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A theoretical model of temperature-modulated differential scanning calorimetry in the glass transition region

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Abstract

A new analysis of an earlier theoretical model of the enthalpic response of glasses to temperature-modulated differential scanning calorimetry in the glass transition region has been made. This yields quasi-continuous values of the complex specific heat capacity, C_p^*, and its in-phase and out-of-phase components, C_p' and C_p'', respectively, as well as those of the phase angle, ϕ. This analysis has been used to predict the effects of three parameters: the period, the amount of annealing, and the non-linearity parameter. Increasing the period reduces the mid-point transition temperature for C_p' in a quantitatively similar way to the effect of cooling rate on T_g, from which a relationship between period and cooling rate has been derived and compared with a fluctuation model for the glass transition. The amount of annealing is shown to have no effect on the area under the C_p'' peak, confirming that this out-of-phase component does not provide information about the enthalpic state of the glass. Finally, the non-linearity parameter has opposite effects on the cooling and heating stages of intrinsic thermal cycles, with reducing x causing the C_p'' peak to broaden on cooling and to sharpen on heating. For these same intrinsic cycles, the area difference under the C_p'' peaks on heating and cooling may be either positive or negative, depending on the value of x. This last observation may have implications for the interpretation of C_p'' in terms of entropy changes occurring during the modulation periods.

Keywords: Enthalpy relaxation; Glass transition; Temperature modulated DSC

1. Introduction

The technique of temperature-modulated calorimetry (TMC) in general, and of temperature-modulated differential scanning calorimetry in particular, has been receiving considerable attention recently by virtue of its exciting potential for enhanced thermal analysis. Its advantages in separating the so-called reversing and non-reversing effects are well known, while a particularly good illustration of its potential is afforded by its application to the study of the isothermal and non-isothermal cure of thermosetting systems [1,2]. In the present context, its application to the glass transition is of particular interest. There has been a number of experimental studies of the glass transition region of polymers by temperature-modulated DSC [e.g. [3–5]], from which some general features are now accepted. These include the following aspects:

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1. the 'total' or 'average' heat capacity, $C_{p,av}$, is very similar to that obtained by conventional DSC at the same average heating rate;
2. the 'in-phase' and 'reversing' components of the specific heat capacity exhibit a sigmoidal change from a glassy value of C_p to a liquid-like value at a temperature that is dependent on the period of the modulations; and
3. the 'out-of-phase' and 'non-reversing' components of C_p, as well as the phase angle between heating rate and heat flow, depart from and then return to zero on passing through the transition region.

The interpretation of these features, both qualitatively and quantitatively in respect of their magnitudes, shapes, and locations on the temperature scale, has only recently begun to be understood. As a means towards this end, a theoretical model was earlier developed [6,7], based upon a single relaxation time model previously used successfully to describe the response of glasses in conventional DSC [8], in order to predict the effects of the various parameters defining the temperature-modulated DSC experiment. This analysis required the numerical integration of an ordinary differential equation, and made use of a 4th–5th order Runge–Kutta solution. Because this procedure involved unequal time steps, the subsequent Fourier transformation of the heating rate and heat-flow modulations was made at intervals of single periods, with the result that the transformed variables (complex C_p, phase angle, etc.) were represented by just one point per cycle. Although this was adequate for describing the general features introduced here, a quantitative analysis of the results was not possible. The object of the present paper is to show the results of an improved method of numerical integration, which allows a quantitative analysis of the transformed data to be made, from which further important predictions of the modulated response are established.

2. Theoretical analysis

2.1. Basic model

As before, the analysis here considers the effects of the kinetics of enthalpy relaxation in the glassy sample in the glass transition region, assuming infinitely good heat transfer. In other words, the sample is assumed to follow exactly the programme temperature, or, alternatively, it is assumed that the instrument can be calibrated for heat-transfer effects. Following an earlier work on modelling the response of glasses in conventional DSC [8], the enthalpic (H) response of a sample to a heating or cooling rate q may be written as:

$$\frac{d\delta}{dt} = -\Delta C_p q - \frac{\delta}{\tau(T,\delta)} \quad (1)$$

where $\delta = H - H_\infty$ is the excess enthalpy and $\Delta C_p = C_{p,l} - C_{p,g}$ is the increment in C_p between glassy ($C_{p,g}$) and liquid-like ($C_{p,l}$) values at the glass transition. For simplicity, a single relaxation time τ is used, which is both temperature (T) and structure (δ) dependent:

$$\tau = \tau_r \exp[-\theta(T - T_r)] \exp[-(1-x)\theta\delta/\Delta C_p] \quad (2)$$

where τ_r is the value of τ in equilibrium at an arbitrary reference temperature, T_r, θ a temperature coefficient related approximately to the apparent activation energy $\Delta h^*(\theta \approx \Delta h^*/RT_g^2)$, and $x(0 \le x \le 1)$ is the non-linearity parameter (smaller values of x implying greater non-linearity) describing the relative contributions of temperature and structure to the relaxation time [9].

