Defect diffusion model for volume and enthalpy recovery in amorphous polymers

J. Perez
Groupe d'Etudes de Métallurgie Physique et Physique des Matériaux, UA CNRS 341, INSA, Bât. 502, 69621 Villeurbanne Cedex, France
(Received 17 August 1987; accepted 25 September 1987)

Glasses are known to undergo spontaneous densification during isothermal annealing. This volume recovery process, which is also an enthalpy recovery process, can be viewed as the collapse of highly disordered sites or 'defects'. We have modelled this physical ageing as a diffusion process in which the positive density fluctuation defects are annihilated by the corresponding negative ones. The diffusion constant depends on the concentration of defects, and each diffusion molecular jump induces hierarchically correlated molecular rearrangements which conform to a stretched exponential law. Good agreement was obtained between the theoretical and experimental volumes as well as enthalpy recovery results for poly(vinyl acetate) including the memory experiment and the variation of the effective relaxation time.

(Keywords: poly(vinyl acetate); ageing; structural relaxation)

INTRODUCTION

It is well known that glasses can undergo spontaneous changes in density during annealing below their glass transition temperature. As shown by Kovacs[1], this volume recovery process exhibits both non-linear and thermal history effects. A review was presented by Struik[2], and it was clear that this phenomenon (which will be called physical ageing or structural relaxation) can be observed in all glassy materials by probing not only their thermodynamic properties (e.g. enthalpy, entropy, volume) but also all properties that depend on molecular mobility (e.g. electrical and mechanical properties).

In order to interpret the experimental results, several authors have developed phenomenological models: the most successful of these are called multiparameter models and were reviewed by Kovacs and coworkers[3]. The essential feature of these models is a distribution of relaxation times, each of which depends upon the instantaneous deviation from the equilibrium volume.

Although phenomenological models reproduce most of the experimental observations, there is a need for models that lead to physical (microscopic) interpretation of recovery processes. Most of the models previously proposed implicitly use the free volume concept[2,3]. Nevertheless, some criticism of the extended use of such a concept has been made[2,4,5]. Thus, Robertson[6] developed a molecular model for the relaxation of internal energy in polymer glasses, by considering the conformational changes of their backbone chains. Such a model is questionable as it is not applicable to non-polymer glasses although the latter exhibit physical ageing phenomena comparable to those observed with polymeric materials. Whereas Robertson considered the local free volume to vary as a consequence of chain conformational changes, Curro *et al.*[7] considered the kinetics of structural relaxation to be controlled by diffusion of free volume. In their approach, the latter authors describe the spatial free volume distribution by a non-linear diffusion equation. The difficulty in this work is related to a length scale for diffusion: the introduction of this length scale is somewhat arbitrary since presently there exists no obvious molecular interpretation for it. Another work that should be mentioned is that of Cunat[8], who presented metallic liquids as mixtures of atoms that can be distinguished by the nature of their degrees of freedom (three degrees of freedom in vibration, or two in vibration and one in translation, or one in vibration and two in translation, or three in translation as their level of enthalpy is increased). Thus, a 'physicochemical' description of the liquid is proposed in terms of thermodynamic equilibrium of each species, depending on the temperature. Consequently, the glass transition corresponds to departure from equilibrium when the temperature is decreased below a value for which the internal timescale becomes longer than the experimental timescale. Unfortunately, the kinetic aspect of Cunat's work remains phenomenological.

In the present investigation, we propose a new interpretation for the enthalpy and volume recovery processes. Specifically, we consider two main assumptions, as follows.

(a) The supercooled liquid has fluctuations in density (i.e. in enthalpy and entropy), called 'defects'. By the usual argument of statistical thermodynamics, the defect concentration is given by[9,10]:

$$C_i = \frac{\exp[\Delta S_F(i)/k_B]\exp[-\Delta H_F(i)/k_B T]}{1+\sum_i \exp[-\Delta S_F(i)/k_B]\exp[\Delta H_F(i)/k_B T]} \tag{1a}$$

and

$$C_d = \sum_i C_i \tag{1b}$$

where $\Delta H_F(i)$ is the enthalpy increment due to broken van der Waals bonds and excited intramolecular bonds, $\Delta S_F(i)$ is the entropy increment related to the different possible states of intramolecular bonds, $1 \leqslant i \leqslant q$ and q is the number of values of $\Delta H_F(i)$ and $\Delta S_F(i)$ proposed in order to describe the microstructure of the polymer. Those defects presented here are merely sites with density

0032-3861/88/030483-07$03.00

fluctuations. Moreover, such fluctuations may be either positive or negative, similar to the p and n defects, respectively, previously introduced by Slorovitz *et al.*[11] for metallic glasses. But in all cases, a defective site implies a positive fluctuation of enthalpy (and entropy). It is, however, worth while to notice that negative density fluctuations can be compared to free volume; nevertheless, the concept of defect might be more useful for at least two reasons: (i) it contains both 'free volume' and 'anti-free volume' concepts and (ii) it takes into account the interaction between structural units, which is strong in condensed matter such as non-crystalline materials near T_g, via enthalpy fluctuations. Thus, at $T > T_g$, there are density, enthalpy and entropy fluctuations and monomers are alternatively either close-packed or they form, with their neighbours, disordered regions or defects. At $T < T_g$, these defects are frozen in, leading to local zones of high molecular mobility, which might be similar to the 'islands of mobility' introduced by Johari in considering β relaxation[12].

