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(11) When the colloid titration curve for weak polyelectrolyte was obtained by using a strongly acidic or basic polyelectrolyte as a titrant, the degree of dissociation (α) for the weak polyelectrolyte can be estimated from the M_s vs. pH curve by $\alpha = (1/M_s)/(1/M_s^0)$, where M_s^0 represents the value of M_s at $\alpha = 1$ (see ref 1 and 2). For polyampholytes, however, the change in M_s with pH in the range $\alpha < 1$ deviates from this relationship because of intramolecular interaction between the anionic and cationic groups. Thus, it is possible to analyze quantitatively the titration data for HSA only under the condition where the M_s value is independent of pH, i.e., $\alpha = 1$.

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Diffusion Model for Volume Recovery in Glasses[†]

John G. Curro* and Robert R. Lagasse

Sandia National Laboratories, Albuquerque, New Mexico 87185

Robert Simha

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106.
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ABSTRACT: Glasses are known to undergo spontaneous densification during isothermal annealing. This volume recovery process can be viewed as collapse of free volume. We have modeled this change in free volume during annealing as a vacancy diffusion process, where the diffusion constant depends on the local free volume (as defined by the Simha–Somcynsky theory) through the Doolittle equation. Good agreement was obtained with estimates of experimental volume recovery results for poly(vinyl acetate). Since volume recovery is sample-size independent, the characteristic length for diffusion cannot be identified with macroscopic dimensions. Several possibilities exist that can reconcile a diffusion picture with the known sample-size independence of the volume recovery process. These possibilities include internal annihilation of vacancies, density fluctuations, and a coupling of diffusive and uniform lattice motions.

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 nonlinear and thermal history effects. Kovacs and co-workers[2] have developed a phenomenological model that reproduces most of the experimental observations. The essential feature of their model is a distribution of relaxation times, each of which depends upon the instantaneous deviation from the equilibrium volume. In the present investigation, we propose a microscopic interpretation for the volume recovery process. Specifically, we consider the kinetics of this process to be controlled by diffusion of free volume. The essential features of our model are that the free volume is localized in the form of vacancies, and these vacancies diffuse to (or from) a boundary where they are annihilated (or created).

Recently, Robertson developed a molecular model for the relaxation of internal energy[3a] and volume[3b] in polymer glasses. In this model, Robertson considers the detailed conformational changes of the backbone chains which are coupled to discrete local free volume states. These coupled motions were analyzed as a stochastic process and the results agree with many of the features observed in volume recovery experiments. In our theory we also allow the local free volume to change. Whereas Robertson considered the local free volume to vary by virture of *chain conformational changes*, we allow the local free volume to change by a *free volume diffusion* process. In essence, we replace Robertson's stochastic equation, which contains the structural details of the chains, by a diffusion equation. Thus in our approach we suppress the structural details considered in the Robertson model.

The idea of free volume diffusion has been applied to glasses before by Hirai and Eyring,[4] who assumed that vacancies can be annihilated by conversion to phonons and vice versa. The entire diffusion and annihilation process was modeled as an activated rate process with an unspecific activation energy. As pointed out by Kovacs,[1] difficulties are encountered when one compares this theory with experiment.

In our approach we describe the spatial free volume distribution by a nonlinear diffusion equation. The only adjustable parameter in our theory is related to a length scale for diffusion. The introduction of this length scale is somewhat arbitrary since there is no obvious molecular interpretation for it. We will discuss some possible interpretations later in this paper.

