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Letter to the Editor

Comments on "A comparison of different evaluation methods in modulated-temperature DSC"

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1. Introduction

A new technique, called Modulated Differential Scanning Calorimetry (MDSC), was introduced a few years ago by the authors of [1–8]. In this technique, the normally linear or isothermal temperature programme used by conventional DSC is modulated by a small perturbation. The response of the sample to the perturbation is deconvoluted from that due to the underlying temperature programme, using an appropriate mathematical procedure. We proposed the use of a sinusoidal perturbation, combined with an averaging procedure and a Fourier transform analysis to perform the deconvolution (though many alternatives are possible). As described in a recent paper [9], Schawe has duplicated the experimental procedure, but claimed a different mathematical treatment and interpretation of data [9]. Here we examine these claims in the light of earlier papers published by Reading and co-workers [1–8]. Since the term Modulated Differential Scanning Calorimetry has now become proprietary, we recommend that our technique should be called Modulated-Temperature Differential Scanning Calorimetry (M-T DSC).

Schawe reproduced some of our data from an earlier publication [5], and correctly pointed out that at 60°C our measurement of heat capacity for PET was in error. We observe that this is also true of his data, which differ from the ATHAS reference data provided by Wunderlich's laboratory [10] for PET by about 15%. What Schawe omitted to mention was that we subsequently presented data that were in good agreement with Wunderlich's values, thus demonstrating the quantitative nature of our technique [6], a fact which others have confirmed [11].

We note that there is no dispute over the fact that the underlying signal produced by averaging over the period of the oscillation is the same for both methods, and that this signal is equivalent to a conventional DSC.

2. Real and imaginary points of difference between our approach to M-T DSC and that proposed by Schawe

There are three points of apparent difference between our approach ([1–8]) to M-TDSC and Schawe's [9];

- the first is that the theoretical basis of his approach appears to be different as he claims his approach has the advantage that it can deal with time-dependent processes such as glass transitions, whereas ours can not
- the second is that our methodology is different in effect, because, he asserts that we are not aware of the importance of the phase lag
- the third is that he believes that the practice of subtracting (to use Schawe's terminology) the storage heat capacity from the total heat capacity

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to derive the non-reversing signal is not a valid procedure.

Although Schawe's theoretical approach is different from ours, it is fairly straightforward to demonstrate that his assertion with regard to the inability of our analysis to deal with glass transitions is incorrect. Whether our two theoretical approaches are in reality fundamentally different or equivalent requires further investigation. It is straightforward to demonstrate that the second point of apparent difference claimed by Schawe is entirely wrong. The third point of difference is more complex as this procedure is valid in a straightforward manner for irreversible processes like cure, loss of volatile, etc., it requires informed interpretation when analysing the glass transition while further work is required to define its quantitative significance in the melting region. We will discuss each of these points in turn.

3. Comparison of theoretical approaches

In the following analysis, we will use the symbols as defined by Schawe in his article [9] except where otherwise stated. As already mentioned, we both agree that the underlying signal contains the same information as a conventional DSC. That a heat flux DSC can be treated as a linear system can be ascertained by consulting standard text books [12]. However, for the purposes of this discussion it is sufficient to observe that the underlying signal can be interpreted in the normal way.

We have always made it clear that we assume the response to the perturbation is linear [1–8]; thus, this assumption does not differentiate Schawe's approach [9] from ours. We start by remarking that in our previous articles we have not ascribed the same meaning to C_p that Schawe ascribes in his [9], thus his comparison of our different methods is not valid. In the past, we have defined it as the heat capacity of the sample due to molecular motions [5,6] (this is, in effect, the same as Schawe's definition of C'). If, at the temperature of the measurement, a motion is frozen (such as in a glassy polymer) then it would not normally be considered to provide a contribution to the heat capacity. Whether a process is considered frozen sometimes depends, of course, on the time scale of the measurement, so this is an inherently time- or frequency-dependent quantity. Here, we will denote this quantity by the same symbol we have used previously [6], $C_{p,t}$, as meaning the heat capacity arising from the part of the molecular motions of the sample that responds rapidly compared with the time scale associated with the measurement (previously, we have used the phrase "practically instantaneously" [6]). We have called this quantity 'thermodynamic' heat capacity [5,6] but this is open to misinterpretation, so we currently prefer the term 'reversing heat capacity'.