(b) The diffusion process results from atomic (molecular) movement presenting a strong correlation effect. Consequently, each atomic (molecular) jump induces some molecular rearrangements in its neighbourhood, and the duration of the whole phenomenon can be given by[10,13,14]:

$$\tau(t) = \tau_{\max}^{b} t^{1-b} \qquad \text{if } t < \tau_{\max} \tag{2}$$

and

$$\tau(t) = \tau_{\max} = [t_1 t_0^{-(1-b)}]^{1/b} \qquad \text{if } t > \tau_{\max} \tag{3}$$

where t_1 and t_0 are characteristic times for the preliminary molecular jump and the subsequent molecular rearrangement, respectively, and $b(0 < b < 1)$ is a parameter characterizing the correlation between the different atomic movements. The cut-off condition $\tau(t) = \tau_{\max}$ when $t = \tau_{\max}$ is implied in equations (2) and (3). Then, the structural relaxation generally observed in glasses could be described in terms of a change in the concentration of these defects produced by a defect diffusion process, each atomic (molecular) jump presenting a strong correlation effect.

A MODEL STRUCTURAL RELAXATION

We propose to present the basic equations for a physical interpretation of the structural relaxation observed in glasses near T_g.

Following assumption (a), a glassy solid at $T < T_g$ can be considered as condensed matter containing frozen-in defects: the consequence is that structural relaxation at $T_1 \lesssim T_g$ can be interpreted in terms of diffusion-assisted annihilation of defects until a new thermodynamic equilibrium is reached at a temperature T_1. The difficulty is that the diffusion kinetics is obviously dependent on the concentration of defects.

In the supercooled liquid, defects result from thermal fluctuations transforming normal sites (NS) into defects, and the following equilibrium equation could be used:

$$2\mathrm{NS} \underset{2}{\overset{1}{\rightleftharpoons}} \mathrm{d}^{+} + \mathrm{d}^{-} + \Delta G \tag{4a}$$

with d^{+} and d^{-} referring to positive and negative density fluctuations, respectively. In agreement with equations (1), one has a set of q equations:

$$2\mathrm{NS} \underset{2}{\overset{1}{\rightleftharpoons}} \mathrm{d}_i^{+} + \mathrm{d}_i^{-} + \Delta G_i \tag{4b}$$

Actually, the situation is much more complicated as other equations such as:

$$\mathrm{d}_i^{+} + \mathrm{d}_j^{-} \rightleftharpoons \mathrm{d}_k^{+} + \mathrm{d}_l^{-} + \Delta G(kl\text{–}ij) \tag{4c}$$

must also be taken into account, with a relation between the integers i, j, k and l (these integers lie between 0 and q, the value 0 corresponding to a normal site).

Working with the whole set of equations (4c) is an overwhelming task; we suggest as an approximation, the use of equation (4b). Thus, direct and reverse structural relaxations correspond to directions 2 and 1, respectively, of the equilibrium described by those equations. In both cases, the kinetics of evolution is governed by the diffusion of defects and the scale for diffusion length can be identified with the mean distance l_m between defects i. Then we have the equation:

$$\frac{\delta C_i}{\delta t} = -\frac{C_i(t) - C_i(\infty)}{\tau_{\mathrm{sr}}} \tag{5}$$

This equation is phenomenological but it is possible to introduce parameters having physical significance. So, the structural relaxation time τ_{sr} can be given by:

$$\tau_{\mathrm{sr}} = l_m^2 / D \tag{6}$$

We now introduce D_i, the coefficient of diffusion of defects i, which can be approximated by λ^2/τ_i, where λ is the mean length of elemental jumps of defects (similar to the single structure unit, or monomer, dimension) and τ_i is the mean duration of those jumps, which can be obtained from equations (2) and (3):

$$\tau_i = t_{1i}(t/t_0)^{1-b} \tag{7}$$

Assuming that $l_m^2/\lambda^2 \simeq C_i(t)^{-2/3}$, equations (5), (6) and (7) lead to:

$$\frac{\delta C_i(t)}{\delta t} = -\frac{[C_i(t) - C_i(\infty)]C_i(t)^{-2/3}}{t_{1i}(t/t_0)^{1-b}} \tag{8}$$

In equation (8), the three parameters t_0, b and t_{1i} are defined as follows.

(i) Parameter t_0 has been defined as the mean duration of the correlated molecular movement. In the paper of Rendell and Ngai[15], where this parameter is discussed in detail, it was identified with the lower end of the two levels system (TLS) spectrum of low-frequency modes. This suggests that t_0 is of the order of 10^{-9} s.