Free Volume Diffusion

Although many different quantitative definitions of free volume have been proposed, the qualitative concept of free volume has been useful in explaining many properties of polymer liquids and glasses.[5] In this work we will define the free volume fraction as the fraction of empty lattice sites or holes in the theory of Simha and Somcynsky[6] for equilibrium polymer liquids. We have recently generalized

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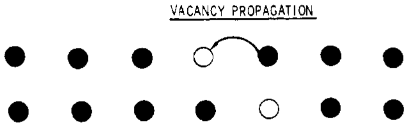

Figure 1. Schematic illustration of vacancy propagation. The free volume represented by an open circle moves to the right in response to a particle (filled circle) moving to the left.

this theory to polymer glasses by allowing the hole fraction to depend on time.[7] Using this approach, we were able to successfully predict the shift in the viscoelastic relaxation spectra of polymer glasses during physical aging from volume recovery experiments. The time-dependent free volume fraction was extracted from volume measurements with the aid of the Simha theory and then used in the Doolittle equation[8] to estimate the shift factors. Good agreement was found with viscoelastic measurements.[7]

In the original theory[6] of Simha, the free volume of equilibrium liquids was found by minimizing the free energy. In our recent generalization[7] to nonequilibrium glasses, this free energy minimization no longer holds and the free volume was simply viewed as a function to be extracted from experiment. In the present work we attempt to make this theory more complete by specifically addressing the time-dependent free volume, rather than regarding it as an experimentally determined parameter.

A rigorous description of the free volume changes must, in general, depend on the detailed molecular dynamics of the system. A considerable simplification can result if it is assumed that the free volume is localized in the form of holes or vacancies, as suggested in the original Simha theory. These vacancies would then diffuse in response to molecular motion (see Figure 1). As mentioned earlier, we will suppress the details of this molecular process by assuming that vacancy motion can be described by a diffusion equation. Thus we assume that the free volume fraction f is given by

$$\partial f/\partial t = \nabla\cdot(D\nabla f) \qquad (1)$$

where D is the diffusion constant for holes and would, in general, depend on free volume. This equation implies that the driving force for vacancy diffusion is a free volume gradient. It should be noted that eq 1 is not tied to the lattice model used in the Simha theory,[6] although the Simha equation of state will be used throughout this paper for converting volume to free volume and vice versa[7] (see below).

A reasonable form to choose for the free volume dependence of the diffusion constant is given by the well-known Doolittle equation[8]

$$D = D_r \exp[-B(f^{-1} - f_r^{-1})] \qquad (2)$$

where for convenience the reference state is taken to be the glass transition temperature and B is a material constant. A theoretical basis for eq 2 is provided by the Cohen–Turnbull[9] theory of liquids. Equation 2 shows that the vacancy diffusion constant can be a very strong function of the free volume. Given appropriate initial and boundary conditions, eq 1 and 2 can then be used to predict the spatial and time dependence of f. The free volume of the sample $\bar{f}$ can then be calculated by averaging over the volume.

$$\bar{f}(t) = \int_V f(r,t)\, \mathrm{d}\vec{r} \qquad (3)$$

In this simple picture, we have assumed that a single or average diffusion mechanism for vacancies applies. In general, we would expect a distribution of such diffusion mechanisms, corresponding to the various molecular motions responsible for causing vacancies to move. This complexity could be introduced into eq 2; however, it would not fundamentally alter the results and is not included in the present investigation. Thus the present model is a single ordering parameter theory with a single relaxation mechanism.

The initial and boundary conditions on the free volume fraction will, of course, depend on the thermal history of the sample. In the case of the conventional volume recovery experiment,[1] the sample is equilibrated at temperature T_0 before an instantaneous temperature jump ΔT is applied. Thus it is reasonable in this case to take the initial condition as

$$f(r,0) = f_0 \qquad (4)$$

where f_0 is extracted[7] from the Simha theory, making use of the experimental volume immediately after quenching. The question of the appropriate boundary condition is a more difficult one. In the present investigation we assume there exists some boundary at which equilibrium is maintained. This allows us to write the boundary condition

$$f(l,t) = f_\infty \qquad t > 0 \qquad (5)$$

in spherical coordinates, where l is a characteristic length for diffusion and f_∞ is the equilibrium free volume fraction at $T_0 + \Delta T$. One possibility would be to identify the characteristic length with the macroscopic dimensions of the sample, in which case vacancies diffuse to (or from) the surface where they are annihilated (or created). At the present time, however, the length l will be kept arbitrary. We will postpone the discussion of this point until we have compared the theory with experiment.

