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A phenomenological model for the enthalpy relaxation of glasses.
Part 2. Effects of a continuous distribution of relaxation times

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Abstract

A multiordering parameter model for the relaxation behaviour of glasses around the glass-transition region is presented. This paper is intended as a generalization of the single order parameter models presented in the first part of this work. It is assumed that each order parameter is associated with a relaxation time of the form suggested by Narayanaswamy and we have adopted a continuous distribution of these relaxation times defined by a single Williams–Watts parameter β. Computer simulations permit predictions of the fictive temperature evolution of glasses, subjected to arbitrary temperature–time histories, in terms of material constants and kinetic parameters such as the activation energy E_a, or the partition factor x. Furthermore, the present model adequately fits the available experimental data obtained from DSC experiments on amorphous selenium and allows us to analyse memory effects (i.e. crossover experiments).

INTRODUCTION

In a previous paper [1] reported as the first part of this work, we have shown that the main features of the enthalpic relaxation around the glass transition can be accounted for by a simple model combining the Kovacs equation and the Narayanaswamy expression for a single relaxation time. Comparisons with DSC measurements performed on amorphous selenium showed good agreement. However, this one parameter theory completely fails to describe the memory effects [2–4] manifested as the influence of heat treatments on the future behaviour of the glass. Otherwise, the agreement with the results on a limited class of experiments was only qualitative. In order to introduce a distribution of relaxation times into the analysis, Kovacs et al. [2] adopted a series of N ordering parameters each

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of which is associated with a specific fraction δ_i of the total departure of the equilibrium δ, so that

$$\delta = \sum_i^N \delta_i$$

The evolution of each δ_i is governed by a kinetic equation

$$\frac{\mathrm{d}\delta_i}{\mathrm{d}t} = -\delta_i/\tau_i - \Delta C_{pi} q \qquad (i = 1, \ldots, N)$$

where ΔC_{pi} is the contribution of the ith process to the total difference between the heat capacity of the liquid and the glass (ΔC_p), q is the heating or cooling rate (depending on the sign) and τ_i is the relaxation time corresponding to the ith process. In the present work we have assumed a relaxation time which depends on both temperature and configuration [5] through

$$\tau_i(T,\delta) = \tau_{i0} \exp(xE_a/kT) \exp((1-x)E_a/kT_f)$$

where x is a partition factor ($0 < x \leqslant 1$), E_a the activation energy near the equilibrium, and T_f is the fictive temperature.

The relaxation time can be handled as follows

$$\begin{aligned}\tau_i(T,\delta) &= \tau_i(T_r,0)\frac{\tau_i(T,0)}{\tau_i(T_r,0)}\frac{\tau_i(T,\delta)}{\tau_i(T,0)}\\ &= \tau_{ir} a_T a_\delta\end{aligned}$$

$\tau_{ir} = \tau_i(T_r,0)$ being the ith relaxation time at a reference temperature T_r in equilibrium; a_T is a temperature-dependent shift factor at equilibrium and a_δ is the structure-dependent shift factor at constant temperature. Hence it is assumed that the relaxation times for the various order parameters differ only in the pre-exponential factor, a condition frequently designated as "thermorheologically simple behaviour".

The set of differential equations mentioned above is called the Kovacs–Aklonis–Hutchinson–Ramos (KAHR) equations [2]. This set of N equations together with the initial conditions

$$\delta_i(t) = \delta_{i0}$$

for $t = t_0$ ($i = 1, \ldots, N$) govern the time and temperature dependence of the system when subjected to any arbitrary thermal history.

The aim of this paper is to assume a continuous integral representation of the set of KAHR equations in order to explore the consequences of a distribution of relaxation times and to compare the theoretical predictions with the calorimetric cyclic experiment on amorphous selenium reported in the previous paper [1]. The numerical simulations were performed by the iterative method proposed by Chow and Prest [6].

THE FUNDAMENTAL EQUATIONS

We have adopted the Narayanaswamy expression [5] for the relaxation times τ_i. Therefore, we write

$$\tau_{i\mathrm{r}} = \tau_{i0} \exp(E_\mathrm{a}/kT_\mathrm{r})$$

$$a_T = \exp\left(E_\mathrm{a}/k\left(\frac{1}{T} - \frac{1}{T_\mathrm{r}}\right)\right)$$

$$a_\delta = \exp\left(-(1-x)E_\mathrm{a}/k\left(\frac{1}{T} - \frac{1}{T_\mathrm{f}}\right)\right)$$

$$a(T,\delta) = a_T a_\delta$$

After examining these expressions it is evident that the KAHR equations cannot be integrated analytically. Nevertheless, they constitute an "autonomous system" [2,7] which is easily simplified. One can introduce the "reduced time" variable as

$$u(t,t') = \int_{t'}^{t} \frac{\mathrm{d}t''}{a[T(t''),\delta(t'')]}$$

$$\frac{\mathrm{d}u}{\mathrm{d}t} = a(T,\delta)^{-1}$$

In terms of u, the KAHR equations for the isothermal case become

$$\frac{\mathrm{d}\delta_i}{\mathrm{d}u} = -\delta_i/\tau_{i\mathrm{r}}$$

which represent a linearized system whose integrations yield

$$\delta_i(u) = \delta_{i0} \exp\left(-\frac{u(t,t_0)}{\tau_{i\mathrm{r}}}\right)$$

By summing the individual contributions we obtain the total departure from equilibrium

$$\delta(u) = \sum_{i=1}^{N} \delta_{i0} \exp(-u/\tau_{i\mathrm{r}}) = \delta_0 \sum_{i=1}^{N} g_i \exp(-u/\tau_{i\mathrm{r}}) = \delta_0 \phi(u)$$

where $g_i = \delta_{i0}/\delta_0 = \Delta C_{pi}/\Delta C_p$ satisfies the normalization condition $\sum_i^N g_i = 1$, and $\phi(u) = \phi(t,t_0)$ is the response function.