(ii) The parameter b characterizes the effectiveness of correlation effects. The stronger the interaction between structure units (i.e. the lower the temperature and consequently the lower the concentration of defects), the lower is the value of b. We propose to relate the parameter b linearly to the total concentration of defects C_d:

$$b = \alpha C_d \tag{9}$$

where the value of the constant α lies between 3 and 4 (since, near T_g, $C_d \simeq 0.1$ (ref. 9)) and b, obtained from a phenomenological treatment of experimental data, is between 0.3 and 0.5 (see, for instance, refs. 2 and 16).

(iii) Finally, the parameter t_{1i} is the duration of the preliminary molecular movement occurring in the defects. In the case of polymer materials, let us consider that this molecular movement is connected to the degree of intramolecular rotational freedom of the smallest subchain atoms further along the chain. Such a possibility, well known as a 'crankshaft' process[17], might be responsible for the β relaxation. Hence, t_{1i} might be similar to the β relaxation time with:

$$t_{1i} = \tau_0 \exp(u_i/k_B T) \qquad (10)$$

It is worth noting that u_i (i.e. t_{1i}) is probably distributed due to the disordered state of matter; nevertheless such a distribution of t_{1i} is much narrower than that of τ_i, which lies between t_1 and τ_{max}.

Thus it is possible to know the kinetics of evolution of the concentration of defects thanks to equations (8), (9) and (10) in relation to the thermal history of the material. But to obtain theoretical results about enthalpy or volume recovery, a link between these properties and defect concentrations is necessary.

For enthalpy, or more precisely the excess configurational enthalpy ΔH, the situation is clear. We have per mole of material:

$$\Delta H = N_A \sum_i \Delta H_F(i) C_i \qquad (11)$$

To establish a relation between C_i (or C_d) and the specific volume is less obvious. When a defect d_i^+ is annihilated with a defect d_i^-, a change of volume can be expected due to anharmonicity; such a feature is to be compared to the phonon thermal expansion coefficient. Then we consider this thermal expansion coefficient of the glass:

$$\alpha_g = \frac{1}{V}\frac{\Delta V}{\Delta T} \quad \text{or} \quad \frac{\Delta V}{V} = \frac{\alpha_g}{k_B} k_B \Delta T \qquad (12)$$

Equation (12) signifies that the volume expansion $\Delta V/V$ results from a change ΔT of temperature inducing an increase $k_B \Delta T$ of the potential enthalpy of interaction between neighbouring units. When creation (or annihilation) of defects is concerned, the change of enthalpy is given by $\Delta H_F(i)$. Thus, the increment of volume per mole due to defects in thermodynamic equilibrium can be derived from equation (12) by:

$$\frac{\Delta V_d(\text{eq})}{V_{eq}} = \frac{\alpha_g}{2k_B} \sum_i \Delta H_F(i) C_i(\infty) \qquad (13)$$

Finally, if the relative change of excess volume, hereafter called $\Delta(t)$, is defined by:

$$\Delta(t) = \frac{\Delta V_d(t)}{V_{eq}} - \frac{\Delta V_d(\text{eq})}{V_{eq}}$$

equation (13) leads to:

$$\Delta(t) = \frac{\alpha_g}{2k_B} \sum_i \Delta H_F(i) [C_i(t) - C_i(\infty)] \qquad (14)$$

In what follows, we shall use equations (8), (11) and (14) to calculate recovery curves in order to compare the present model with the experimental results. But these equations are highly non-linear and not amenable to analytical solution. As a result we resort to numerical techniques.

PREDICTIONS OF THE DEFECT DIFFUSION MODEL: COMPARISON WITH EXPERIMENT

Numerical calculations have been made after adjusting the values of $\Delta H_F(i)$; once having arbitrarily chosen $q = 20$ ($1 \leqslant i \leqslant 20$) and taken $\Delta S_F(i) = (2 + 0.03i)k_B$ (ref. 9), this adjustment is possible by comparing experimental $\Delta C_p = C_p(\text{liq}) - C_p(\text{glass})$ values with the value obtained from equation (11): $C_p = \mathrm{d}\Delta H/\mathrm{d}T$. Owing to the number of results published in the case of poly(vinyl acetate), mainly by Kovacs (see, for instance, ref. 1), we propose to do, as an example, calculations applicable to this polymer, but this does not reduce the generality of the model presented here so that it could be extended to other materials as well.

For poly(vinyl acetate), $\Delta C_p(\text{exp}) = 12.4\,\text{cal mol}^{-1}\,\text{K}^{-1}$ (ref. 18), giving $\Delta H(i) = (0.15 + 0.005i)\,\text{eV}$. We also need to know u_i. Internal friction experiments on poly(vinyl acetate)[19] indicate that β relaxation obeys an Arrhenius law (equation (10)) with $\tau_0 = 10^{13 \pm 1}$ and $u = (0.55 \pm 0.05)\,\text{eV}$. Thus, the values $u_i = (0.55 - 0.005i)\,\text{eV}$ need to be used. This means that the higher the disorder (i.e. $\Delta S_F(i)$ and consequently $\Delta H_F(i)$ are high), the higher is the molecular mobility in defects. To sum up, the relevant parameters for poly(vinyl acetate) used for the calculations are given in *Table 1*. It is worth noting that the parameters $\Delta H_F(i)$, u_i, α_g and α were adjusted from independent experiments (calorimetry, mechanical spectroscopy, dilatometry and form of the relaxation function, respectively); t_0 could be an adjustable parameter but the value quoted in ref. 15 has been chosen to calculate volume recovery curves.