The nonlinear diffusion equation in eq 1 and 2 can now be solved using eq 4 and 5 for specified thermal histories. The *equilibrium* free volume in eq 5 can be computed from the Simha theory[6] through free energy minimization. Once the spatial and temporal free volume fractions have been obtained, the average free volume can be computed from eq 3 as a function of time. The time-dependent specific volume can then be calculated from the average free volume using the Simha theory according to the method outlined in our previous publication.[7] The reducing parameters in the Simha theory, T^* and V^*, as well as B in the Doolittle equation can be determined from measurements on the equilibrium liquid.[7] The only adjustable parameter we will have in the glass is the characteristic time τ, defined by

$$\tau = l^2/D_r \qquad (6)$$

Experimental Results for Poly(vinyl acetate)

Rather than reading the volume measurements from published figures, we deemed it more convenient to compute the specific volumes by means of the phenomenological theory of Kovacs et al.[2] This empirical representation is thought[2b] to reproduce most of the important features of the experimental data. The relevant parameters for poly(vinyl acetate)[2a] are shown in Table I. In addition, the distribution of relaxation times in the phenomenological representation was taken from Figure 5 of ref 2a.

For comparison with the theoretical results, the specific volumes obtained from the phenomenological representation were then converted to free volume fractions $f(t)$, using the Simha theory as outlined in ref 7. This procedure is equivalent to, but computationally simpler than, converting the theoretically obtained free volumes to specific volumes for comparison. Thus in the present investigation

Table I
Experimentally Determined Parameters for PVAc

type	values	ref
phenomenological model	$\Delta\alpha = 4.0 \times 10^{-4}$ K^{-1} $\theta = 1.0$ K^{-1} $x = 0.4$	2a, p 1114
Simha theory	$T^* = 9471$ K $V^* = 0.81386$ cm^3/g	11
Doolittle equation	$B = 10.5$	11
present theory	$\tau = l^2/D_r = 7800$ s	

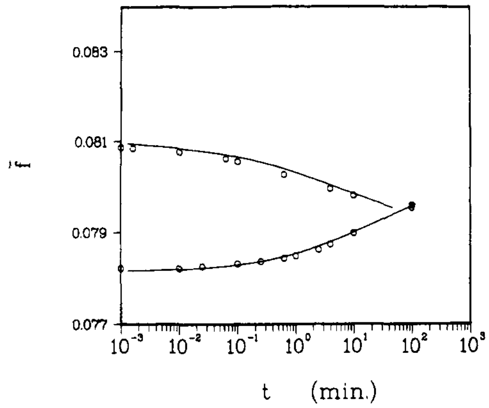

Figure 2. Comparison of free volume fractions during volume recovery of poly(vinyl acetate) predicted by the phenomenological theory (circles) and the present diffusion model (curves). The upper points (and curve) correspond to a sample equilibrated at 38 °C and brought to 35 °C at $t = 0$. The lower points (and curve) correspond to a sample equilibrated at 32 °C and brought to 35 °C at $t = 0$. The parameter τ was adjusted to 7800 s in order to fit the data.

a comparison is made between the free volume fractions derived from experiment and those computed on the basis of the diffusion model.

The required Simha parameters T^* and V^* were determined from equilibrium volume–temperature values for the liquid. These data were estimated from the thermal expansion coefficient ($\alpha_l = 6.9 \times 10^{-4}$ K^{-1}, ref 11, p 159) and specific volume at 35 °C ($v_l = 0.8445$ cm^3/g, ref 11, Figure 15) of poly(vinyl acetate) from the data of Kovacs, Ferry, and Stratton.[11] V^* and T^* were found by a least-squares fit of ln V vs. $T^{3/2}$, making use of the approximate relationship[12a]

$$\ln V = \ln V^* - 0.1033 + 23.834(T/T^*)^{3/2} \qquad (7)$$

which is valid in the range $0.0165 < T/T^* < 0.0703$. The parameters resulting from this procedure are shown in Table I. The values agree with those obtained by McKinney and Simha[12b] ($V^* = 0.8141$ cm^3/g, $T^* = 9419$ K) on poly(vinyl acetate).