We can now restate the starting equation Schawe used as being:

$$\mathrm{d}Q/\mathrm{d}t = C_{p,t}\mathrm{d}T/\mathrm{d}t + f(t,T) \tag{1}$$

Where $C_{p,t}$ is the reversing heat capacity and not the static heat capacity denoted by C_p in Schawe's article, because it is potentially a time-dependent quantity.

It is appropriate to define what we consider to be a reversing quantity. $C_{p,t}$ would normally be constant over a small interval of time and temperature. Thus we assume that, at any time and temperature, there is a process that provides a reversible contribution to the heat flow that is directly proportional to and synchronous with the heating rate. It should be noted that, by definition, the in phase (with $\mathrm{d}T/\mathrm{d}t$) component of the cyclic signal (see below) that arises from molecular motions is a reversing quantity.

The signal which is expressed through $f(t,T)$ constitutes the kinetic or non-reversing contribution. We use the terms reversing and non-reversing, rather than reversible and irreversible, to avoid confusion with transitions like cold crystallisation. These are often reversible events but, at the time and temperature they are occurring, the enthalpy associated with crystallisation is non-reversing, whereas $C_{p,t}$ is always reversing.

The fact that $C_{p,t}$ is allowed to be a time-dependent quantity is consistent with the well-known frequency dependence of the glass transition that we have demonstrated with M-T DSC [8]. Similarly, it allows for different values of $C_{p,t}$ for the single frequency of the modulation and for the underlying heating rate (to which the sample responds as it would to some equivalent frequency or distribution of modulation frequencies [8]). For processes other than melting and the glass transition, where the sample is not in equilibrium but is moving toward equilibrium at a rate governed by some kinetic equation, we obtain from Eq. (1), under a modulated heating programme with ramp rate β, the following:

$$\mathrm{d}Q/\mathrm{d}t = \beta \cdot C_{p,t} + \bar{f}(t,T) \ldots\ldots\ldots \quad \text{(the underlying signal)} \qquad (2)$$

$$+C_{p,t} \cdot T_a \cdot \omega \cos \omega t + C \cdot \sin \omega t \ldots\ldots\ldots \quad \text{(the cyclic signal)} \qquad (3)$$

where $f(t,T) = \bar{f}(t,T) + C \sin \omega t$ =the kinetically-hindered response of the sample$\bar{f}(t,T)$ is the average of $f(t,T)$ over one, or more modulation periods, and C=the amplitude of the kinetic response to the sine wave modulation. In general, C will be a slowly varying function of t and T, but can be considered constant over at least one modulation period. It is true that $f(t,T)$ can also provide a cosine contribution [13], and therefore Eqs. (2) and (3) is an approximate expression. However, provided the amplitude of the modulation is small and there are many oscillations during the course of the transition, we have found it to be an excellent approximation for most polymer transitions. We have provided a complete mathematical analysis for chemical reactions and crystallisations, including criteria for when Eqs. (2) and (3) cease to be valid, elsewhere [13]

A M-T DSC experiment comprises two different time scales; that is associated with the frequency of the modulation and that associated with the heating/cooling rate (T). We can explicitly express the requirement that $C_{p,t}$ may have to take a range of values depending on the time scale of the measurement, as follows:

$$\mathrm{d}Q/\mathrm{d}t = \beta C_{p,\beta} + \bar{f}(t,T) + C_{p,\omega} T_a \omega \cos \omega t + C \sin \omega t \qquad (4)$$

Thus, Eq. (4) generalises Eqs. (2) and (3). It should be noted that in our previous articles, C has been described simply as the kinetic (or kinetically hindered) response to the modulation. We have never stated or implied that it is in all cases $a_f T_a$ (where a_f is the slope of a graph of $f(t,T)$ against T) as implied by Schawe ([9] Eq. (3)). To illustrate a different possibility, we can consider a simple model for the glass transition based on that employed by Hutchinson and Montserrat [17]. This takes the enthalpy difference δ of the sample from its equilibrium value ($=TC_{pl}$, where C_{pl} is the specific heat capacity of the liquid) to satisfy a law

$$\mathrm{d}\delta/\mathrm{d}t = -\Delta C_p \mathrm{d}T/\mathrm{d}t - \delta/\tau \qquad (5)$$

where $\Delta Cp = C_{pl} - C_{pg}$ is the difference between the heat capacity of the liquid and that of the glass. We assume that the relaxation time τ has an Arrhenius dependence upon temperature, $\tau = \tau_g e^{E/RT}$, and that the activation energy is large (E/RT >>1). Using the alternative variable $\eta = \delta + T\Delta C_p$=the enthalpy–the glass value (TC_{pg}) and making an approximation based on high activation energy we obtain [14];

$$\begin{aligned} \mathrm{d}\eta/\mathrm{d}t &= (e^{KT}/\tau_0)(T\Delta C_p - \eta) && (6)\\ &= (1/\tau_0)\exp[K\beta t + KT_a \sin \omega t] \\ &\quad \times (\beta t \Delta C_p + T_a \Delta C_p \sin \omega t - \eta) && (7) \end{aligned}$$