Such curves are shown in *Figure 1*. Several remarks have to be made about these results by comparing them with the experimental data of Kovacs[20]. First of all one can see that the calculated $\Delta(t)$ scales rather well with the experimental values; the agreement is not so good with

Table 1

Parameter	Value	Ref.
Enthalpy of formation defects	$\Delta H_F(i) = (0.15 + 0.005i)\,\text{eV}$	
Entropy of formation of defects	$\Delta S_F(i) = (2 + 0.03i)k_B$	9
Activation energy of preliminary molecular movement in defects (from activation energy of β relaxation)	$u_i = (0.55 - 0.005i)\,\text{eV}$	19
$C_p(\text{liq}) - C_p(\text{glass})$	$\Delta C_p = 12.4\,\text{cal mol}^{-1}\,\text{K}^{-1}$	18
Thermal expansion coefficient (glassy state)	$\alpha_g = 1.9 \times 10^{-4}\,\text{K}^{-1}$	3
Coefficient relating b to C_d (equation (12))	$\alpha = 3$	
Coefficient relating $\Delta(t)$ to $\Delta H_F(i)$ $[C_i(t) - C_i(\infty)]$ (equation (17))	$\frac{\alpha_g}{2k_B} = 1.1$	
τ_0	$10^{-13}\,\text{s}$	19
t_0	$10^{-9}\,\text{s}$	15

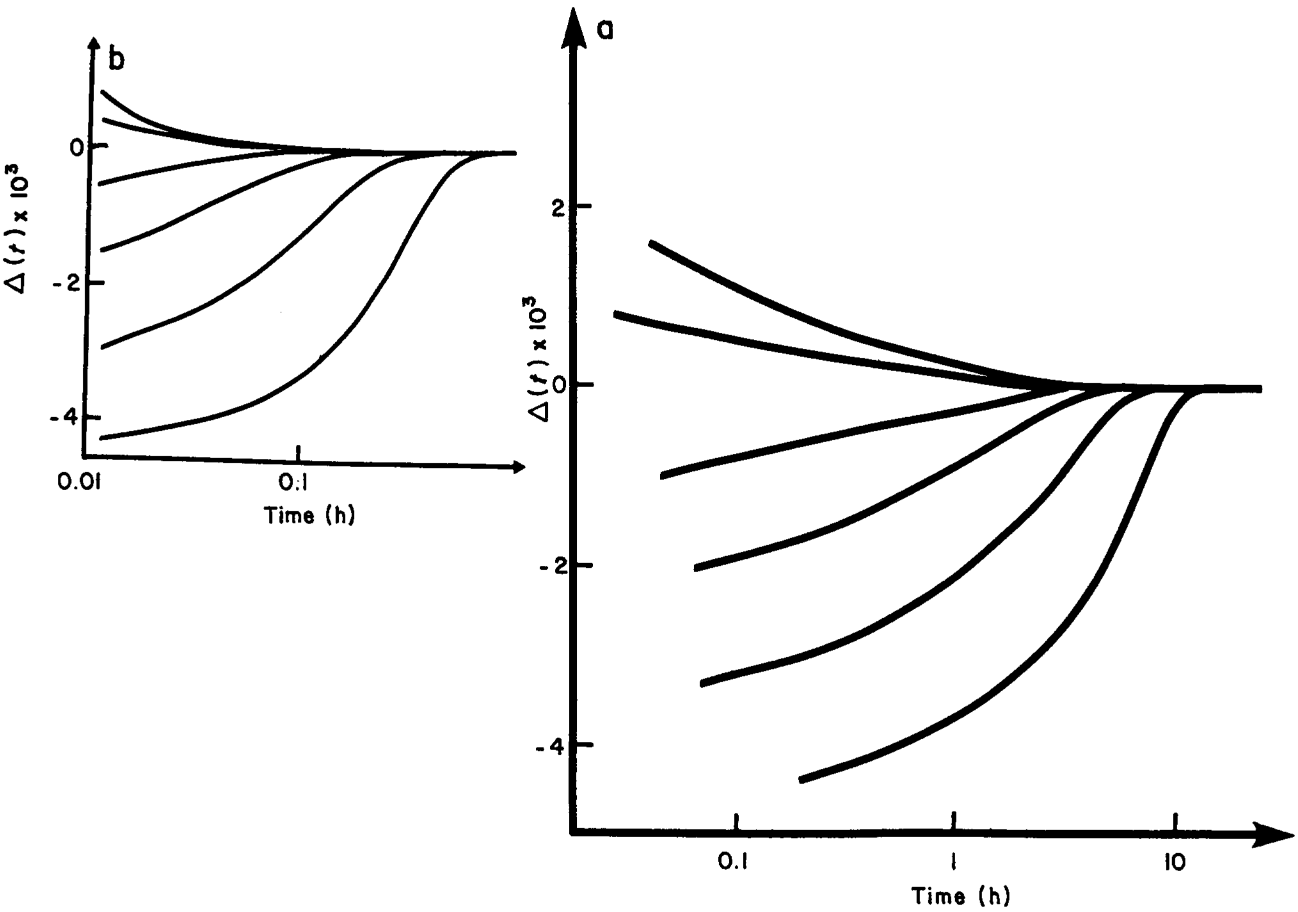

Figure 1 (a) Calculated variation of the relative excess volume $\Delta(t)$ with time of annealing at 40°C. (b) Experimental results redrawn from ref. 20. In both cases, annealing treatments are made on a specimen previously in equilibrium at (from bottom to top) 30, 32.5, 35, 37.5, 42.5 and 50°C