The results from the above procedure are shown as points in Figures 2 and 3 for simple volume recovery experiments on poly(vinyl acetate). These figures represent experiments in which equilibrated samples were jumped to 35 °C from above and below.

In previous studies,[1,2] volume recovery data were analyzed in terms of an effective relaxation time, defined as

$$\tau_{\text{eff}}^{-1} = -\mathrm{d} \ln \delta / \mathrm{d}t \qquad (8)$$

where

$$\delta = V(t)/V_\infty - 1$$

This effective relaxation time, which is related to the slopes of the curves in Figures 2 and 3, is though to be a more sensitive test for a volume recovery model than the time-dependent volume itself. τ_{eff} was obtained directly from the phenomenological model for poly(vinyl acetate) at 35 °C and is shown as the points in Figure 4.

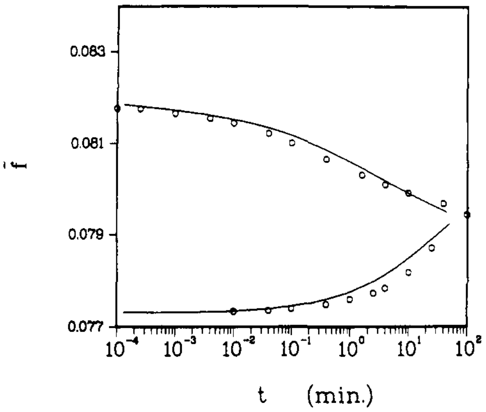

Figure 3. Comparison of free volume fractions during volume recovery of poly(vinyl acetate) predicted by the phenomenological theory (circles) and the present diffusion model (curves). The upper points (and curve) correspond to a sample equilibrated at 40 °C and brought to 35 °C at $t = 0$. The lower points (and curve) correspond to a sample equilibrated at 30 °C and brought to 35 °C at $t = 0$. The parameter τ was the same as in Figure 2.

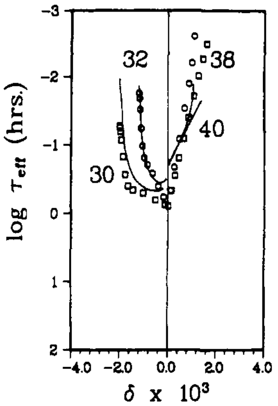

Figure 4. Comparison of τ_{eff} of poly(vinyl acetate) at 35 °C predicted by the phenomenological theory (points) and the present diffusion model (curves). The temperatures from which the samples were brought are shown. The parameter τ was the same as in Figure 2.

An interesting example[1] of the temperature–history dependence of the physical aging process is provided by the "memory experiment". In this case a glass is allowed to relax isothermally at some temperature below T_g. Before the glass reaches its equilibrium volume, it is heated to the temperature at which the volume is at its equilibrium value. It is typically observed[1] that the volume, even though it is at its equilibrium value, first increases and then decreases back to the equilibrium value. The behavior of poly(vinyl acetate), as predicted by the phenomenological model and expressed in terms of free volume fraction, is shown in Figure 5.

Predictions of the Diffusion Model for Poly(vinyl acetate)

The diffusion equation in eq 1 and 2 is highly nonlinear and not amenable to analytical solution. As a result we resorted to numerical techniques. For this purpose we used a finite element code[10] which was applicable to nonlinear two-dimensional or axisymetric problems. For simplicity, a spherical geometry was assumed.