In the simplest approach, namely that involving only a single relaxation time, these two equations are sufficient to describe the response of the sample to any prescribed thermal history. In reality, the response is determined, in addition, by a distribution of relaxation times which may be included either as a discrete distribution [9] or, more commonly, by the use of a stretched exponential response function. The inclusion of a distribution within the model introduces non-exponentiality to the response besides non-linearity and will be the subject of a later paper.

For the present purposes, therefore, the response is defined by Eqs. (1) and (2). For temperature-modulated DSC, the heating rate is:

$$q = q_{av} + A_T\omega\cos(\omega t) \quad (3)$$

and the modulation is defined by three experimental variables, namely: q_{av}, the average heating (or cooling) rate; A_T, the amplitude of temperature modulations; and ω, the frequency of the modulation (or alternatively the period defined by $t_p = 2\pi/\omega$).

2.2. Solution of model

The set of Eqs. (1)–(3) is solved using a method appropriate to stiff problems, involving a quasi-constant step size (here, typically 0.1 s, giving 24 001 points for a temperature interval of 20 K and an average heating rate of 0.5 K min^{-1}) implementation of numerical differentiation formulae, and available as code 'ode15s' in Matlab software. The material constants are the same as the ones used before [6,7]:

$$C_{\mathrm{p,l}} = 1.6\,\mathrm{J\,g^{-1}\,K^{-1}}$$

$$C_{\mathrm{p,g}} = 1.3\,\mathrm{J\,g^{-1}\,K^{-1}}$$

$$\Delta C_{\mathrm{p}} = 0.3\,\mathrm{J\,g^{-1}\,K^{-1}}$$

$$\tau_{\mathrm{r}} = 100\,\mathrm{s}$$

$$x = 0.4\ \text{(unless otherwise stated)}$$

$$\theta = 1.0\,\mathrm{K^{-1}}\ \ (\Delta h^* \approx 1200\,\mathrm{kJ\,mol^{-1}},\ \text{for } T_{\mathrm{g}} = 105^\circ\mathrm{C})$$

while the experimental conditions are defined by a temperature range from $T_{\mathrm{r}} - 10\,\mathrm{K}$ to $T_{\mathrm{r}} + 10\,\mathrm{K}$, and with various values for the initial excess enthalpy δ_0 at $T_{\mathrm{r}} - 10\,\mathrm{K}$. The temperature T_{r} is the temperature at which the relaxation time in equilibrium ($\delta = 0$) is equal to 100 s (τ_r), and may be considered as an arbitrary glass transition temperature.

The solution of the foregoing equations gives the response of the excess enthalpy δ as a function of time or temperature, from which the heat flow is evaluated as:

$$HF = C_{\mathrm{p,l}}q + \mathrm{d}\delta/\mathrm{d}t \tag{4}$$

The resulting modulations of excess enthalpy and of heat flow have been shown previously as functions of time and temperature [6,7], from which the glass transition is evident as: (i) a change in the average value of the heat flow; (ii) a change in the amplitude of the heat flow; and (iii) a phase difference between the heating rate and the heat flow, the former leading the latter.

2.3. Fourier transformation

A sliding Fourier transformation is made of single cycles of the heating rate and of the heat flow. With typically 600 points per cycle for 40 cycles, the sliding transform is made every 20 points, which would yield 1171 points (after truncation) for the transformed variables over the 20 K temperature interval. The Fourier transformation gives the following quantities:

$\langle q \rangle$ = average value of heating rate ($= q_{\mathrm{av}}$)

$\langle \mathrm{HF} \rangle$ = average value of heat flow

A_q = amplitude of heating rate

A_{HF} = amplitude of heat flow

ϕ = phase angle between heating rate and heat flow.