Here $\tau_0 = \tau_g e^{KT_g} e^{E/RT_g}$, $K = E/RT_g^2$ and $\tau_g E\beta/RT_g^2 = \exp(-ER/T_g)$, ($T_g$ is the underlying glass transition temperature for the rate β). It is convenient to write

$$\eta = \bar{\eta} + T_a R\{\eta^* \exp(i\omega t)\} \qquad (8)$$

where $\bar{\eta}$ is the underlying part of η and satisfies

$$\mathrm{d}\bar{\eta}/\mathrm{d}t = (e^{Kbt}/\tau_0)(\beta t \Delta C_p - \bar{\eta}) \qquad (9)$$

η^* is the complex amplitude that gives the amplitude and phase of the cyclic part of η. Assuming many cycles over the transition and small amplitude for T_a it can be shown that

$$\mathrm{d}Q/\mathrm{d}t = \beta C_{pg} + \mathrm{d}\bar{\eta}/\mathrm{d}t \ldots\ldots \quad \text{(the underlying signal)} \qquad (10)$$

$$+ \omega T_a[(C_{pg} - \mathrm{Im}\{\eta^*\})\cos \omega t - \mathrm{Re}\{\eta^*\}\sin \omega t] \ldots \text{(the cyclic signal)} \qquad (11)$$

We can identify

$$C = -\omega T_a \mathrm{Re}\{\eta^*\} \qquad (12)$$

$$C_{p,\omega} = C' = C_{pg} - \mathrm{Im}\{\eta^*\} \qquad (13)$$

$$C'' = C/T_a\omega = -\mathrm{Re}\{\eta^*\} \qquad (14)$$

where C' and C'' are the real and imaginary parts of the complex heat capacity described by ourselves [7] and by Schawe [9]. It should be noted that the C_{p_ω} term is reversible and derived from molecular motions and thus corresponds to our definition of a reversing heat capacity. The C term arises because part of the response of the sample is sufficiently fast for it to be detectable but is still too slow to keep pace with $\mathrm{d}T/\mathrm{d}t$ as it does above the transition. The C term is therefore a function of the degree to which the sample response is kinetically hindered. Clearly Schawe's interpretation of C (see his Eqs. (3) and (4) from [9]) does not conform to this simple and more general description. If we wish to invoke a frequency–heating rate equivalence, then this can be used to determine $C_{p,\beta}$ (i.e. $C_{p,\beta} = h(C_{p,\omega}, \beta)$). We will publish further on this in the future.

Inspection of Eq. (4) shows that we have obtained an expression that is very similar to the equation we used in our early articles [1–8], except that it explicitly allows for a different reversing heat capacity for β and ω, something that is essentially implicit in our definition of C_{pt} ($=C_p$ in [1–5]). Schawe's analysis fails because he assumes meanings for the symbols and functions we have used that are different from those we gave and intended.

We have also made use of complex notation for the cyclic signal in Eq. (3) to obtain the equation we have already presented [7] as our approach for modelling the response to the glass transition, viz.:

$$\mathrm{d}q/\mathrm{d}t = \beta C_{p,\beta} + \bar{f}(t,T) + T_a\omega(C'\cos\omega t + C''\sin\omega t) \qquad (15)$$

Our use of complex notation did not, and does not constitute a new or changed theory, it is merely the adoption of a different mathematical formalism as a matter of convenience. Here, as already noted, $C''=C/T_a\omega$ and our interpretation, that this represents the kinetically hindered response of the sample, is the same.