According to Chow and Prest [6], when N is large and g_i very small, the solution of the linearized KAHR equations for the non-isothermal case ($q \neq 0$) is

$$\delta_i(t) = \delta_{i0} \exp(-u(t,t_0)/\tau_{i\mathrm{r}}) - \Delta C_{pi} q \int_{t_0}^{t} \exp(-u(t,t')/\tau_{i\mathrm{r}})\, \mathrm{d}t'$$

$$(i = 1, \ldots, N)$$

Therefore, by summing all the individual terms we obtain

$$\delta(t) = \delta_0 \phi(t,t_0) - \Delta C_p q \int_{t_0}^{t} \phi(t,t')\,\mathrm{d}t'$$

The above equation, for both isothermal ($q = 0$) and non-isothermal ($q \neq 0$) treatments, may be adequately written in different forms depending on the parameter chosen to describe the progress of the relaxation. Frequently it is convenient to characterize the change by the fictive temperature T_f at temperature T [8], which is defined by

$$T_\mathrm{f} = T + \delta/\Delta C_\mathrm{p}$$

On inserting the above expression into the equation providing the total departure from equilibrium $\delta(t)$, and taking account of the simple relationship $\mathrm{d}t = \mathrm{d}T/q$, we are left with the fundamental equation

$$T_\mathrm{f}(T) = T + (T_{\mathrm{f}0} - T_0)\phi(T,T_0) - \int_{T_0}^{T} \phi(T,T')\,\mathrm{d}T'$$

which for the isothermal case ($q = 0$) adopts the simpler form

$$T_\mathrm{f}(t) = T_0 + (T_{\mathrm{f}0} - T_0)\phi(t,t_0)$$

and where T_0 and $T_{\mathrm{f}0}$ are the initial conditions.

The integration of the above equations demands that we should propose a model for the response function ϕ. In fact, we have adopted the Williams–Watts expression for $\phi(T,T')$ [6,9]

$$\phi(T,T') = \exp\left(-\left(1/q \int_{T'}^{T} \frac{\mathrm{d}T''}{\tau_0(T'',T_\mathrm{f}(T''))}\right)^{\beta}\right)$$

where β is a constant ($0 < \beta \leqslant 1$); τ_0 follows the Narayanaswamy form and may be expressed as

$$\tau_0 = \gamma \exp\left(\frac{xE_\mathrm{a}}{kT} + \frac{(1-x)E_\mathrm{a}}{kT_\mathrm{f}}\right) = \tau_{0\mathrm{r}} a_T a_\delta$$

$\tau_{0\mathrm{r}}$ being a reference relaxation time at T_r in equilibrium and a_T and a_δ being the corresponding shift factors. At this point our model differs from the model of Chow and Prest [6] in that they adopt the simpler form of Ritland [10] for the relaxation time. As showed by Ngai et al. [11] the characteristic relaxation time τ_0 is coupled with the mean value $\langle \tau \rangle$ by the relation

$$\langle \tau \rangle = (\tau_0/\beta)\,\Gamma(1/\beta)$$

By introducing the non-dimensional parameters

$$A = (T_\mathrm{r} - T)/T_\mathrm{r}$$

$$B = (T_\mathrm{r} - T_\mathrm{f})/T_\mathrm{r}$$

and

$$C = T_{\mathrm{r}} q^{-1} \tau_{0\mathrm{r}}^{-1}$$

one can obtain, for the non-isothermal evolution, the equation

$$B(A) = A - (A_0 - B_0)\phi(A_0, A) + \int_A^{A_0} \phi(A', A)\, \mathrm{d}A'$$

with

$$\phi(A', A) = \exp\left(- \left(C \int_A^{A'} \frac{\mathrm{d}A''}{a(A'', B(A''))} \right)^{\beta} \right)$$

and

$$a(A, B) = a_T(A) a_\delta(B)$$

$$= \exp\left(\frac{E_{\mathrm{a}}}{kT_{\mathrm{r}}} \frac{A}{1 - A} \right) \exp\left(-(1 - x) \frac{E_{\mathrm{a}}}{kT_{\mathrm{r}}} \frac{A - B}{(1 - A)(1 - B)} \right)$$

However, for the isothermal response we have

$$T_{\mathrm{f}}(t/\tau_{\mathrm{D}}) = T_0 + (T_{\mathrm{f}0} - T_0) \exp\left(- \left(\int_{t_0/\tau_{\mathrm{D}}}^{t/\tau_{\mathrm{D}}} \frac{\mathrm{d}t'}{a_\delta(T_{\mathrm{f}}(t'))} \right)^{\beta} \right)$$

with $\tau_{\mathrm{D}} = \tau_{0\mathrm{r}} a_T$.

Because of the strong dependence of the relaxation times upon the structure and temperature we must pay special attention to the stability of the solutions. In order to solve the integral equation we have adopted the iterative method proposed by Chow and Prest [6] and Carnahan [12] where all integrations are evaluated by a double-precision 32-point Gaussian quadrature.

EFFECT OF THE ADJUSTABLE PARAMETERS ON THE C_p VERSUS T DEPENDENCE

The theoretical model exposed above allows us to evaluate the $T_{\mathrm{f}}(T)$ dependence on the basis of four adjustable parameters, namely (i) the partition factor x, (ii) the activation energy E_{a}, (iii) the relaxation time of the Williams–Watts law at a reference temperature $\tau_{0\mathrm{r}}$, and (iv) the fractional exponential decay parameter, β, of the Williams–Watts law.