From these transformed quantities, various different heat capacities can be defined. Adopting the approach suggested by Schawe [10], one can define an 'average' or 'total' heat capacity, $\langle C_{\mathrm{p}} \rangle$ or $C_{\mathrm{p,ave}}$, and a complex heat capacity, C_{p}^*, the latter being separated into real (in-phase), C_{p}', and imaginary (out-of-phase) C_{p}'' components, as follows:

$$\langle C_{\mathrm{p}} \rangle = C_{\mathrm{p,ave}} = \langle HF \rangle / \langle q \rangle \tag{5}$$

$$C_{\mathrm{p}}^* = A_{HF}/A_q \tag{6}$$

$$C_{\mathrm{p}}' = C_{\mathrm{p}}^* \cos\phi \tag{7}$$

$$C_{\mathrm{p}}'' = C_{\mathrm{p}}^* \sin\phi \tag{8}$$

Alternatively, one can define reversing and non-reversing components, $C_{\mathrm{p,rev}}$ and $C_{\mathrm{p,non-rev}}$, respectively, as follows:

$$C_{\mathrm{p,rev}} = A_{\mathrm{HF}}/A_q \tag{6$'$}$$

$$C_{\mathrm{p,non\text{-}rev}} = \langle C_{\mathrm{p}} \rangle - C_{\mathrm{p,rev}} \tag{9}$$

It should be noted that $C_{\mathrm{p,rev}}$ is identical to the complex heat capacity, C_{p}^*, and is approximately equal to the in-phase component, C_{p}', when the phase angle ϕ is small, which is the case in the glass transition region; thus, at the glass transition, the values of $C_{\mathrm{p,rev}}$, C_{p}^*, and C_{p}' will be essentially indistinguishable. On the other hand, $C_{\mathrm{p,non\text{-}rev}}$ and C_{p}'' are certainly not equal in the glass transition region, as has been shown previously [10].

3. Results and discussion

The foregoing analysis has used to predict the response to modulated heating and cooling through