Schawe Eq. (21) in [9] writes for his approach

$$\mathrm{d}Q/\mathrm{d}t = \Phi(T(t)) = C_\beta(T) + \omega T_a|C(T,\omega)|\cos(\omega t - \phi) \qquad (16)$$

By an elementary transformation:

$$\mathrm{d}Q/\mathrm{d}t = C_\beta(T)\beta + T_a\omega(C'\cos\omega t + C''\sin\omega t) \qquad (17)$$

By comparing Eqs. (4),(10),(11)–(15) and (17) the similarity between our approaches as regards analysing the response to the modulation becomes self-evident. Leaving aside differences in nomenclature, Schawe describes cosine components in the heat flow as being due to "molecular motion" [9], and we too defined cosine components as being due to "molecular motions" [5]. Schawe describes the sine component as arising from dissipation or loss processes. Any analogy with DMA and dielectric spectroscopy should not be taken too far. With these techniques mechanical or electrical energy is lost. Generally in calorimetry, with endothermic processes such as glass transitions, energy is lost from the sample only if the heating rate becomes negative, whereas the 'loss' component is present even when the heating rate is at all times positive. We describe the sine term as arising from processes that are kinetically hindered. In reality we see no difference between the physical origins of the sine wave component as defined by us and as defined by Schawe.

Notwithstanding possible differences in interpretation, Schawe's claim that our analysis "represents a special case, which is only valid for time-independent events" is obviously false. Similarly, his claim that our approach develops "problems of interpretation" at the glass transition is spurious. Differences between our approach and Schawe's emerge when we consider the underlying signal, viz.:

$$\text{underlying signal (Schawe)} = C_\beta(T)\beta \qquad (18)$$

We equate it to

$$\text{underlying signal (Reading)} = \beta C_{p,\beta} + \bar{f}(t,T) \qquad (19)$$

We divide it into (a) a response that is reversing ($= \beta C_{p,\beta}$), i.e. arising from molecular motions that respond effectively instantaneously at the "frequencies" within the distribution implied by the underlying heating rate and, (b) a response that is kinetically hindered ($=\bar{f}(t,T)$); Schawe, however, does not. We contend that generally it must be true that, if the response to the perturbation comprises an instantaneous reversing component, $T_a\omega C''$ cos ωt, and a kinetically hindered component, $T_\mathrm{a}\omega C''$ sin ωt, then, in general, this will also be true for the underlying signal.

To avoid future misunderstandings, it is appropriate that we present the outline of our approach to polymer melting. It is here that we use our alternative starting equation [3], which we restate as being:

$$\mathrm{d}Q/\mathrm{d}t = \mathrm{d}T/\mathrm{d}t(C_{p,t} + g(t,T)) + f(t,T) \qquad (20)$$

where, for the sake of clarity, we use different symbols for the functions having different dimensions (i.e. $g(t,T)$ instead of $f_1(t,T)$ as used by Schawe [9]). In an earlier article, where we used the phase lag to examine the in- and out-of-phase response in the cyclic signal in the melt region for PET [2], we observed, "If the crystallite melting temperatures have a distribution and they are able to melt rapidly without extensive superheating, something that would normally be true given their instability, then at least part of the signal will be in phase with dT/dt, as this determines the speed with which a fresh population of crystallites find themselves at their melting temperature". This means that there is a contribution to Eq. (20) from melting as expressed in $g(t,T)$. However, this will not be a reversing contribution as, the heating rate becomes negative, the process of melting is not symmetric due to supercooling (we have demonstrated this point with a new data-analysis method called parsing which analyses the heat, cool and reheat portions of a modulation cycle independently [14]). Consequently, the assumption of linear response is violated in this case. The melted material may then participate in reorganisation which will be a kinetic process. It is therefore convenient to define a composite kinetic function that includes all terms other than the reversing $C_{p,t}$ itself, viz.:

$$f_2(t,T) = g(t,T)\mathrm{d}t/\mathrm{d}t + f(t,T)) \tag{21}$$

where, under modulated conditions,

$$f_2(t,T) = \bar{f}_2(t,T) + D\sin(\omega t) + \omega T_a E\cos(\omega t) \tag{22}$$

Therefore

$$\mathrm{d}Q/\mathrm{d}t = \beta C_{p\beta} + \bar{f}_2(t,T) + \dots \quad \text{(the underlying signal)} \tag{23}$$

$$+\, \omega T_a(C_{p\omega} + \mathrm{E})\cos(\omega t) + D\sin(\omega t) \ \dots\dots \text{(the cyclic signal).} \tag{24}$$