In order to compare the numerical calculations with the experimental results we have investigated the effect of each adjustable parameter on the $C_p(T)$ dependence during the heating stage of the cyclic experiment described in ref. 1. The conversion of the $T_{\mathrm{f}}(T)$ dependence into the $C_p(T)$ description (the usual in calorimetric experiments) is straightforward

$$C_p(T) = C_{pg} + \Delta C_p\, \mathrm{d}T_{\mathrm{f}}/\mathrm{d}T$$

where C_{pg} is the glassy heat capacity.

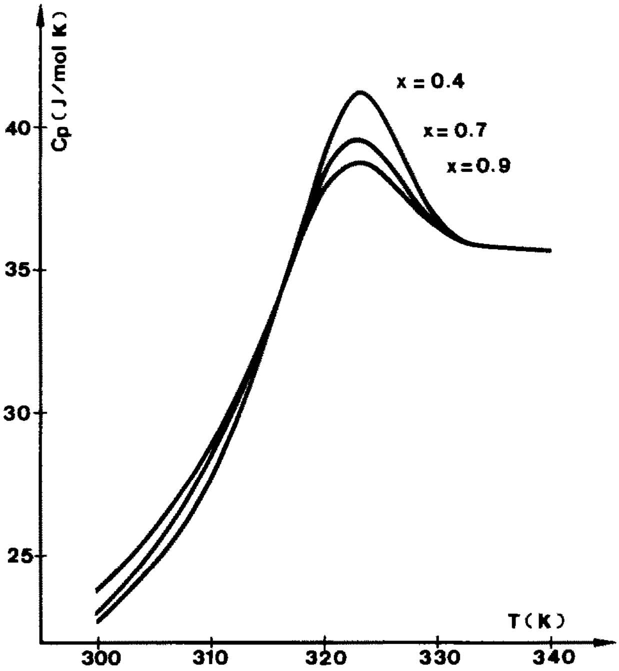

Fig. 1. Temperature dependence of the heat capacity C_p in the glass transition range. The simulated experiments show the effect of the partition parameter x on the $C_p(T)$ curve.

Our numerical calculations attempt to simulate the behaviour of amorphous selenium around the glass transition temperature T_g. We have reported in Table 1 of the first paper [1] the main material constants of this amorphous solid. Unless otherwise specified we adopt the following set of initial values for the adjustable parameters: $x = 0.7$; $E_a = 2.7$ eV at^{-1}; $\tau_{0r} = 4.3 \times 10^{-4}$ s; and $\beta = 0.4$.

Figure 1 illustrates the changes produced in the heat capacity when the partition parameter x is varied about its standard initial value. Sharper peaks are observed for smaller values of x. Nevertheless, the position of the peak is unaffected. Similar results were obtained from the one-parameter model in ref. 1. Figure 2 displays the effect of the activation energy: as the values of E_a are increased a significant shift of the C_p peak towards higher temperatures is observed. Moreover, the C_p peak becomes slightly narrower and the peak height increases. Figure 3 demonstrates the effect of τ_{0r}: as this parameter increases the C_p peak occurs at higher temperatures but its shape remains very nearly unaffected. Finally, Fig. 4 shows the effect of the non-dimensional parameter β: the C_p peak becomes sharper and occurs at lower temperatures as β increases.

In practice we perform an iterative sequence of steps in order to determine the adequate parameters of the model fitting an experimental relaxation maximum: (i) x, E_a and τ_{0r} remain constant while we change β

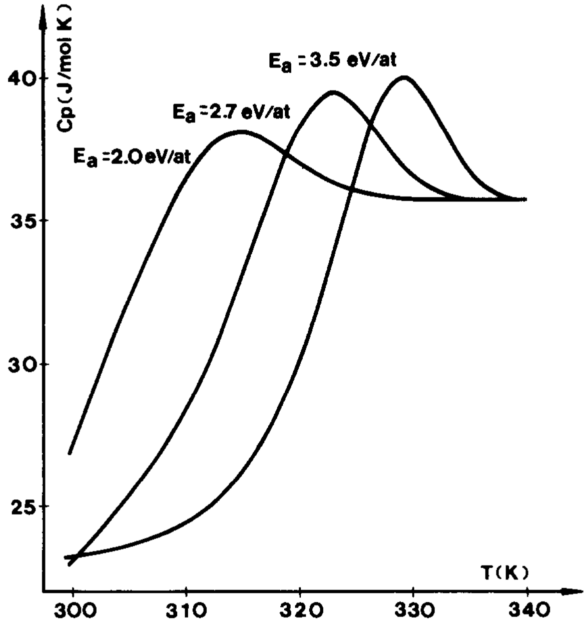

Fig. 2. Heat capacity C_p versus temperature in the region of T_g. The simulated experiments show the effect of the activation energy E_a on the $C_p(T)$ curve.

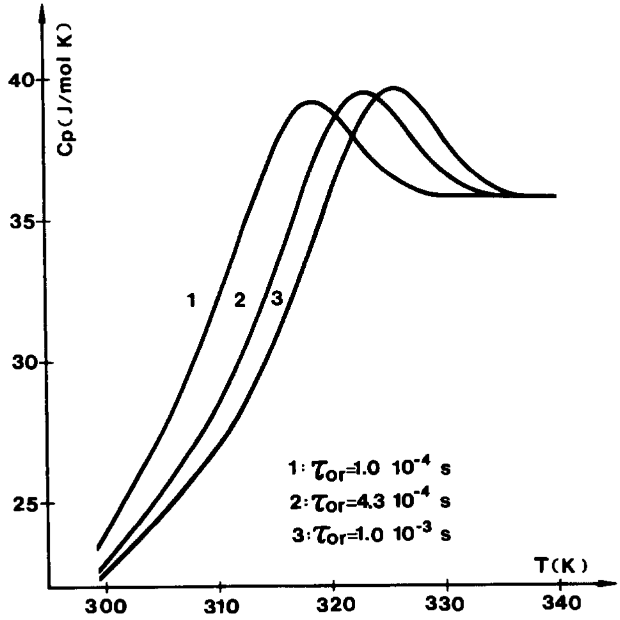

Fig. 3. Temperature dependence of the heat capacity C_p in the glass transition range. The simulated experiments show the effect of τ_{0r} on the $C_p(T)$ curve.