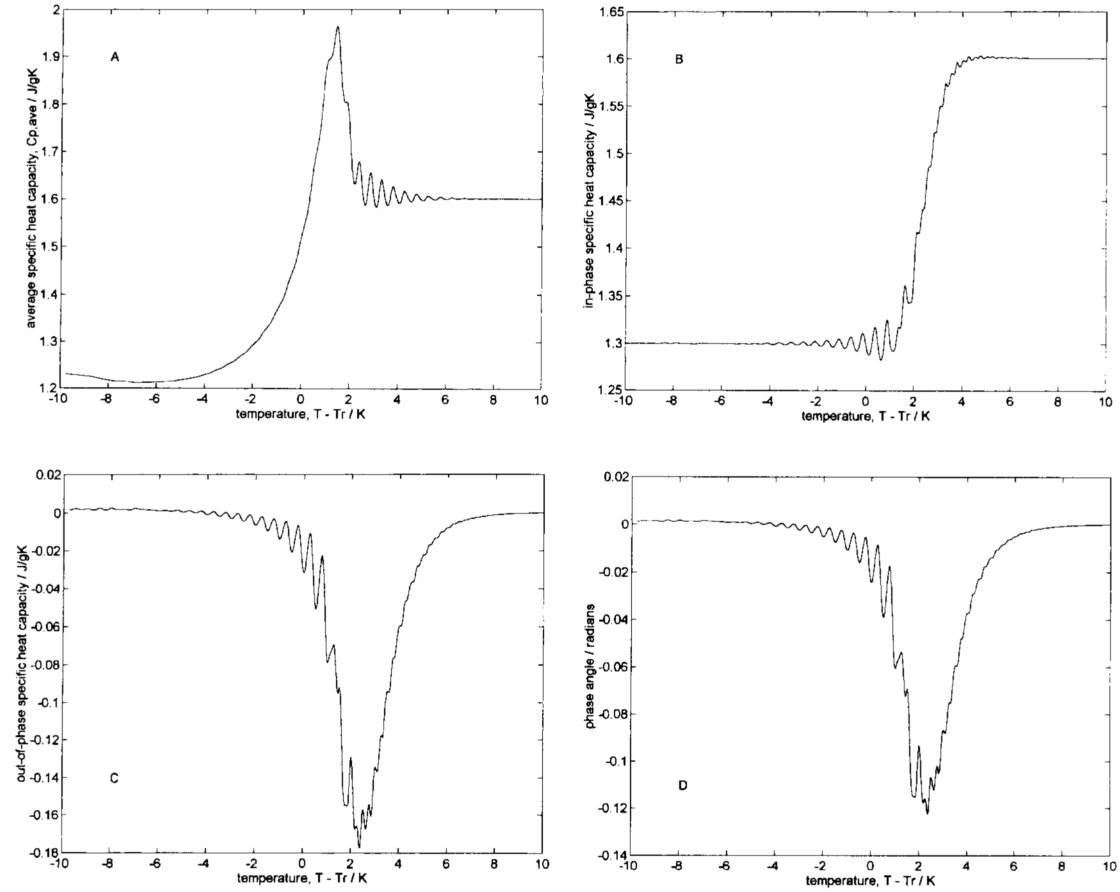

Fig. 1. Model predictions for : (a) $C_{p,ave}$; (b) C'_p; (c) C''_p ; and (d) ϕ. Modulation conditions : $t_p = 60$ s; $q_{av} = 0.5$ K min^{-1}; $A_T = 0.25$ K; and $\delta_0 = 3.0$ J g^{-1}.

the glass transition region for various combinations of the experimental variables (period, q_{av} and A_T) and conditions (δ_0). For example, a typical result is shown in Fig. 1. These curves show all the features obtained previously [6,7], but now with additional detail. In particular, there are clear modulations in these unsmoothed traces, which are also seen in unsmoothed experimental data. In the transition interval, the frequency of these modulations is twice the frequency of the heating rate modulations, for both the model predictions and the experimental data. The analysis of these modulations in the transformed data is the subject of a separate paper in this issue [11].

Because the curves such as those shown in Fig. 1 are now quasi-continuous, it is possible to examine more precisely than before [6,7] the predictions for the effects of some of the experimental variables and material parameters. Here, we present the results for three of these: the period, the amount of annealing prior to the heating scan, and the non-linearity parameter x.

3.1. Effect of modulation period

A ‘mid-point glass transition temperature’, T_{mid}, is defined as the temperature at which the in-phase heat capacity, C'_p, passes midway between the glassy and liquid-like values. When this temperature is examined as a function of the modulation period in the modelling of both heating and cooling experiments, it is found that T_{mid} decreases as the period increases. This is illustrated in Fig. 2, where $T_{mid} - T_r$ is plotted as a function of ln (t_p), and it can be seen that there is a good agreement between the values for heating and

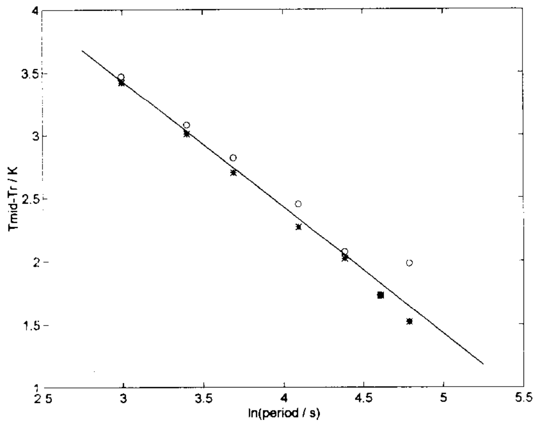

Fig. 2. Model predictions for dependence of $T_{\mathrm{mid}} - T_{\mathrm{r}}$ on $\ln(t_{\mathrm{p}})$ for both heating (circles) and cooling (asterisks) experiments. The full line is drawn with slope $-\theta$. Parameter values: $q_{\mathrm{av}} = \pm 0.5\,\mathrm{K\,min^{-1}}$; $A_T = 0.25\,\mathrm{K}$; $T_0 - T_r = \pm 10\,\mathrm{K}$; and $\delta_0 = 3.0\,\mathrm{J g^{-1}}$ (heating) or $0\,\mathrm{J\,g^{-1}}$ (cooling).

cooling experiments. Furthermore, the full line represents a slope of $-\theta$ and well describes the dependence, implying that a value of θ and, hence, of activation energy, can be obtained from such experimental data. This kind of behaviour has been observed experimentally [4,5,12], but the range of periods (or frequencies) available in temperature-modulated DSC is rather limited, so that the accuracy of determination of the activation energy in this way is compromised; the so-called 'fictive temperature method' [13] in conventional DSC remains a better method for its evaluation.