We can still use Eq. (15), except that now:

$$\mathrm{d}Q/\mathrm{d}t = \beta C_{p,\beta} + \bar{f}_2(t,T) + T_a\omega(C'\cos\omega t + C''\sin\omega t) \tag{25}$$

where f_2 includes non-reversing quantities that are proportional to $\mathrm{d}T/\mathrm{d}t, C'_\omega = C_{p\omega} + E$ and $C''_\omega = D/\omega T_a$. Thus, the form of the equation remains the same but the interpretation is different. We will be publishing further papers on the melt region in the near future. In conclusion, we can express Eq. (25) as:

$$\mathrm{d}Q/\mathrm{d}t = \beta(C_{p,\beta} + C_E) + T_a\omega(C'_\omega\cos\omega t + C''_\omega\sin\omega t) \tag{26}$$

where $C_\mathrm{E} = \bar{f}_2(t,T)/\beta$ =the non-reversing or excess heat capacity.

4. The use of the phase lag

Schawe claims that we do not use the phase lag to calculate C' (in our analysis=$C_{\mathrm{p},\omega}$) and $C''(= C/\omega T_a \, or \, D/\omega T_a$ over a melting transition). In an early article [2], we defined and demonstrated a 'simple' deconvolution procedure which did not use the phase lag but we also defined and demonstrated a 'complete' deconvolution that did use the phase lag, as can be demonstrated by the following quotation: "A further deconvolution step is required to distribute the AC (cyclic) component of the heat flow components that are in phase with the dT/dt signal or in phase with the absolute temperature, respectively... The AC 'reversing' signal is divided between the in-phase (with the dT/dt modulation) and the out-of-phase (with the dT/dt modulation) according to the expressions.

$$\text{in-phase} = (\text{AC Component})\,\text{Cos}(\text{phase lag peak height})$$

$$\text{out-of-phase} = (\text{AC component})\,\text{Sin}(\text{phase lag peak height})$$

The non-reversing signal is now obtained by subtracting the in-phase reversing signal from the total heat flow".

In this article we plotted the in-phase reversing signal (=$\beta C'$) and the out-of-phase signal (=$\beta C'$) to illustrate the type of results this procedure gives. We also presented results for the non-reversing signal (equal to the underlying heat flow minus $\beta C'$). In terms of the methodology there is, therefore, no fundamental difference at all between our approach and that of Schawe with regard to the use of the phase angle. It should be noted that our work predates his by some considerable time [2,9]. We have used the simple (approximate) deconvolution in much of our work to date because it makes perfectly valid measurements possible in most circumstances when dealing with polymer transition. Where the change in phase lag during the transition is small, the C'' term must be correspondingly small, so we can make the approximation.

$$|C| \approx C' \text{ i.e. } C'' \approx 0 \qquad (27)$$

To quote from [5]:

"It is important to realise that this cyclic measurement comprises a contribution from the thermodynamic heat capacity (denoted C_{pt} above) plus a contribution from any kinetic event... arising from C... The cosine wave contribution is always present and is, in the case of PET, by far the major part of the cyclic component in the heat flow signal for all of the transitions except the melting. We have generally found this to be the case for all of the polymer samples we have looked at... Thus, for many kinetically controlled phenomena, C can be approximated to zero" (note that we use the term thermodynamic heat capacity; we currently prefer the term reversing heat capacity, see above).

The maximum error involved in making this approximation from the data Schawe presents [9] is less than 0.2% (it should be remembered that it is the ratio of the squares of C' and C'' that is important when calculating this quantity). Schawe states "In the case of the time-dependent thermal events in the sample, a_f... cannot be neglected" [9]. The simple fact is that it can, when C'' is small enough, as his own data demonstrate very well. In general, for glass transitions, crystallisation, the loss of volatiles, etc. in polymer systems, we have found the error to be less than 1%. This approximation, as we have made clear [2,5,6], is not valid during the melt which always exhibits a large shift in phase lag, but we have not attempted to make a detailed quantitative discussion of M-T DSC results during the melt as we are of the opinion that further theoretical work is required before this will be possible. We have now provided the first part of this analysis [13]. Systematically presenting C' and C'' data for these transitions (or $\beta C'$ and $\beta C''$) before providing the basis of a theoretical approach would have been of little practical value.