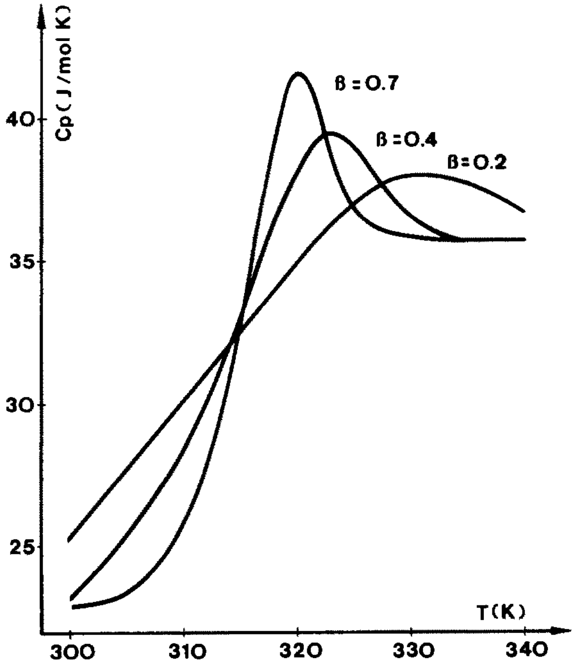

Fig. 4. Heat capacity C_p versus temperature in the region of T_g. The simulated experiments show the effect of the non-dimensional parameter β on the $C_p(T)$ curve.

to adjust the shape of the peak; (ii) then we change E_a and τ_{0r} to adjust the position of the maximum (in fact these parameters do not appreciably affect the shape of the peak); (iii) after that we change the partition parameter x to adjust the height of the peak; and finally (iv) we return to (i) until convergence is ensured.

It is convenient to stress the connection of β with its associated distribution of relaxation times $G(\tau)$

$$\phi(u) = \exp\left(-(u/\tau_{0r})^{\beta}\right) = \int_0^{\infty} G(\tau)(\exp(-u/\tau))\,\mathrm{d}(\ln \tau)$$

At first thought the $G(\tau)$ distribution could be obtained by the Laplace inversion of $\exp(-v^{\beta})$, where $v = u/\tau_{0r}$. Nevertheless, this task is far from a trivial problem. According to Pollard [13] $G(\tau)$ may be obtained as

$$G(s) = (1/\pi)\int_0^{\infty} \exp(-z)\left(\exp\left(-(zs)^{\beta} \cos \pi\beta\right)\right) \sin\left((zs)^{\beta} \sin \pi\beta\right)\,\mathrm{d}z$$

where $s = \tau/\tau_{0r}$ is a non-dimensional variable. This integral may be evaluated by a Gauss–Laguerre quadrature. Figure 5 shows the calculated $G(s)$ distribution for different values of β. It is evident that for larger β the distribution becomes narrower approaching a single relaxation time. An alternative method of obtaining $G(s)$ is due to Cost [14] which considers the solution of a Fredholm integral equation of the first kind by numerical

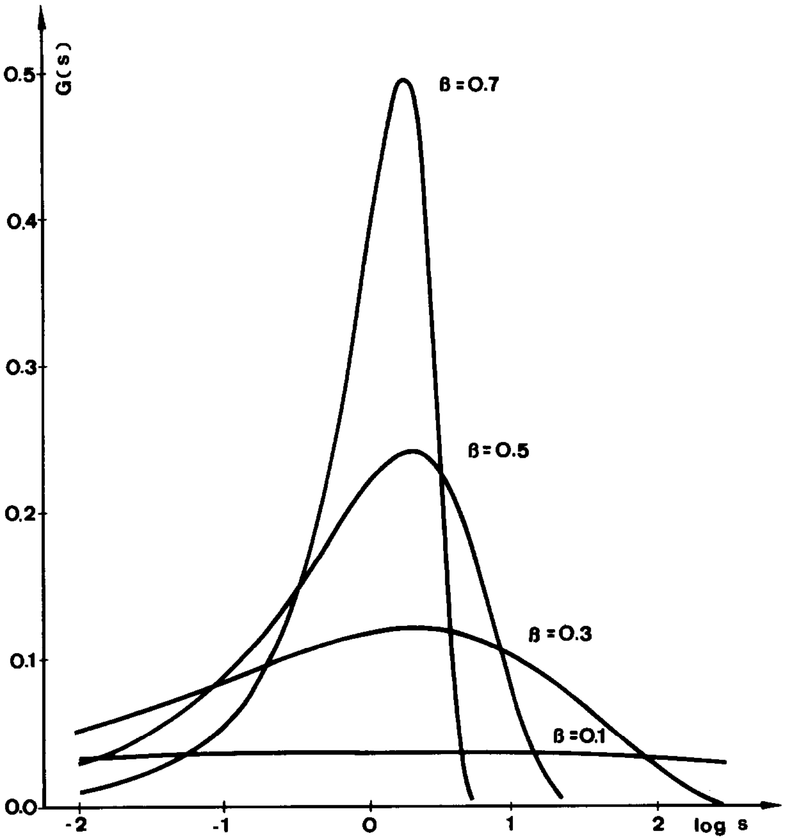

Fig. 5. Distribution of relaxation times for different values of the parameter β of the Williams–Watts law.

computations. His method involves unfolding the integral equation using non-linear regression least-squares.