It is interesting also to examine the relationship between period and cooling rate in respect of their effects on T_{mid}, since T_{mid} depends on both $\ln(t_{\mathrm{p}})$ and $-\ln(|q_{\mathrm{av}}|)$ in the same way. Defining a glass transition temperature, T_{g}, as the temperature at which C_{p} passes midway between $C_{\mathrm{p,l}}$ and $C_{\mathrm{p,g}}$ on cooling at constant rate in conventional DSC, the difference Δ between $\ln(t_{\mathrm{p}})$ and $-\ln(|q_{\mathrm{av}}|)$ in order to obtain $T_{\mathrm{mid}} = T_{\mathrm{g}}$ is shown in Table 1 as a function of the non-linearity parameter x. This relationship between period and cooling rate has been derived theoretically by Donth [14,15] on the basis of a fluctuation model for the glass transition, and can be written as:

$$t_{\mathrm{p}}|q_{\mathrm{av}}| = 2\pi a \delta T \tag{10}$$

with period in units of seconds and cooling rate in units of $\mathrm{Ks^{-1}}$. In this equation, δT is the mean temperature fluctuation, of the order of 2 K, and a is a constant, of the order of unity. Using Eq. (10), values of $a\delta T$ have been calculated, and are included in Table 1. From these results, it can be seen that $a\delta T$ decreases with increasing x, implying that the temperature fluctuations are greater for the more non-linear glassy systems, as would be anticipated intuitively. In fact, x has much more effect on the shape of the $C_{\mathrm{p}} - T$ curve in conventional DSC, broadening the transition region as x decreases, than it does on the $C'_{\mathrm{p}} - T$ curve in temperature-modulated DSC. Within the range of values of x normally encountered for polymer glasses (0.3 → 0.6), the values of $a\delta T$ listed in Table 1 agree well with the mean temperature fluctuation $\delta T = 2.5\,\mathrm{K}$ found by Hensel et al. [5] for polyvinyl acetate if the constant a is of the order of unity, as is expected [14].

Table 1
Difference, Δ, between $\ln(t_{\mathrm{p}}/\mathrm{s})$ and $-\ln(|q_{\mathrm{av}}|/\mathrm{K\,s^{-1}})$ to obtain $T_{\mathrm{mid}} = T_{\mathrm{g}}$, and temperature fluctuation term $a\delta T$ [5,14,15] as function of non-linearity parameter x

x	Δ	$a\delta T/\mathrm{K}$
0.2	3.70	6.44
0.3	3.45	5.01
0.4	3.25	4.10
0.6	2.85	2.75
1.0	2.40	1.75

3.2. *Effect of annealing*

Temperature-modulated DSC scans from an initial temperature $T - T_{\mathrm{r}} = -10\,\mathrm{K}$ have been modelled for various different conditions defined by the initial excess enthalpy, δ_0. The reference, 'unannealed', state is taken as that with $\delta_0 = 3.0\mathrm{Jg^{-1}}$, which corresponds approximately to cooling at $-5\mathrm{K\,min^{-1}}$ from equilibrium at $T_{\mathrm{r}} + 10\,\mathrm{K}$, with the usual material parameter values. Annealing is effected by reducing the value of δ_0. A typical example of the effect of annealing on the out-of-phase heat capacity is shown in Fig. 3 for two different values of δ_0. It can be seen that, as δ_0 decreases, the transition narrows, and C''_{p} departs increasingly from zero; the same effect is seen for the phase angle ϕ, while the in-phase heat capacity also shows a narrowing of the transition. Experimental data showing these effects have been obtained by

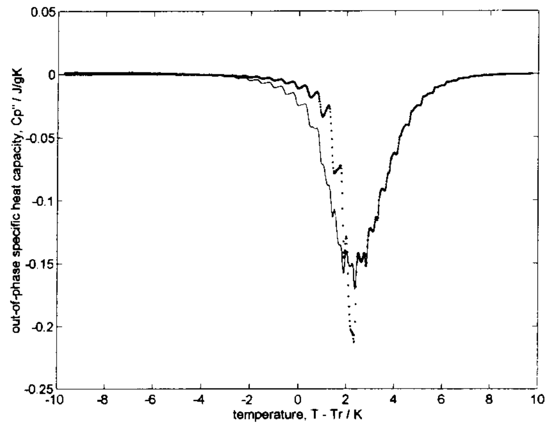

Fig. 3. Model predictions for the effect of annealing on C''_p for the following modulation conditions: $q_{av} = 0.5\,K\,min^{-1}$; $t_p = 60\,s$; $A_T = 1.0\,K$; and for two different values of initial excess enthalpy: $\delta_0 = 3.0\,Jg^{-1}$ ('unannealed'), full line; $\delta_0 = 1.8\,Jg^{-1}$, dotted line.