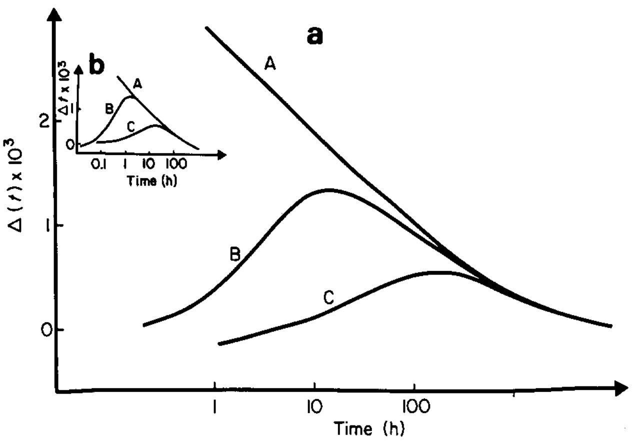

Figure 2 (a) Calculated memory effect. (b) Experimental results redrawn from ref. 3. In both cases, $\Delta(t)$ is obtained at $T_3 = 30$°C (curve A) or after equilibrium at 40°C and a subsequent annealing at $T_2 = 15$°C (curve B) or at $T_2 = 25$°C (curve C)

time. Calculated volume recovery phenomena occur in a timescale that is about one order longer than that observed experimentally. In fact, this agreement is not so bad considering the high sensitivity of the timescale to parameters such as u_i, t_0 and b. For instance, if α is increased by only 10% (thus increasing b), the right order of timescale is found. Nevertheless, it is worth noting the good agreement at the level of the whole set of curves: calculated volume recovery is neither linear nor symmetric as shown experimentally, a feature typically known as specific in the case of structural relaxation.

An interesting example of the temperature–history dependence of the physical ageing process is provided by the so-called 'memory (or crossover) experiment'. In this case, a glass previously in equilibrium at $T_1 > T_g$ is allowed to relax isothermally to some temperature T_2 below T_g. Before the glass reaches its equilibrium volume at T_2, it is heated to the temperature T_3 at which the volume is at its equilibrium value. It is typically observed that the volume, even though it is at its equilibrium value, first increases and then decreases back to the T_3 equilibrium value with kinetics agreeing with that observed during direct relaxation to T_3 from T_1. The behaviour of poly(vinyl acetate) expressed in terms of diffusion-assisted creation and annihilation defects is shown in *Figure 2*. It can be seen that the magnitude of the calculated memory effect is comparable to the experimental results[3]. However, the maximum occurs at a larger time after the second temperature jump. But, as just commented, the difference is not important with regard to the absence of adjustable parameters in the calculation.

In previous studies[3,21], volume recovery data were analysed in terms of an effective relaxation time defined as:

$$\tau_{\text{eff}}^{-1} = -\mathrm{d} \ln \Delta(t)/\mathrm{d}t$$

Plotting this effective relaxation time *versus* $\Delta(t)$ for many simple approach experiments gives a very sensitive test for