In Schawe's comparison, he represents our simple (approximate) method as being our general method. A proper reading of our work makes it clear that this is incorrect. The reason we have chosen to use this approximation is best summarised by a quote from [6]: "In principle the phase lag measurement could be used to separate the cyclic C_p into the in- and out- of-phase components of the response to the perturbation. However, before doing this, ways must be found of properly calibrating and testing this signal... The key to progress is a proper understanding of how real calorimeters and samples behave when subjected to a cyclic perturbation." In other words, although we were the first to offer a theoretical framework that describes the importance of the phase lag and the first to illustrate how it can be used in practice [2], we nevertheless advised caution in using it systematically, because there are special difficulties in taking account of the instrumental effects that influence this measurement. There are also problems with any subsequent testing of the values obtained to ascertain their accuracy. What, for example, would be used as a standard? For the underlying signal and $C_{p\omega}(=C')$ we can answer these questions. Much less certainty surrounds $C(=T_a\omega\, C')$. Given that there is, at this stage, no clear practical use for this quantity, we have chosen to focus our attention in our published work on the reversing (from C') and non-reversing signals.

We have preferred to wait until the completion of a rigorous mathematical analysis of the behaviour of a DSC cell under M-T DSC conditions before presenting further data on the C'' (or C) term. This work has now been completed [13]. The conclusion from this analysis is that the methodology we proposed in [2] has been shown to be valid provided certain precautions are taken experimentally. Now that we have provided the theoretical background, we will be publishing further data on C'' and discussing its significance.

The basic point that emerges from this discussion is that the methodology of our approach and that of Schawe are identical; he has simply duplicated our approach. Thus any dispute must be confined to the *interpretation* that is ascribed to the three basic signals: the underlying heat flow, the in-phase (with $\mathrm{d}T/\mathrm{d}t$) component of the heat flow, and the out-of-phase (with $\mathrm{d}t/\mathrm{d}T$) component of the heat flow, whether these quantities are expressed as heat flows [2] or heat capacities [9]. The debate will also be about the significance of the calculated quantity, the non-reversing signal.

5. The non-reversing signal

Except in the region of glass transition it will normally be the case in Eq. (4) that:

$$C_{p\beta} = C_{p\omega} \tag{28}$$

Therefore Eqs. (2) and (3) applies. If we take, for example, the heat capacity of an inorganic solid, within the bounds of the frequencies accessible to current M-T DSC technology, we would not expect C_{pt} to vary with frequency. If this solid undergoes an irreversible chemical reaction, such as a decomposition, then, even during the reaction, the sample will have at any point in time, a heat capacity associated principally with the vibrational modes available to the sample. This heat capacity is reversible without hysteresis. Thus, during a conventional scanning DSC experiment, at any point during the reaction, the total heat flow will comprise a contribution from the enthalpy of the reaction and a contribution from this reversible C_{pt}. We know that when using M-T DSC the cyclic heat capacity calculated just from the amplitude of the response to the modulation, if C is small, will be, to a good approximation, a measure of the reversible C_{pt}. Alternatively, if C is large, the phase lag can be used as described above to calculate C_{pt} despite the fact a chemical reaction is occurring at the same time. Thus the reversible and irreversible processes can be separated. We have demonstrated that this is possible experimentally [8], thus both theory and experiment agree.

Schawe criticised the use of the non-reversing signal and used as his example a glass transition. We have not yet offered a detailed discussion of the interpretation of M-T DSC results at the T_g. However, in order to respond to Schawe's comments, we will offer a brief explanation here. More details will be given in a future article [14]. We have already proposed that, to simplify the interpretation during the glass transition that we explicitly allow for different reversing heat capacities for the underlying and the cyclic measurements to account for the different effective frequencies of these two aspects of the sample response [7], as expressed in Eq. (4). The question then arises of what is the relationship between $C_{p\beta}$ and C'. This will be addressed in more detail in our forthcoming paper [14]. Where the relationship between $C_{p\beta}$ and C' is not known, we must assume that $C_{p\beta}=C'$. This does then lead to a peak in the non-reversing signal even when the sample is being cooled as Schawe has demonstrated. This reflects the difference in enthalpy of motions that are reversing at or faster than the frequency of the modulation and the total enthalpy associated with the frequency, or distribution of frequencies represented by the underlying cooling rate. It does not mean that the area under the non-reversing signal is not related to the relaxation enthalpy in an annealed sample; on the contrary, it has been clearly demonstrated that it is [15,16]. It simply means that there is an additional term that must be taken into account. In Fig. 1 we present the results of a complete deconvolution for a sample of quenched polystyrene. To obtain these results we used the procedure already demonstrated in [2], except that there we expressed the results in terms of heat flows, whereas here we express them as heat capacities (heat flow =– underlying heating rate × heat capacity). It can be seen that they are very similar to the results given by Schawe [9]. This sample should have no relaxation endotherm, yet it has a non-reversing peak. The reason for this is similar to that given earlier for the cooling experiment (although there is also the possibility of annealing as the sample is heated). We propose that this represents the zero-point measurement for subsequent measurements of relaxation enthalpy. This is a somewhat simplified argument, and we will be discussing these issues in greater detail in our forthcoming article. However, what we hope to make clear is that the observation about the existence of a non-reversing component when cooling the sample or heating a quenched sample is not evidence that it cannot be used to measure relaxation enthalpies – it simply means that the informed use of a reference measurement is required or a more detailed knowledge of the relationship between $C_{p\beta}$ and C' is needed.