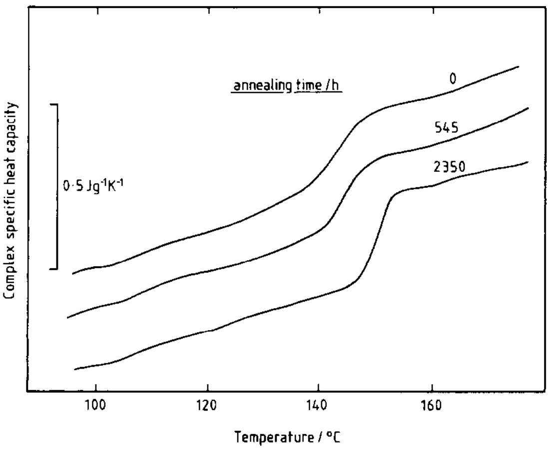

Fig. 4. Complex specific heat capacity of polycarbonate as a function of annealing time (shown against each curve, in hours) at 120°C. Data obtained using Mettler–Toledo ADSC with $q_{av} = 1\ K\ min^{-1}$, $A_T = 0.5\ K$, and $t_p = 60\,s$. Samples, of ≈12 mg, were in the form of discs, 5 mm diameter and 0.5 mm thick, machined from solid polycarbonate (Tecanat, Ensinger GmbH) rod of 40 mm diameter.

Schawe [3] for polystyrene and also in the present work for polycarbonate (see Fig. 4).

The area differences under the C''_p and $C_{p,ave}$ curves, relative to the unannealed state, have been evaluated for increasing amounts of annealing, $\Delta\delta_0$, and are plotted in Fig. 5 as a function of $\Delta\delta_0$. As expected, since $C_{p,ave}$ corresponds closely to C_p from a conventional DSC experiment, the area difference for $C_{p,ave}$ is essentially equal to the enthalpy loss on annealing, as indicated by the full line with slope unity. On the other hand, the area difference for C''_p is essentially constant for enthalpy losses up to 1.4 Jg^{-1}, increasing slightly for greater losses. In fact, this slight increase for C''_p at large values of $\Delta\delta_0$ reduces as the period is reduced, and is likely to be a result of insufficient periods in the transition region which, as has already been pointed out, narrows significantly with increasing annealing. The interesting observation from these results is therefore that the area under the peak of the out-of-phase component of the complex specific heat capacity is not related to the enthalpic state of the sample.

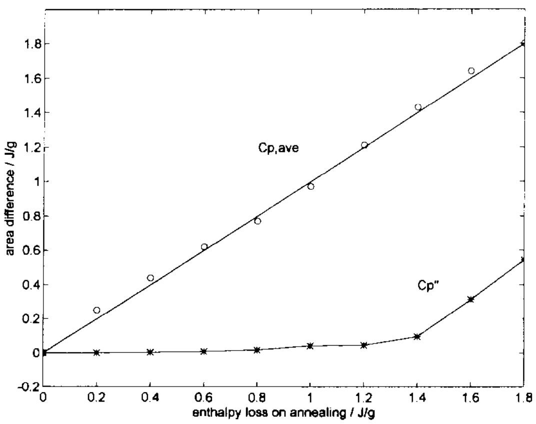

Fig. 5. Differences in area under (○) $C_{p,ave}$, and (*) C''_p traces, relative to the unannealed curve ($\delta_0 = 3.0\,Jg^{-1}$), as a function of the enthalpy loss during annealing, $\Delta\delta_0$. The temperature-modulated DSC conditions were: $q_{av} = 0.5\ K\ min^{-1}$, $A_T = 0.25\ K$, and $t_p = 60s$.

3.3. *Effect of non-linearity parameter*

The non-linearity parameter, x, is determined by the particular glassy material under investigation, and is not a parameter that can be varied experimentally. It is interesting, however, to examine its effect on the temperature-modulated DSC response, in order to predict the behaviour of glasses with different x values. Fig. 6 shows the model response on cooling from equilibrium at $T - T_r = 10\,K$, for two extreme values of x (0.2 and 1.0), from which it can be seen that the transition in C''_p is broadened slightly as x decreases. To examine the effect of x on the response