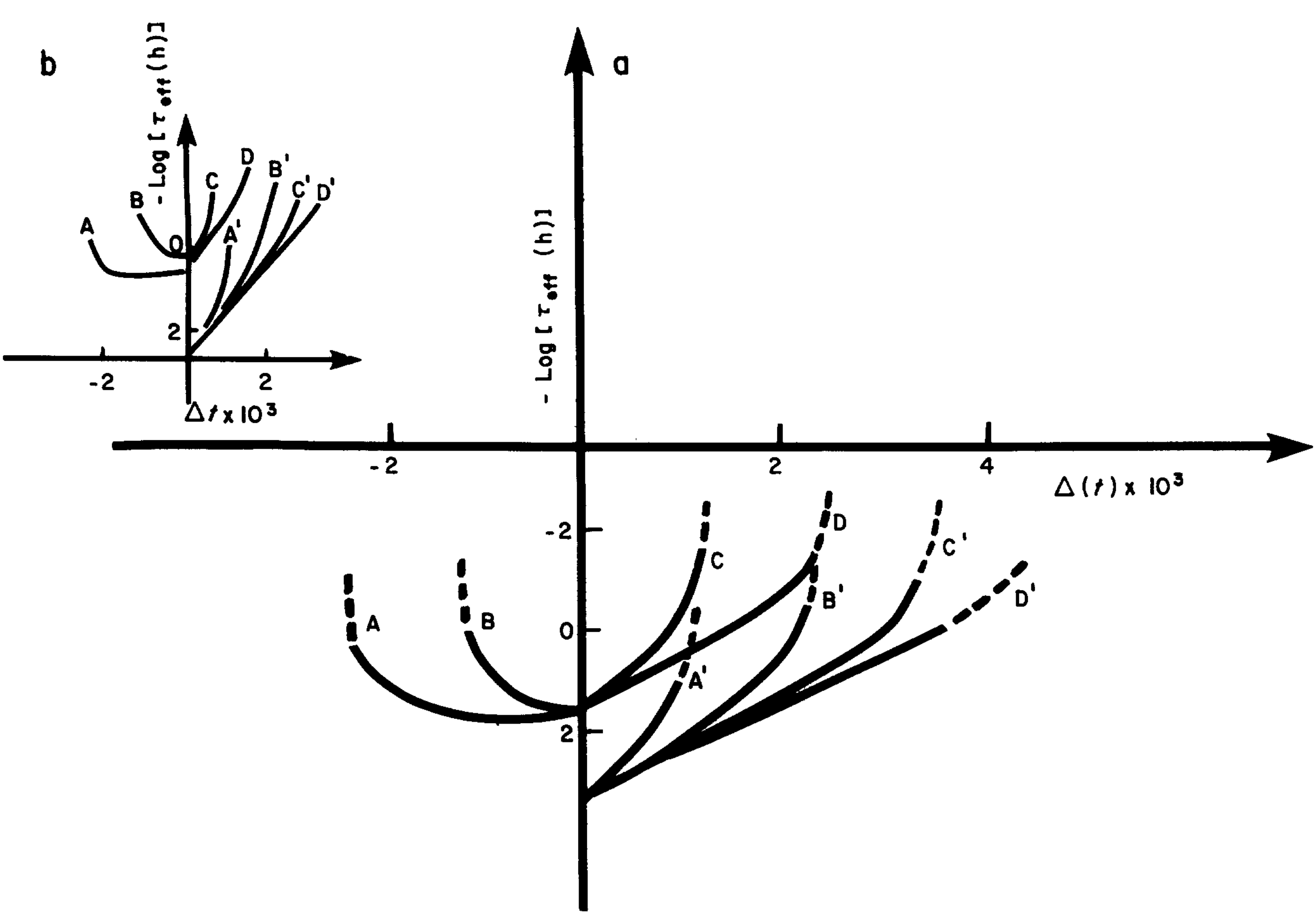

Figure 3 (a) Calculated curves of effective relaxation time as a function of relative excess volume. (b) Results from experiments redrawn from ref. 3. Isothermal annealing is either at 35°C after equilibrium at 30 (A), 32.5 (B), 37.5 (C) or 40°C (D) or at 30°C after equilibrium at 32.5 (A′), 35 (B′), 37.5 (C′) or 40°C (D′)

a volume recovery model. Such plots are shown in *Figure 3*. Once more, the main experimental features are reproduced by the calculated curves: note, in particular, the asymmetry between the down-jump and up-jump experiments. As for the preceding results, even the calculated experimental[3] values of time τ_{eff} are not too different (less than one order of magnitude).

Thus, it can be considered that volume recovery experiments are interpreted rather well by the defect diffusion model. It is also interesting to test this model with calorimetric results. So, we have calculated curves $C_p(T)$ corresponding to isobaric cooling through the glass transition region at a constant rate $p = dT/dt$ and subsequently reheating through the same temperature interval at the same rate. A particular case corresponds to cooling at a high value of p (quenching) followed by isothermal annealing with a low value of p for calorimetric measurements. Calculated curves of C_p *versus* T are shown in *Figure 4*: no new adjustable parameters, but only the values presented in *Table 1*, were used in this calculation. Comparison with the experimental results quoted in ref. 8 has to be made: as C_p has been used in order to adjust $\Delta H_F(i)$, only the other features observable in *Figure 4* will be commented upon. (i) The general evolution of the calculated curves with annealing time t_a is very similar to that obtained experimentally. The maximum is first observed at a lower or similar temperature after the first annealing and then at higher temperature when t_a is long. (ii) The maximum value of calculated C_p is comparable to the experimental values. (iii) The temperature at which the maximum C_p is observed is only slightly higher (2 to 5 K) in the case of the calculated curves: this point is related to the timescale difference as discussed above.