RESULTS AND DISCUSSION

Theoretical simulations of the cyclic experiment reported in ref. 1 (cooling from equilibrium → ageing → reheating) based on the above equations will be presented and compared with a cyclic DSC experiment on amorphous selenium In Figs. 6 and 7 the calculations were based on the following input parameters: $T_r = 350$ K, $\tau_{0r} = 4.3 \times 10^{-4}$ s, $x = 0.75$, $\beta = 0.5$, $E_a = 2.7$ eV at^{-1}. Both Figs. 6 and 7 depict the $T_f(T)$ representation for several cooling rate/heating rate ratios. Some relevant differences may be found with respect to the same curves evaluated by the simpler models previously presented (figs. 5, 6, 11 and 12 of ref. 1): the fundamental aspect is the widening of the region where the glass transition takes place. This may be explained by considering that the slower processes (those with

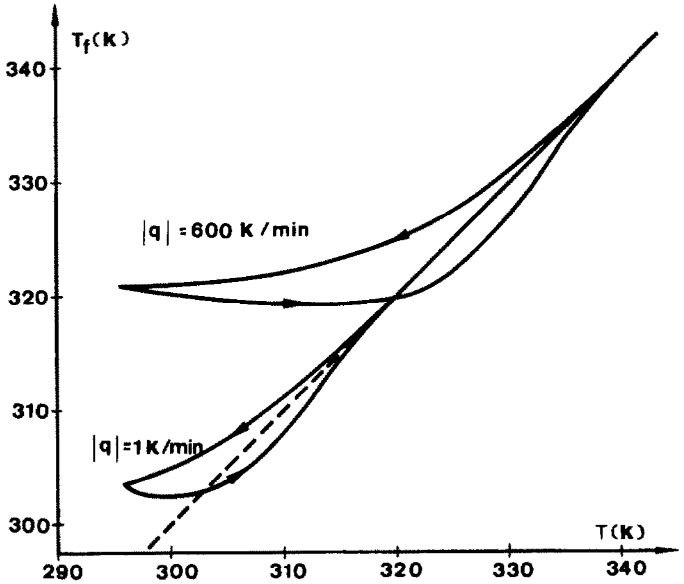

Fig. 6. Fictive temperature versus temperature for several cooling rate/heating rate ratios. Computer simulations of rapid–rapid and slow–slow processes.

larger τ_i) are prematurely frozen, during the cooling step, involving a fast departure from the equilibrium $T_f = T$ line. The opposite effect occurs at the lower threshold of T_g where the faster processes still persist and they

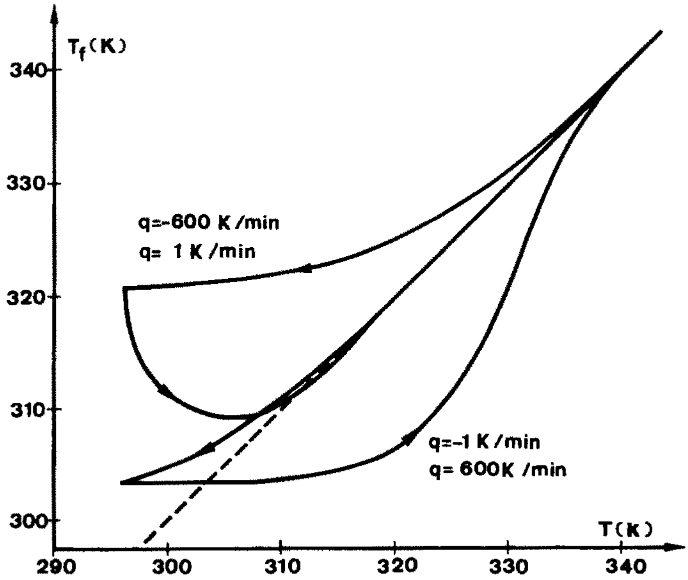

Fig. 7. Fictive temperature versus temperature for several cooling rate/heating rate ratios. Computer simulations of rapid–slow and slow–rapid processes.