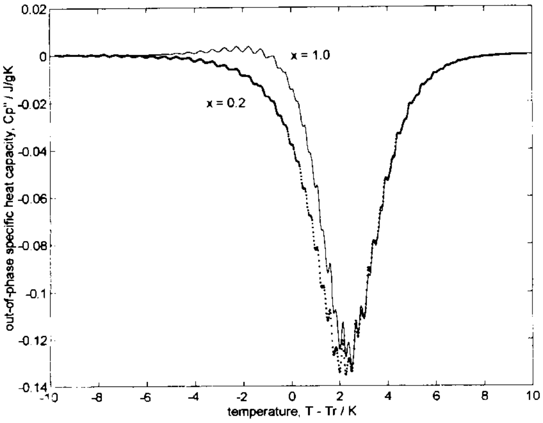

Fig. 6. Response of out-of-phase specific heat capacity during cooling with the following parameter values: $q_{\mathrm{av}} = -0.5\,\mathrm{K\,min^{-1}}$, $A_T = 0.5\,\mathrm{K}$, $t_{\mathrm{p}} = 60\,\mathrm{s}$, and $\delta_0 = 0\mathrm{Jg^{-1}}$. Full line $x = 1.0$; dotted line $x = 0.2$.

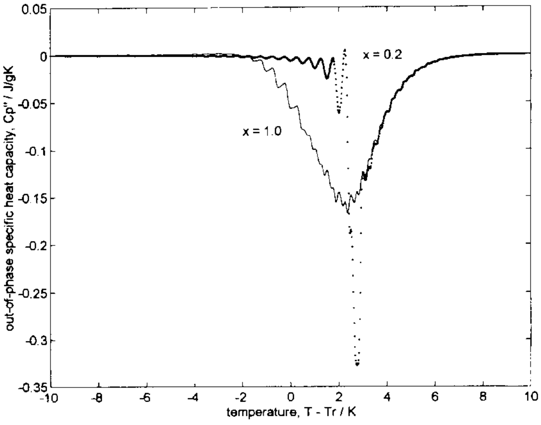

Fig. 7. Response of out-of-phase specific heat capacity during heating with the following parameter values: $q_{\mathrm{av}} = 0.5\,\mathrm{K\,min^{-1}}$, $A_T = 0.5\,\mathrm{K}$, $t_p = 60s$, and $\delta_0 = 2.7865\,\mathrm{Jg^{-1}}$ for $x = 1.0$ (full line), or $\delta_0 = 2.1472\,\mathrm{Jg^{-1}}$ for $x = 0.2$ (dotted line).

on heating is more difficult, since the heating trace depends on the initial state (see previous section), which itself depends on x through the influence of x on the prior cooling state (cf. Fig. 6). The easiest approach is to consider 'intrinsic cycles' [9], for which the heating scan immediately follows the cooling stage, with no annealing. Such intrinsic heating scans, immediately following the cooling stages relevant to Fig. 6, are shown in Fig. 7 for the same values of x (0.2 and 1.0). The most obvious feature from a comparison of Figs. 6 and 7 is that, on heating, the effect of decreasing x is to sharpen rather than broaden the response. This is an example of the asymmetry [16] introduced by the non-linearity parameter. Also the greater magnitude of the absolute departure of C''_{p} from zero for $x = 0.2$ implies that the phase angle departs from zero on heating by a greater amount for $x = 0.2$ than it does for $x = 1.0$. This results from the more rapid approach to equilibrium of the enthalpy in the former case by virtue of the greater non-linearity.

The absolute magnitudes of the areas under these C''_{p} peaks are as follows: 0.37 J g^{-1} and 0.54 J g^{-1} for $x = 1.0$, and 0.47 J g^{-1} and 0.35 J g^{-1} for $x = 0.2$, for the cooling and heating stages, respectively. Since these are intrinsic cycles, the difference between the areas (heating–cooling) under the average specific heat capacity, $C_{\mathrm{p,av}}$, curves for each value of x would be (and indeed is) zero, as there is no enthalpy loss at $T - T_{\mathrm{r}} = -10\,\mathrm{K}$.

The present results show, in contrast, that the circular integral of the imaginary component of the complex specific heat capacity, C''_{p} , is positive (+0.17 J g^{-1}) for $x = 1.0$ but negative (−0.12 J g^{-1}) for $x = 0.2$. This may have implications for the interpretation of the physical significance of C''_{p} in terms of entropy changes during the modulations. To understand these changes, we must return to fundamental thermodynamics [e.g. [17]], and recognise that the change of entropy of a closed system is:

$$\mathrm{d}S = \mathrm{d}S_{\mathrm{i}} + \mathrm{d}S_{\mathrm{e}} \tag{11}$$

where $\mathrm{d}S_{\mathrm{i}}$ is the entropy generated in the system as a consequence of irreversible processes, and $\mathrm{d}S_{\mathrm{e}}$ the thermal entropy flux due to the exchange of heat (δQ). Thus:

$$\mathrm{d}S = \mathrm{d}S_{\mathrm{i}} + \frac{\delta Q}{T} \tag{12}$$

For reversible processes, $\mathrm{d}S_{\mathrm{i}} = 0$ and $\mathrm{d}S = \delta Q/T$. For cyclic reversible processes:

$$\oint \mathrm{d}S \equiv \oint \frac{\delta Q}{T} = 0 \tag{13}$$

whereas for cyclic irreversible processes:

$$\oint \mathrm{d}S \equiv \oint \mathrm{d}S_{\mathrm{i}} + \oint \frac{\delta Q}{T} = 0 \tag{14}$$