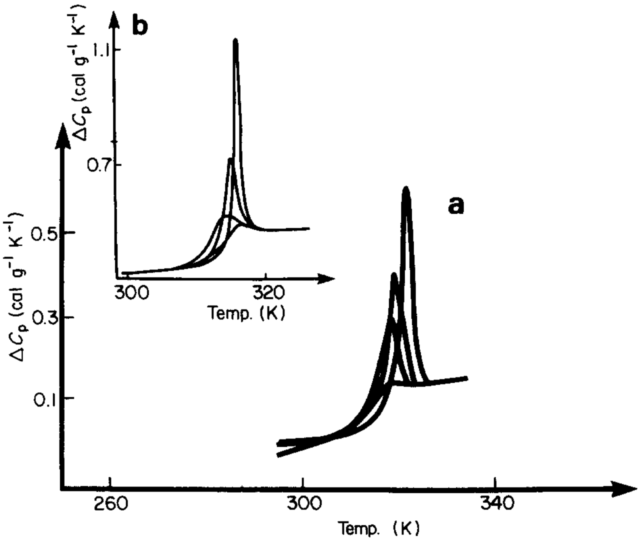

Figure 4 (a) Calculated curves of C_p as a function of temperature. (b) Experimental results redrawn from ref. 8. In both cases, curves correspond to a heating rate $p = 0.5\ K\ min^{-1}$ after isothermal annealing treatment at 294 K for 0, 17 h, 48 h and 7 days (corresponding to increasing height of the C_p peak)

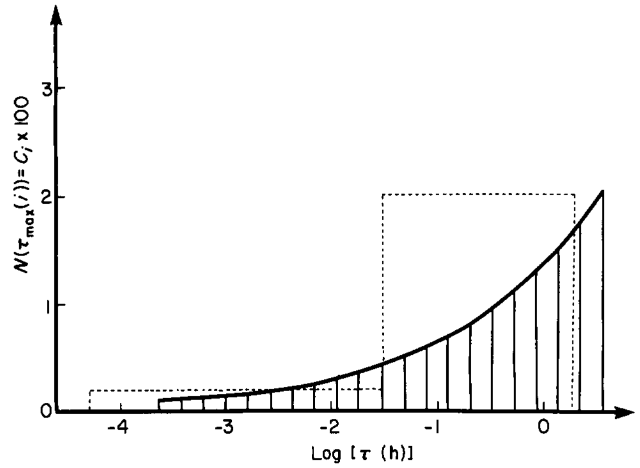

Figure 5 Distribution of times $\tau_{max}(i)$ related to characteristics of defects i. The broken line shows the two-box distribution function considered by Kovacs[3]

DISCUSSION AND CONCLUSIONS

It can be seen from *Figures 1* to *4* that a comparison can be made between the predictions of our defect diffusion model and the main experimental results. However, our purpose was not, strictly speaking, to obtain a fit between both series of curves. This work is an attempt to give insight into recovery phenomena, on a clear physical basis. The concept of defects, as proposed here, generalizes that of free volume, which was proposed earlier only for supercooled liquids at a temperature higher than T_g (ref. 22). Thus, on the one hand, kinetics governed by molecular jumps over potential energy barriers is introduced naturally and, on the other, the length scale for diffusing species is obviously defined as the mean distance l_m between defects resulting from positive and negative density fluctuations. This seems to solve the difficulty encountered by Curro *et al.*[7] in identifying this diffusion length scale, which is well known to be independent of sample size. Moreover, by calculating $l_m = \lambda C_i^{-1/3}$ we find 2.5 nm in the case of the most numerous defects ($i = 1$), and this value is increased to 6.9 nm for $i = 20$. These results should be compared to the size of regions of cooperative rearrangement calculated by Donth[23] through a thermokinetic fluctuation theory for the glass transition. This author found 3.6 nm for the case of poly(vinyl acetate). Moreover, assuming that these defects are sites where molecular movements inducing β relaxation occur leads us to understand why ageing phenomena are not observed when the temperature is lower than the temperature of β relaxation[2].

Relaxation phenomena in glasses are generally described with stretched exponential decay functions. In the model presented here, the physical origin of such stretched functions is mainly due to hierarchic correlated molecular movements (from this point of view, the present work is linked to papers recently published[10,13,14,24,25] in order to give a physical basis to the stretched exponentials generally used in the physics of glassy solids), but it results also from the distribution in the values of activation energy of the preliminary molecular movement ($0.55\,\mathrm{eV} > u_i > 0.45\,\mathrm{eV}$). It is worth while, then, to take notice of the distribution $N(\tau_{max}(i))$ by taking the concentration of defects i as a statistical weight factor. From equations (1a) and (3) the curve $N(\tau_{max}(i)) = C_i$ as a function of $\log \tau_{max}(i)$ is obtained. As shown in *Figure 5*, it appears that the timescale is similar to that considered by Kovacs with a two-box distribution function[3]. Furthermore, the curve of *Figure 5* is rather well approximated by the two distribution functions studied by Ng and Aklonis[21], i.e. the Williams–Watts and positive-slope ramp distribution, which appear to lead to the best fit of the data over a wide range of behaviour. Nevertheless, these authors concluded that no distribution could adequately describe the experiments; a temperature history effect at equilibrium for the up (down) jump is sometimes mentioned[7,21] with reference to experimental results corresponding to the curves of *Figure 3*. The defect diffusion model predictions of τ_{eff} (*Figure 3*) do not seem to show evidence of such an effect. Thus, we are forced to conclude either that this is a shortcoming of the model or, as experimentally shown by Calemzuck[26], that the τ_{eff} derived from experimental dilatometric data may be subject to large uncertainties in the region of $\Delta(t) \sim 0$.