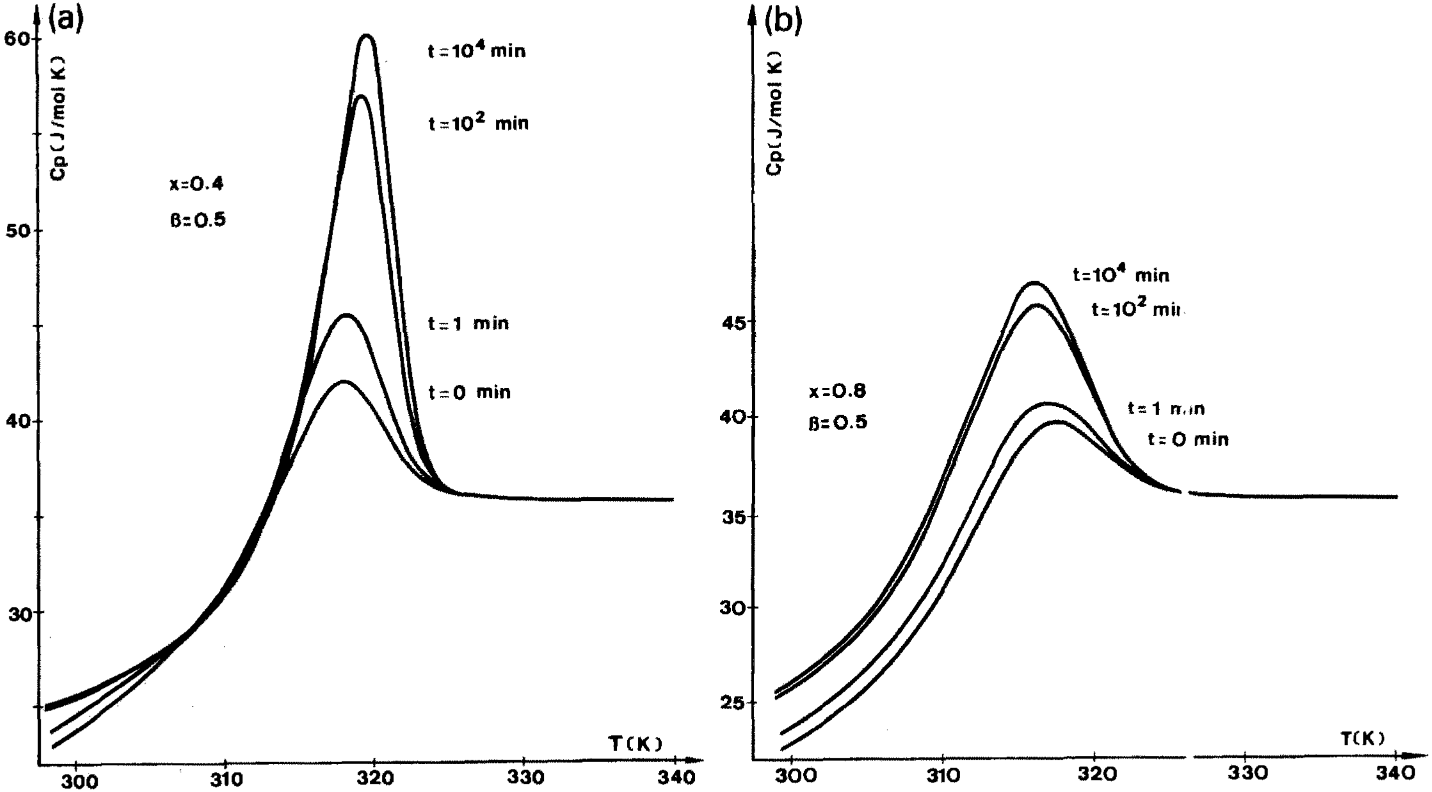

Fig. 8. Heat capacity C_p versus temperature in the region of T_g after different elapsed times at 296 K: (a) computer calculations with $x = 0.4$; (b) computer calculations with $x = 0.8$.

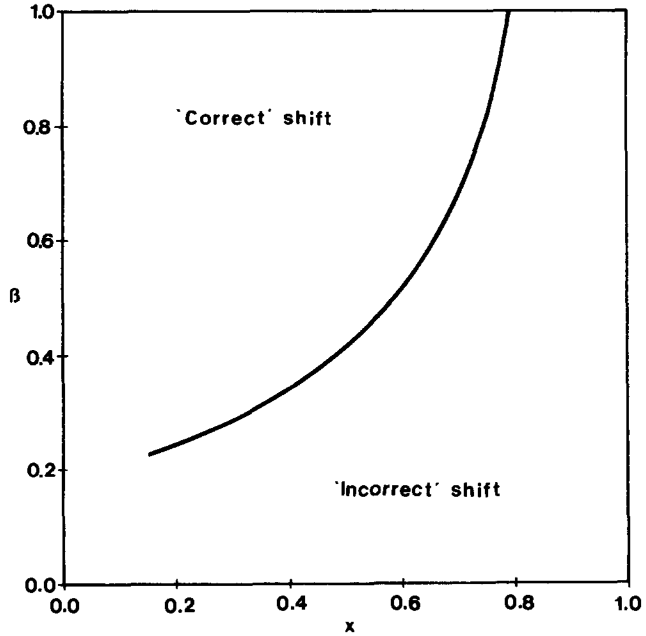

Fig. 9. β versus x regions of "correct" and "incorrect" shift of the temperature at the maximum of the relaxation peak when annealing time increases. Prediction of the model for isothermal holding at the ageing temperature $T_v = 296$ K.

are the last to be quenched. Another relevant feature is the change of curvature at the beginning of the heating line; this behaviour indicates a vigorous initial approach towards the equilibrium which is gradually weaker as we approach it.

Figure 8 (a), (b) illustrates the influence of the isothermal holding at the ageing temperature on the $C_p(T)$ curve. In the first part of this work [1] special attention was devoted to analysing the consequences of the time of isothermal holding during a cyclic experiment on the shift of the relaxation peak. From the single relaxation time model $\tau = \tau(T,\delta)$ already considered, the real importance of the x parameter on the direction of the displacement was evident. Moreover, the universally observed trend indicates that the temperature of the maximum increases as δ decreases (with the progress of relaxation) although a reverse effect was reported for B_2O_3 [15] and more recently for the glassy alloy $GeSe_2$–$GeTe$–Sb_2Te_3 [16]. Our results reveal a correct evolution in Fig. 8(a) with $x = 0.4$ and a reverse one for $x = 0.8$ (Fig. 8(b)). In fact, Fig. 9 displays a β versus x chart where the boundary has been sketched between the "correct" and "incorrect" regions (e.g. for $\beta = 0.5$ a value $x < 0.6$ is required for the correct shift, thus suggesting a pronounced non-linear behaviour). For $\beta = 1$ we go back over the single relaxation time model $\tau = \tau(T,\delta)$ for which we confirm the $x = 0.8$ limit.