When applied to melting, the term non-reversing loses the simple meaning it has during chemical reactions, loss of volatiles, crystallisation and glass transitions. It is also true that the approximation made in Eq. (24) will generally not be valid, so that it is essential to use the phase lag to obtain quantitative values as we have made clear [2]. We will be discussing the melt region further in future articles.

Schawe asserts that "the non-reversing component is determined by subtracting two logically different quantities" which were obtained under "dissimilar

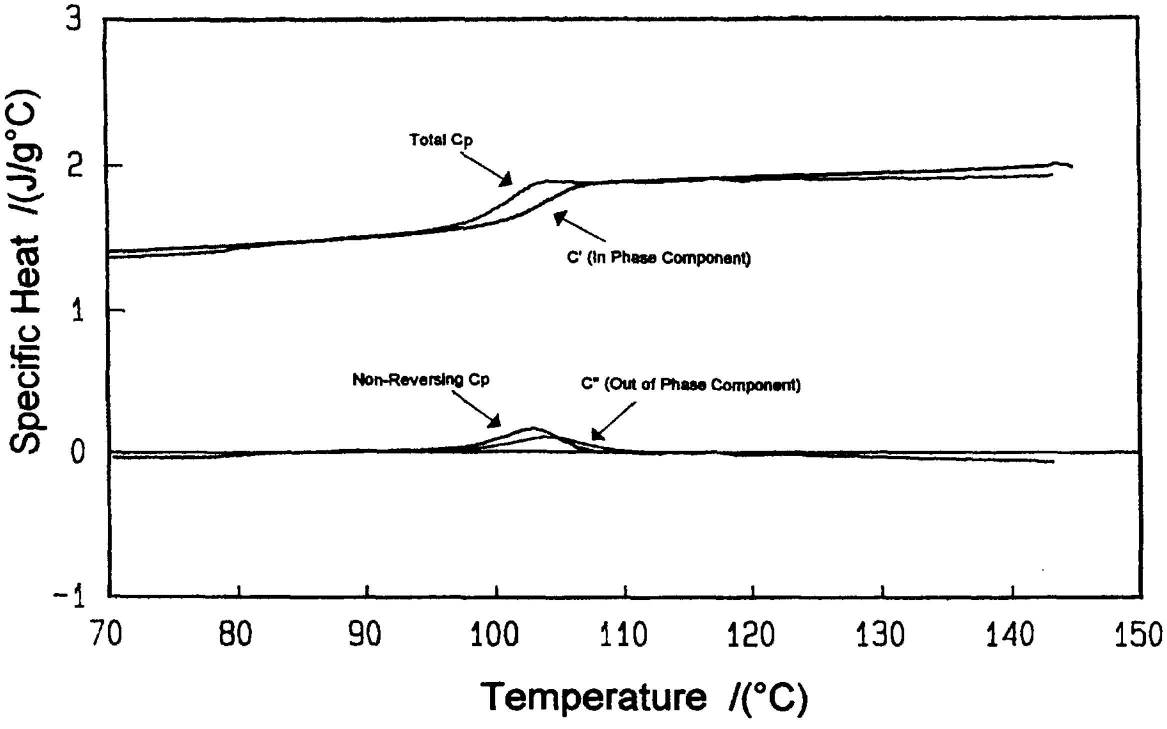

Fig. 1. MTDSC results for quenched polystyrene using the method proposed by Reading et al. [2].

measurement conditions" and are not directly comparable. There must be a relationship between the response of the sample to the modulation and its response to the underlying heating programme. Given this fact, comparing them cannot be an illogical thing to do. Excepting melting, for many transitions the simple analysis obtained by combining Eqs. (2)–(3) and (27) will apply and the meaning of the non-reversing signal is clear. For other transitions, where $C_{p\beta}$ and C' are not equal (see Eq. (15)), it is still possible to interpret the non-reversing signal in a useful and meaningful way as discussed above.