In order to utilize eq 2 for the diffusion constant, we determined the parameter B for poly(vinyl acetate). This was found from shift factors obtained on equilibrated poly(vinyl acetate) in the region of the glass transition.[11]

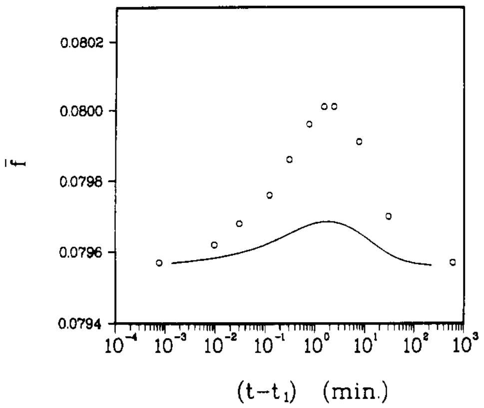

Figure 5. Comparison of the free volume fractions during a memory experiment on poly(vinyl acetate) predicted by the phenomenological thoery (points) and the present diffusion model (curve). The results correspond to a sample equilibrated at 38 °C, quenched to 32 °C, and held for a time $t_1 = 9.12$ min. At $t = t_1$ the sample is brought to 35 °C, where the average free volume is at its equilibrium value. Note that $\bar{f}$ first increases and then decreases to the equilibrium value. The parameter τ was the same as in Figure 2.

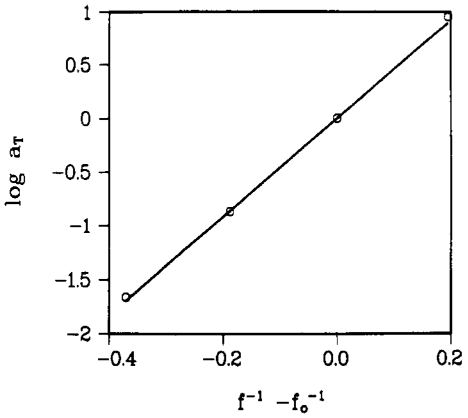

Figure 6. Determination of the B parameter in the Doolittle equation for poly(vinyl acetate). log a_T from ref 11. Free volume fractions from equilibrium Simha theory.[6] A least-squares fit yields $B = 10.5$.

These shift factors (log a_T) were calculated for different temperatures from an equation that represented measurements obtained by Kovacs, Stratton, and Ferry.[11] The equilibrium free volume fractions $f_\infty(T)$ were then computed at these temperatures from the Simha theory. B was obtained from a least-squares fit to an alternate form of the Doolittle equation.[8]

$$\log a_T = 0.4343B\{[f_\infty(T)]^{-1} - [f_\infty(308\ \mathrm{K})]^{-1}\} \tag{9}$$

A plot of these data is shown in Figure 6. Although the value of B is higher than often quoted values, it is nevertheless consistent with the free volume quantity employed by us.[7]

The results from solving the nonlinear diffusion equation for poly(vinyl acetate) are shown in Figures 2 and 3 as the solid lines for the simple volume recovery experiments. The characteristic time τ in eq 6 was determined from the 3 °C temperature jump data in Figure 2 by shifting along the log (time) axis. The value of τ obtained is shown in Table I and was held *fixed* in the remainder of this study.

The diffusion model prediction for the effective relaxation time is obtained by numerically differentiating the curves in Figures 2 and 3. In order to compute τ_{eff} according to eq 8 we make use of the approximation

$$V(t) = V_\infty(T) + A(\bar{f} - \bar{f}_\infty) \tag{10}$$

At $T = 35$ °C, eq 10 fits $V(t)$ to within $\pm 10^{-5}$ cm^3/g, for $V/V_\infty < 1.002$ with $A = 0.7558$. Equation 8 can then be written as

$$\tau_{\mathrm{eff}}^{-1} = \frac{-0.4343}{f - f_\infty}\frac{\mathrm{d}\bar{f}}{\mathrm{d}\log t} \tag{11}$$

τ_{eff} was calculated for our diffusion model using eq 11 and the curves in Figures 2 and 3. The slopes were obtained numerically using cubic splines. These results are shown in Figure 4 as the solid lines. Considerable numerical difficulties in evaluating τ_{eff} wer experienced near $\delta = 0$ since the calculation in eq 11 involves taking the ratio of two quantities which are both approaching zero. In order to overcome these difficulties, the diffusion equation in eq 1 and 2 could be solved to yield τ_{eff} directly; however, this is beyond the scope of the present investigation.