It is interesting to calculate $\Delta\alpha = \alpha_l - \alpha_g$: with the parameters indicated in *Table 1*, we find $\Delta\alpha = 5.3 \times 10^{-4}\,\mathrm{K}^{-1}$, which is not too different from the value of $4.5 \times 10^{-4}\,\mathrm{K}^{-1}$ given by Kovacs[3].

Finally, we have to mention the paper of Bendler and Ngai[27], who utilized an equation similar to (5) applied directly to the variable physical property (H or V) with τ_{sr} also including the correlation effects. Their results are very similar to those presented here (e.g. same τ_{eff} behaviour), but the microstructural content of their description is not clear. The important common point between both works is that the parameter b appears to be dependent on the microstructure (b decreases with structural relaxation as represented by C_d in the present work and as $(1-n)$ in ref. 28). This is in agreement with the conclusion of Kovacs *et al.*[29], although the thermorheological simplicity is often admitted[2]. This was discussed by Kovacs *et al.*[30], who claimed that the dependence of τ_{eff} on thermal history is a feature that cannot be resolved by appropriate choice of an invariant distribution function.

To conclude, we feel that diffusion-assisted creation and annihilation of defects through correlated molecular movements occurring in those defects can lead to the complete description of enthalpy or volume recovery experiments on polymeric glasses. The case of poly(vinyl acetate), taken as an example, shows convincing arguments about such a physical approach, which could be seen as an extension of well known recovery phenomena studied in the case of crystals, although some features are clearly specific to glasses.

REFERENCES

1 Kovacs, A. J. *Adv. Polym. Sci.* 1963, **3**, 394
2 Struik, L. C. E. 'Physical Aging in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978
3 Kovacs, A. J., Aklonis, J. J., Hutchinson, J. M. and Ramos, A. R. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 1907
4 Anderson, P. W. 'La Matière Mal Condensée' (Ed. R. Balian), Les Houches, 1979, 162
5 Perez, J., Cavaille, J. Y., Fouquet, F. and Guyot, F. *Ann. Phys.* 1983, **8**, 417
6 Robertson, R. E. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 597
7 Curro, J. G., Lagasse, R. R. and Simma, R. *Macromolecules* 1982, **15**, 1621

8 Cunat, C. Thesis, Nancy, 1985

9 Perez, J. *Rev. Phys. Appl.* 1986, **21**, 93

10 Perez, J., Cavaille, J. Y., Etienne, S. and Jourdan, C. Int. Conf. Viscoel. Polym. Liq., Huez, 1986

11 Slorovitz, D., Maeda, K., Vitek, V. and Egami, T. *Phil. Mag. A* 1981, **44**, 847

12 Johari, G. P. 'Plastic Deformation of Amorphous and Semicrystalline Materials' (Eds. B. Escaig and C. G'Sell), Editions de Physique, Les Houches, 1982, p. 109

13 Palmer, R. G., Stein, D. L., Abrahams, E. and Anderson, P. W. *Phys. Rev. Lett.* 1984, **53**, 958

14 Ngai, K. L. and White, C. T. *Phys. Rev. B* 1979, **20**, 2475

15 Rendell, R. W. and Ngai, K. L. 'Relaxations in Complex Systems' (Eds. K. L. Ngai and G. B. Wright), Naval Research Laboratory, 1984, p. 309

16 Ngai, K. L. *Polym. Prep.* 1981, **22**, 289

17 Roberts, G. E. and White, E. F. T. 'The Physics of Glassy Polymers' (Ed. R. N. Haward), Applied Science, London, 1973, p. 153

18 Adam, G. and Gibbs, J. M. *J. Chem. Phys.* 1965, **43**, 139

19 Cavaille, J. Y., Jourdan, C., Kong, X. Z. and Perez, J. *Polymer* 1986, **27**, 693

20 Kovacs, A. J. 'Phenomènes de Relaxation et de Fluage en Rhèologie Non Linèaire', CNRS, 1961, p. 191

21 Ng, D. and Aklonis, J. J. 'Relaxations in Complex Systems, (Eds. K. L. Ngai and G. B. Wright), Naval Research Laboratory, 1984, p. 53

22 Cohen, M. H. and Turnbull, D. *J. Chem. Phys.* 1959, **31**, 1164

23 Donth, E. *J. Non Cryst. Solids* 1982, **53**, 325

24 Ngai, K. L. and Wright, G. B. (Eds.), 'Relaxation in Complex Systems', Naval Research Laboratory, 1984

25 Rammal, R. *J. Phys.* 1985, **46**, 1837

26 Calemzuck, R. Thesis, Grenoble, 1977

27 Bendler, J. T. and Ngai, K. L. *Polym. Prep.* 1981, **22**, 287

28 Ngai, K. L. and Manning, I. *J. Phys.* 1982, **12**, C9-607

29 Kovacs, A. J., Stratton, R. A. and Ferry, J. D. *J. Phys. Chem.* 1963, **67**, 152

30 Kovacs, A. J., Hutchinson, J. M. and Aklonis, J. J. 'The Structure of Non-crystalline Materials' (Ed. P. M. Gaskell), London, 1977, p. 153