6. Conclusions

A proper review of our work clearly shows that Schawe's methodology is identical to ours. We have been well aware of the significance of the phase lag right from the time we introduced our new technique (now called M-T DSC) and presented data in 1992 for the in- and out-of-phase components of the response to the perturbation equivalent to that presented by Schawe in 1995. We have used an approximate method in many of our articles but we have made our simplifying assumptions clear, and this is and will remain a perfectly valid method where the phase lag change during a transition is small. In his article, Schawe incorrectly represented our approximate approach as being our general approach. Consequently Schawe's claim that "Reading's separation method has an empirical basis: consequently the equations and quantities contain little information. Our (Schawe's) evaluation method is based on well-known linear response theory and we have relaxation theory and irreversible thermodynamics at our disposal for the interpretation of the measured quantities" is entirely spurious while his table of comparisons is inaccurate and misleading. We present a more accurate version in our Table 1. It is not clear that his theoretical approach is fundamentally different from ours and more discussion will be required to elucidate this point. Certainly his assertion that our

Table 1
Comparison of the different methods

	Reading et. al.'s method	Schawe's method
Underlying or averaged heat flow	Same information as conventional DSC	Same information as conventional DSC
Amplitude of the cyclic response and the phase lag	Divided into in and out of phase responses by use of the phase lag unless the phase shift is small in which case the out of phase component can be neglected	Divided into in and out of phase responses by use of the phase lag
Theory	Kinetic approach based on differentiating between fast responses (equilibrium behaviour) and slower kinetically hindered processes including irreversible processes	Based in irreversible thermodynamics and linear response theory
Chronology	Details of the methodology including use of the phase lag given in 1992	Some information given in 1994 with further details in 1995

approach cannot adequately deal with glass transitions is incorrect.

We have chosen to refrain from systematically providing C'' (or $\beta C''$) for all of our M-T DSC measurements, because of the difficulties associated with assuring that this signal has been measured with a quantitative correction for instrumental factors together with the fact that at this stage there is no clear, practical value in measuring C''. Schawe has provided no evidence that he has addressed the important issue of correcting instrumental factors and so his data is suspect. In contrast, we have now completed and submitted for publication a rigorous mathematical analysis of DSC cell behaviour under M-T DSC conditions and confirmed the validity of the method we proposed in 1992 [2]. Consequently we will be providing more data on C'' in the future, although our approximate treatment will continue to be a valid alternative in many cases.

References

[1] J.C. Seferis, I.M. Salin, P.S. Gill and M. Reading, Proceedings of the Academy of Athens, Athens, Greece (1992).

[2] M. Reading, D. Elliott and V. Hill, Proceedings of the 21st North American Thermal Analysis Society Conference (1992) pp.145–150.

[3] M. Reading, D. Elliott and V.L. Hill., 10th ICTAC August 24–28 (1992) J. Therm. Anal. (1993) 949–955.

[4] P.S. Gill, S.R. Saurbrunn and M. Reading, 10th ICTAC August 24–28 (1992), J. Therm. Anal. (1993) 931–939.

[5] M. Reading, Trends Polym. Sci., (1993) 248.

[6] M. Reading, A. Luget and R. Wilson, Thermochim. Acta., (1994) 238.

[7] M. Reading, R. Wilson and H.M. Pollock, Proceedings of the 23rd North American Thermal Analysis Society Conference (1994) pp.2–10.

[8] M. Reading, K.J. Jones and R. Wilson, Netsu Sokutie, 22 (1995) 83–84.

[9] J.E.K. Schawe, Thermochimica Acta (1995) in press.

[10] B. Wunderlich, personal communication.

[11] Y. Yin, A Boller and B. Wunderlich, Proceedings of the 22nd North American Thermal Analysis Society Conference (1993) pp.59–63.

[12] B. Wunderlich, Thermal Analysis, Academic Press (1990).

[13] A. Lacey, C. Nikolopoulos and M. Reading, submitted to J. Therm. Anal.

[14] K. Jones, M. Reading and H.M. Pollock, in preparation.

[15] A. Boller, Y. Jin and B. Wunderlich, J. Therm. Anal., 42 (1994) 277.

[16] Y. Yin, A. Boller and B. Wunderlich, Proceedings of the 22nd North American Thermal Analysis Society Conference (1993) 59–64.

[17] J.M. Hutchinson and S. Montserrat, preprint.