The predicted results for the memory experiment are shown in Figure 5 for poly(vinyl acetate). The thermal history of the memory experiment was incorporated into the theory by using the following initial and boundary conditions. For the initial recovery from the 38–32 °C temperature jump we used

$$f(r,0) = f_0 \tag{12a}$$

$$f(l,t) = f_\infty(32\ ^\circ\mathrm{C}) \tag{12b}$$

for $0 < t < t_1$. At the time $t = t_1$ the temperature was instantaneously jumped to 35 °C. The free volume also experiences an instantaneous response Δ

$$f(r,t_1^{+}) = f(r,t_1^{-}) + \Delta \tag{13a}$$

where t_1^- and t_1^+ refer to times just before and after the temperature is jumped to 35 °C. Δ was adjusted so that the average free volume matched the result derived from the experimental volume at t_1^+. The boundary condition for $t > t_1$ is then given by

$$f(l,t) = f_\infty(35\ ^\circ\mathrm{C}) \tag{13b}$$

The characteristic time τ was held fixed at the previous value shown in Table I.

Discussion

It can be seen from Figures 2 and 3 that good agreement is obtained between the predictions of the diffusion model and the phenomenological results.

In the case of the average relaxation times in Figure 4, the diffusion model and phenomenological results are similar; however, significant deviations are seen to occur near equilibrium ($\delta = 0$). The phenomenological model is known[2] not to give quantitative agreement with experimentally determined τ_{eff} values. This can be seen by comparing the points in Figure 4 with the data of Kovacs shown in Figure 7. Note, in particular, the asymmetry between the down-jump and up-jump experiments and that the equilibrium ($\delta = 0$) τ_{eff} depends on the starting temperature in the up-jump experiment. The phenomenological model does not reproduce this last feature and predicts the same equilibrium τ_{eff} regardless of the starting temperature. Note also that the diffusion model predictions of τ_{eff} in Figure 4 seem to show some evidence of a temperature history effect at equilibrium for the up-jump experiment. We feel that we cannot say with certainty whether this effect is real or due to the numerical difficulties near $\delta = 0$ mentioned earlier. It should also be mentioned that the τ_{eff} derived from experimental dilatometric data may also be subject to the same numerical uncertainties in the region of $\delta \sim 0$.

We expect to find memory effects in the diffusion model since free volume gradients can exist in the glass even

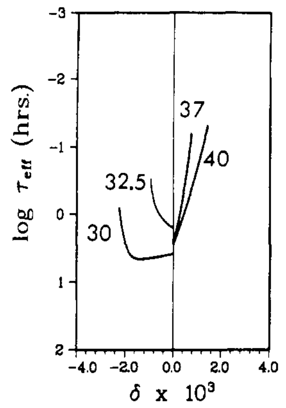

Figure 7. τ_{eff} from experimental data of Kovacs[1] for poly(vinyl acetate) at 35 °C. The temperatures from which the samples are brought are shown. Note the history dependence of τ_{eff} at equilibrium ($\delta = 0$) for the up-jump experiment.

though the average free volume is at its equilibrium value. It can be seen in Figure 5 that the magnitude of the memory effect is significantly smaller than the phenomenological prediction; however, the maximum occurs at the correct time after the second temperature jump. No new adjustable parameters are used in this calculation. We found that the amplitude of the peak in the calculation was insensitive to the value of τ, B, or the Simha parameters T^* and V^*. One possible source of the discrepancy (which we have not investigated) is the fact that our model contains only a single diffusion mechanism.

It can be seen by a comparison of the present diffusion model with the phenomenological predictions that our model is in semiquantitative agreement with the essential dilatometric observations made on glasses. We feel that this is significant in view of the simplicity of the model and strongly suggests that volume recovery occurs by a vacancy diffusion process. The only feature of this model that we find unsatisfying is the introduction of an arbitrary length scale for diffusion. We will now speculate on its possible origin.

