed from the heat-flow and temperature amplitudes (see Eqs. (10)–(12) and their temperature analogs) [12], only the heat flow corresponding to the apparent heat capacity $C' = C_0 \cos \delta$ is available from the experiment and can be “seen” (and is used for the evaluation of the hole theory parameters in Ref. [23]). The loss part of the complex heat capacity is computed *via* Eq. (9) as $C_0 \sin \delta$. It corresponds to a virtual loss that has occurred because the apparent heat capacity could not increase the enthalpy (hole energy) to the equilibrium value of Eq. (13). While the loss modulus in DMA corresponds to a real loss (work to heat conversion), the loss due to heat capacity does not. This finding diminishes, perhaps, the importance of the discussion of a complex heat capacity outside of its use in simplifying computations.

5. Conclusions

MDSC based on heat flux is basically linear. Provided sufficient care is taken to stay in steady state and to satisfy the condition of negligible temperature gradient within the sample reversible heat capacities can be measured. Only a single calibration constant is needed to assess the thermal conductivity and geometry of the calorimeter. The modulation permits separation of heat losses of frequency different from the modulation and thus increases the accuracy of the measurement. Transitions that can be described by linear kinetics expressions can also be followed quantitatively by MDSC as long as steady state is maintained within acceptable error limits. Quantitative separations may be possible to relatively high levels of lag, but the total enthalpy integrated over the complete transition region is always quantitative (within the limits if standard DSC). Finally, the introduction of complex variables for temperature, heat flow, and heat capacity facilitates computations. The imaginary part of the heat capacity C'' seems, however, to have no measurable effect, in contrast to the loss modulus determined in DMA.

Acknowledgments

The authors gratefully acknowledge constructive discussions with Dr. M. Reading, ICI Paints, Messrs. L. Thomas and B.S. Crowe of TA Instruments, R. Truttmann of Mettler-Toledo, and all attendees of the Third Lähnwitz Seminar, 1994. This work was financially supported by the Div. of Materials Res., NSF, Polymers Program, Grant # DMR 90–00520 and the Div. of Materials Sci., Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC05–84OR21400 with Lockheed Martin Energy Systems. Support for instrumentation came from TA Instruments, Inc. and Mettler-Toledo, Inc. Research support was also given by ICI Paints, Exxon Res. and Eng. Co., Shell Development Co., and the Toray Research Center.

References

- [1] B. Wunderlich, *Thermal Analysis*, Academic Press, Boston, 1990.
- [2] T. Ozawa, *Bull. Chem. Soc. J.* 39 (1966) 2071.
- [3] B. Wunderlich, *Differential Thermal Analysis*, in A. Weissberger and B.W. Rossiter (Eds.), *Physical Methods of Chemistry* Vol. 1, Part V, John Wiley and Sons, Inc., New York, 1971, Chapter 8, p. 427.
- [4] N. Hirai and H. Eyring, *J. Appl. Phys.*, 29 (1958) 810., *J. Polym. Sci.* 37 (1959) 51.
- [5] B. Wunderlich, D. M. Bodily and M.H. Kaplan, *J. Appl. Phys.*, 35 (1964) 95.
- [6] F.H. Müller and H. Martin, *Kolloid Z.Z. Polymere*, 172 (1960) 97; 192 (1963) 1.
G. Adam and F.H. Müller, *Kolloid Z.Z. Polymere*, 192 (1963) 29.
- [7] E.S. Watson, M.J. O'Neill, J. Justin and N. Brenner, *Anal. Chem.*, 36 (1964) 1233; US Patent 3,263,484.
- [8] G.Davis and R.S. Porter, *J. Therm. Anal.*, 1 (1969) 449.
- [9] T. Ozawa and K. Kanari, *Thermochim. Acta*, 253 (1995) 183.
- [10] W.Hemminger and G. Höhne, *Calorimetry, Fundamentals and Practice*, Verlag Chemie, Weinheim, 1984, Sect. 6.3.
- [11] M. Reading, *Trends Polym. Sci.* 1 (1993) 248.

- M. Reading, B. Hahn and B.S. Crowe, US Patent 5,224,775 (July 6, 1993).
M. Reading, D. Elliott, and V. Hill, Proc. 21st NATAS Conf. in Atlanta GA, Sept. 13–16, 1992, 145–149.
- [12] B. Wunderlich, Y. Jin and A. Boller, *Thermochim. Acta*, 238 (1994) 277.
- [13] T.A. Instruments, Inc. 109 Lukens Drive, New Castle, DE 19720.
- [14] A. Boller, Y. Jin and B. Wunderlich, *J. Therm. Anal.* 42 (1994) 307.
- [15] Perkin Elmer Corp., Norwalk, CT 08659–0012.
- [16] A. Mehta, R.C. Bopp, U. Gaur and B. Wunderlich, *J. Therm. Anal.*, 13 (1978) 197.
- [17] See, for example, the ADSC (Alternating DSC) of Mettler-Toledo, available since 1995.
- [18] See, for example, I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*. J. Wiley and Sons, New York, 1967, or Sect. 2.1.2 of Ref. [1].
- [19] See, for example, B. Wunderlich, *Macromolecular Physics*, Vol. 3, Crystal Melting, Academic Press, New York, 1980.
- [20] See WWW(Internet), URL: <http://funnelweb.utcc.utk.edu/~athas>. For a general description see also, B. Wunderlich, *Pure Appl. Chem.*, 67 (1995) 1919.
- [21] See, for example, B. Wunderlich, *Macromolecular Physics*, Vol. 2, Crystal Nucleation, Growth, Annealing, Academic Press, New York, 1976.
- [22] The first description of superheating of macromolecules was given by E. Hellmuth and B. Wunderlich, *J. Appl. Phys.*, 36 (1965) 3039.
- [23] B. Wunderlich, A. Boller, I. Okazaki and S. Kreitmeier, *J. Therm. Anal.*, submitted (1995).
A. Boller, I. Okazaki and B. Wunderlich, *J. Therm. Anal.*, submitted (1995).
Preliminary long abstract: B. Wunderlich and A. Boller, Proc. 24th NATAS Conf., in San Francisco, CA, Sept. 10–13, 1995.
- [24] J.E.K. Schawe, *Thermochim. Acta*, to be published, (1995). (MDSC measurements, the influence of the experimental conditions).
- [25] G.W.H. Höhne and J.E.K. Schawe, *Thermochim. Acta*, 229 (1993) 27.