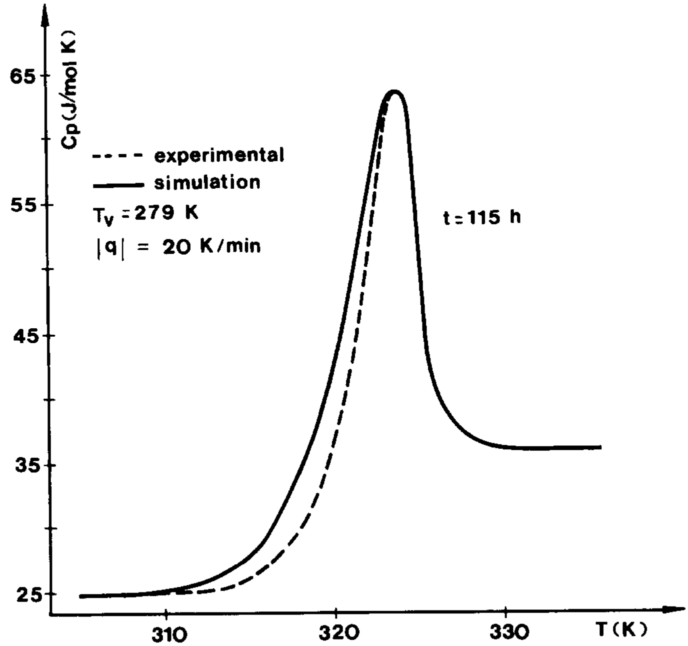

Fig. 10. Heat capacity C_p versus temperature in the region of T_g for an annealing time of 115 h at $T_v = 279$ K: (— — — —) experimental result for amorphous selenium; (———) computer simulation.

Finally, we show in Fig. 10 the best simulation obtained for the abovementioned cyclic experiment (figs. 10 and 15 in ref. 1). The schedule of this experiment included 115 h of isothermal holding at the ageing temperature $T_v = 279$ K. A good agreement may be observed between model predictions and experiment which, in any case, is far better than that obtained for single relaxation time models. The refined parameters obtained from the fit were $\tau_{0r} = 8.1 \times 10^{-4}$ s, $E_a = 2.67$ eV at^{-1}, $x = 0.65$ and $\beta = 0.7$. Subsequent attempts to improve the fit (e.g. to narrow the width of the peak) by varying the model parameters compromise the quality of the fit and were unsuccessful. After examining these results we emphasize the following points.

(i) The activation energy ($E_a = 2.67$ eV at^{-1}) remains much the same just as for the single relation time models $\tau = \tau(T)$ and $\tau = \tau(T,\delta)$. In fact, this kinetic parameter is closely bound up with the observed T_g, as shown in ref. 1.

(ii) The model is satisfactory for describing the kinetics of the phenomena related to the glass transition, at least insofar as the Narayanaswamy form for τ is consistent with the experimental viscosity of the system.

(iii) Since we are considering a distribution of relaxation times, for the theoretical viewpoint the model can account for memory effects. This last point is largely discussed in the next section.

Figure 11 shows the schedule of a crossover experiment involving two consecutive T-jumps of opposite sign. It has been shown [2] that for complex thermal treatments including n consecutive T-jumps, the amount of disequilibrium after the elapsed reduced time u is

$$\delta(u) = -\Delta C_p \sum_{j=1}^{n} \Delta T_j \phi(u - u_{j-1})$$

u_j being the reduced time at the end of the j isotherm.

Then, for the crossover experiment we have

$$\delta(u \geqslant u_1, T_2) = -\Delta C_p((T_1 - T_0)\phi(u) + (T_2 - T_1)\phi(u - u_1))$$

and adopting the T_f representation besides the Williams–Watts form for the $\phi(u)$ response function, we obtain

$$T_f(u \geqslant u_1, T_2) = T_2 - \left((T_1 - T_0)\exp\left(-(u/\tau_{0r})^\beta\right) + (T_2 - T_1)\exp\left(-\left(\frac{u - u_1}{\tau_{0r}}\right)^\beta\right)\right)$$

From the above relationship one can infer the reduced time u_1 of isothermal holding at T_1 so that an instantaneous T-jump allows us to reach T_2 within an initial equilibrium state

$$u_1 = \tau_{0r}\left(\ln\frac{T_0 - T_1}{T_2 - T_1}\right)^{1/\beta}$$

Figure 12 shows the simulation of several crossover experiments, similar to those represented in Fig. 11. The intermediate temperature T_1, in the

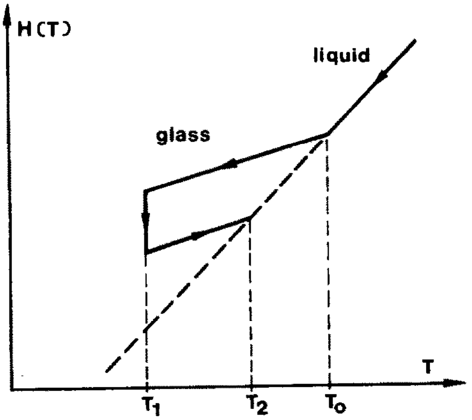

Fig. 11. Schematic diagram of enthalpy versus temperature showing a crossover experiment involving two consecutive T-jumps of opposite sign.