Perhaps the most physically appealing approach would be to simply identify the length scale l with the macroscopic dimensions of the sample. This would imply that vacancies would be annihilated or created at the surface of the glass sample. If this were the case, however, the relaxation time τ in eq 6 would depend on the dimensions of the sample. No evidence is found in the literature for such a size-dependent effect on physical aging experiments. In fact, a number of years ago Kovacs performed dilatometric experiments[13] on bulk and powdered samples of polystyrene and found no size dependence of the magnitude predicted by eq 6. Note, moreover (from eq 6), that a macroscopic value for l (e.g., $l \sim 1$ cm) would require $D_r \sim 10^{-4}$ cm^2/s for poly(vinyl acetate), which appears to be an impossibly large value for a defect diffusion mechanism. On the other hand, if we assume an internal length scale, e.g., $l \sim 10^{-5}$ cm, then $D_r \sim 10^{-14}$ cm^2/s.

There are at least two possible speculations for the existence of such an internal length scale: internal annihilation (or creation) of vacancies and inhomogeneous structure. The former mechanism would imply significant overlapping of the particles, resulting in enhanced local strain energy. Hirai and Eyring[4] suggested that vacancies can be converted to phonons which propagate to the surface at the speed of sound and (vice versa). A similar idea was employed by Montrose and Litovitz,[14] who interpreted ultrasonic measurements in liquids as a diffusion process with a characteristic time representing the lifetime of a hole.

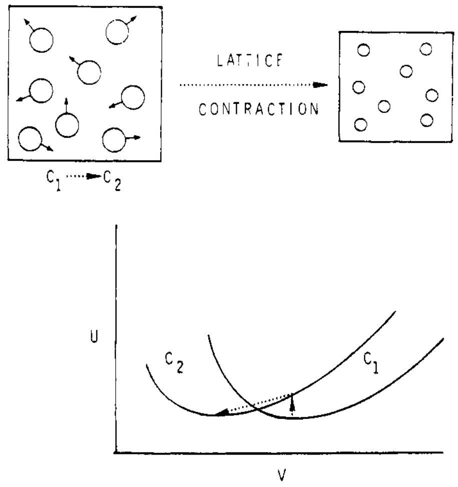

Figure 8. Schematic illustration of coupling between uniform lattice contraction of holes and vacancy diffusion. Vacancies (open circles) in configuration C_1 have a free volume determined by the minimum in the potential energy. Vacancies then diffuse slowly (as shown by arrows) to a new configuration C_2 having a different potential energy minimum. The system responds quickly to this new minimum by undergoing a uniform lattice contraction, resulting in all the holes being reduced in volume by the same fraction.

The question of inhomogeneous structure in glasses is controversial. Yeh[15] and co-workers suggested such a nonhomogeneous structure in polymer glasses on the basis of electron microscopy results. This interpretation has been criticized by Thomas.[16] Goldstein[17] has postulated an inhomogeneous structure in order to explain his results on small-molecule glasses. Others, based on computer simulation of dense packing,[18] have suggested that large-scale amorphous structures are a possibility. It appears as if the possibility of structural inhomogeneities in glasses is still very much an open question.[19] If, for example, spatial density fluctuations persist in the glass at equilibrium, then we would expect regions of high and low mobility. Because of the highly nonlinear diffusion constant, small fluctuations in density lead to large fluctuations in mobility. Based on the Doolittle equation, eq 2, with reasonable parameters, we estimate that a factor of 10 change in diffusion constant can result from a fluctuation as small as 0.15% in density. Such small density fluctuations would be difficult to observe by most techniques. Diffusion in and out of these regions of low mobility (if they exist) could be the rate-determining process leading to changes in total free volume. It sould be mentioned that Robertson[3a] also introduced an internal length scale into his model. Robertson's length scale is associated with the size of the "relaxation environment" of a chain segment.