On the other hand, the work dissipated during the irreversible process is related to the entropy generated:

$$d|W_{\mathrm{diss}}| = TdS_{\mathrm{i}} \tag{15}$$

and

$$|W_{\mathrm{diss}}| = \int T\mathrm{d}S_{\mathrm{i}} \tag{16}$$

which must always be a positive value for an irreversible process. Now, according to Schawe [18] the entropy production during one cycle, under quasi-isothermal conditions (underlying heating rate = 0), is:

$$\Delta S_{\mathrm{i}} = 2\pi C''_{\mathrm{p}} \tag{17}$$

while according to Schawe and Höhne [19], the work dissipated is:

$$|W_{\mathrm{diss}}| \propto A_T C''_{\mathrm{p}} \tag{18}$$

where C''_{p} is, presumably, an average value for the cycle. We calculate the circular integral of C''_{p} which may be written $\oint C''_{\mathrm{p}} dT$, which (from Eq. (18)) is proportional to the work dissipated in the complete intrinsic cycle (cooling and heating stages, starting and finishing in equilibrium at the same temperature above T_{g}) as a consequence of the irreversibility of the process, and is also proportional to the circular integral $\oint T\mathrm{d}S_{\mathrm{i}}$. Thus, we may write:

$$m \oint C''_{\mathrm{p}}\mathrm{d}T \equiv \oint T\mathrm{d}S_{\mathrm{i}} = |W_{\mathrm{diss}}| \geq 0 \tag{19}$$

where m is a constant of proportionality. The thermodynamic requirement is, therefore, that $\oint C''_{\mathrm{p}}\mathrm{d}T$ be positive, whereas the model predicts a negative result for small values of x. This could be interpreted as implying forbidden values of x at the lower end of the range (approaching zero), though the model predictions in this respect will almost certainly depend on the existence of a distribution of relaxation times (not included in the present single relaxation time analysis). It is interesting to note, though, that values of x as low as 0.2 are not often reported in the literature, and that some very low values have not always been supported by other workers (e.g. compare the value $x = 0.10$ for polyvinyl chloride found by Hodge [20] with $x = 0.27$ obtained for the same polymer by Pappin et al. [21]).

4. Conclusions

The present model of the response of glasses to temperature-modulated DSC in the transition region gives quasi-continuous curves for the various specific heat capacities, $C_{\mathrm{p,av}}$, C'_{p}, C''_{p}, and the phase angle ϕ. The model response correctly describes typical experimental data, and can be used to predict the effects of some of the parameters; here, these are the period, the amount of annealing, and the non-linearity parameter.

As was shown previously, the model predicts a decreases in T_{mid} with increasing ln (t_{p}), quantitatively similar to the decrease of T_{g} with decreasing $\ln(|q_{\mathrm{av}}|)$. By analysing these dependences for different values of x, the relationship between period and cooling rate has been compared with the predictions of Donth's fluctuation model of the glass transition. This comparison yields magnitudes of temperature fluctuations which increase in the approximate (2–6) K range as x decreases, of the same magnitude as those reported earlier [5].

The effect of annealing is to cause the area under the $C_{\mathrm{p,av}}$ peak to increase by just the amount of enthalpy lost during annealing, as for conventional DSC, thus confirming the equivalence between $C_{\mathrm{p,av}}$ from temperature-modulated DSC and C_{p} from conventional DSC. On the other hand, the area under the C''_{p} peak remains essentially constant with annealing, indicating that the out-of-phase component of the complex heat capacity is not related to the enthalpic state of the glass.

Finally, the effect of non-linearity in intrinsic cycles is shown to introduce an asymmetry in the response: the peak in C''_{p} on cooling broadens as x decreases, whereas it sharpens on heating. In addition, the area difference under the C''_{p} peaks on heating and cooling depends on the value of x, and can even be of opposite sign for different values of x. This may have implications for the interpretation of the significance of C''_{p} in terms of entropy changes during the modulation periods.

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