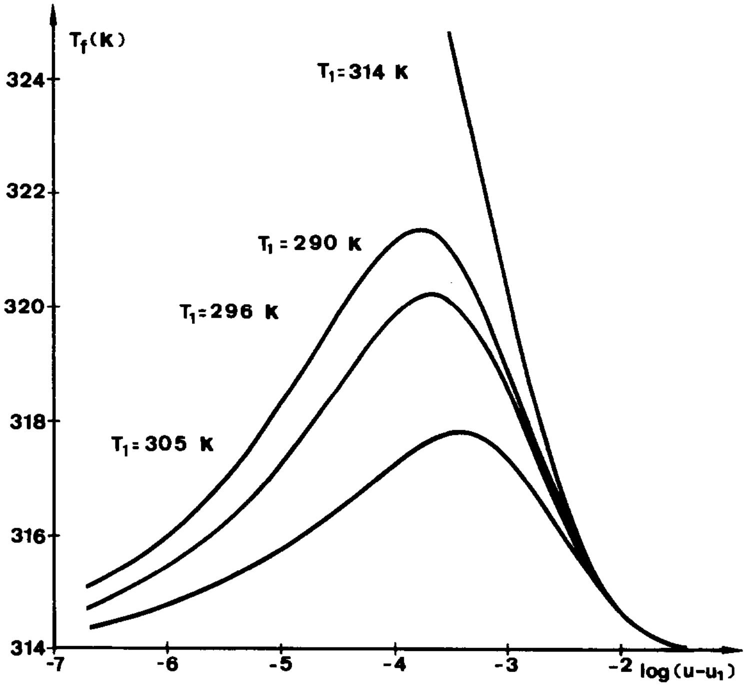

Fig. 12. Fictive temperature T_f versus $\log(u - u_1)$ in crossover experiments. Simulations for several values of the intermediate temperature T_1.

above experiments, was scanned from 290 to 314 K. The parameters of the simulation were $\tau_{0r} = 4.3 \times 10^{-4}$ s, $\beta = 0.4$, $T_0 = 340$ K and $T_2 = 314$ K. From the curves in Fig. 12 we can observe that the system departs from its apparent equilibrium ($T_f = T_2$), passes through a maximum in T_f, which increases in magnitude and occurs at shorter times ($u - u_1$) as T_1 decreases, and then approaches true equilibrium (in fact, $\phi(\infty) = 0$, then we find again $T_f = T_2$). The departure from equilibrium is a consequence of the contribution of all the rapid processes until the contribution of the slow processes compensates this departure and restores the equilibrium.

Furthermore, at long times ($u \gg u_1$) we have $\phi(u) \approx \phi(u - u_1)$; thus

$$T_f(u \gg u_1, T_2) = T_2 - (T_2 - T_0)\phi(u)$$

and this explains why all the isotherms asymptotically approach that obtained by quenching the sample directly from T_0 to T_2 ($T_1 = T_2 = 314$ K).

The influence of β on the evolution of T_f is shown in Fig. 13 for the following parameters. As β increases, involving a narrower distribution of relaxation times, the crossover maximum becomes shallow and vanishes for $\beta = 1$. In fact, for $\beta = 1$ we have

$$\phi(u - u_1) = \phi(u)\frac{T_0 - T_1}{T_2 - T_1}$$

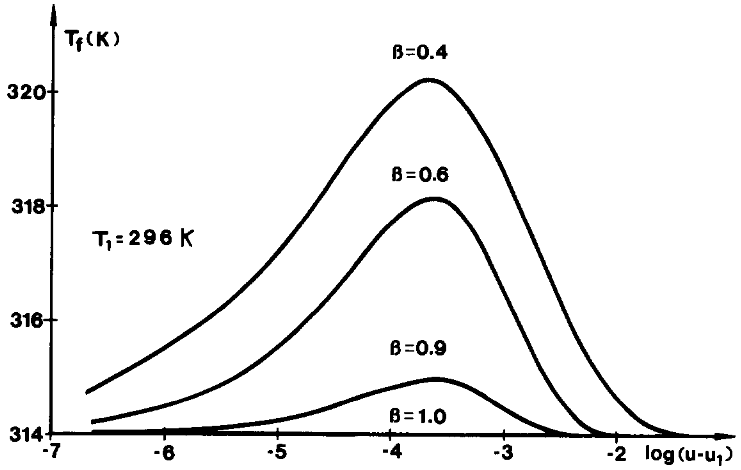

Fig. 13. Fictive temperature T_f versus $\log(u - u_1)$ in crossover experiments. Simulations for several values of the non-dimensional parameter β.

and, consequently, $T_f = T_2 = \text{constant}$. Therefore, for a single relaxation time, the system remains in equilibrium at temperature T_2 and the crossover effect is not observed.

CONCLUSIONS

Our previous work describing the relaxation in glasses (particularly in amorphous selenium) by means of a single relaxation time, has been generalized by allowing for a distribution of relaxation times. We have developed a phenomenological approach of increasing complexity in terms of kinetic parameters such as the activation energy E_a and the partition parameter x both included in the Narayanaswamy expression for the relaxation time. In addition, the general $T_f(T)$ solution is expressed in terms of a distribution of relaxation times characterized by the Williams–Watts parameter β. Moreover, the existence of memory effects requires a distribution of order parameters describing the state of the system. It may well be that order parameters do not have their counterparts in physical reality as underlying processes but rather should be a consequence of a relaxation which is inherently non-exponential. In any case, the relevant matter is that evolution of the order parameters towards equilibrium is kinetically impeded. Comparison between the prediction of this model and a well-known cyclic experiment on enthalpic relaxation was made. The obtained activation energy was very close to that obtained by means of single relaxation time models. Nevertheless, the quality of the fit is far superior for the present model. Furthermore, this study improves our understanding that the relaxation is strongly influenced by the non-equilibrium structural dependent part of the relaxation time. Finally, and as pointed out in our previous work, the activation energy obtained from the simulations supports the view that the breaking and reconstruction of trigonal chains plays the dominant role in the relaxation of amorphous selenium.

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