Another vacancy diffusion mechanism that is not sample-size dependent and does not involve an internal length arises from a coupling between lattice contraction and diffusion processes. Consider an amorphous system containing a distribution of hole sizes (free volume). If the temperature of the system is suddenly changed to some new value, the lattice will rapidly contract (or expand), resulting in a uniform contraction (or expansion) of the holes. One would expect that this contraction would be such that the potential energy at *constant configuration* would be minimized. If the holes are allowed to diffuse, a new constrained potential energy curve, characteristic of the new configuration, would result (see Figure 8). The system would then respond by undergoing another uniform lattice contraction, resulting in a further uniform reduction in hole size. These two processes, hole diffusion and lattice contraction, would occur simultaneously in a relaxing glass. This uniform lattice contraction could be the mechanism by which the overall free volume changes. Since diffusion of holes would be expected to occur slowly in the glassy state, this hole diffusion would be the rate-determining step. Well above the glass transition the hole diffusion and uniform contraction would occur at comparable rates.

Conclusion

We have presented a simple, nonlinear diffusion model that semiquantitatively reproduces the major phenomena observed during physical aging of glasses. We have also speculated on how a diffusion picture can be reconciled with sample-size independence of these annealing effects. Further work clearly needs to be done to elucidate the details of the diffusion mechanism. Nevertheless, we feel that the agreement with the phenomenological model strongly suggests that volume recovery behavior in glasses is due essentially to a diffusion process.

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Local Configuration of Poly(L-proline) in Dilute Solution

J. A. Darsey and Wayne L. Mattice*

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803.

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ABSTRACT: Representative poly(L-proline) chains containing peptide bonds in the trans configuration have been generated using a conformational energy surface that successfully reproduces the unperturbed dimensions in dilute solution. Representative chains have also been generated using selected portions of that surface in order to assess the influence of various features on the local conformation. Approach of the X component of the end-to-end vector to its asymptotic limit has been characterized for these same cases. In dilute solution, the overall configuration for chains containing as few as 70 prolyl residues is that of a random coil. Within the chain can be found a few short sequences that adopt a threefold left-handed helical structure reminiscent of that seen in the solid state. Threefold helices containing more than two turns are not seen in chains representative of the ensemble found in dilute solution. Helices do not extend further due to a continuous bending of the chain and, to a lesser extent, because of the presence of occasional sharp turns. The flexibility of the pyrrolidine ring plays a role in limiting the size of recognizable threefold helices.

Poly(L-proline) forms either of two ordered conformations in the solid state. Form I is a rather compact right-handed helix in which peptide bonds adopt the cis configuration,[1] and form II is a comparatively extended left-handed helix containing peptide bonds in the trans configuration.[2,3] In dilute solution there is a pronounced tendency for all peptide bonds to adopt the same configuration.[4-10] A reversible interconversion between the two forms can be produced by appropriate changes in solvent composition.[6,7,10] The configuration containing cis peptide bonds is favored in poor solvents. The tendency for aggregation in these solvents has prevented an extensive physical characterization of the solution conformational properties of form I. Good solvents support the chain configuration containing trans peptide bonds. Samples with weight-average molecular weights ranging from 4000 to 100000 have been studied in five solvents that favor the form containing trans peptide bonds.[11] Behavior of the intrinsic viscosity over this molecular weight range demonstrates that the overall configuration is that of a random coil in a good solvent. The asymptotic limit for the characteristic ratio, $C = \langle r^2 \rangle_0 / n_p l_p^2$, is found to be 14 in water and 18–20 in three organic solvents at 25 °C.[11] Here $\langle r^2 \rangle_0$ denotes the mean square unperturbed end-to-end distance and n_p is the number of virtual bonds of length l_p. Virtual bonds extend from C^α of residue i to C^α of residue $i + 1$. They have length 380 pm.[12]

Measured characteristic ratios are rationalized by a conformational energy surface that incorporates consequences of flexibility in the pyrrolidine ring.[13] The major feature in the conformational energy surface is an area of low energy that includes the conformation adopted by a prolyl residue in the solid state. This low-energy region has an extension of about 80° for the C^α–C' dihedral angle, ψ, and an extension about half as large for the C^α–N dihedral angle, ϕ. The limiting characteristic ratio for