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Microscopic Approach to Volume Recovery of Polymers

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ABSTRACT: A theory of volume relaxation following step temperature jumps near T_g is derived on the basis of a fractional exponential autocorrelation function $g(t)$ for backbone bond transitions in amorphous polymers. The exponent describing the time dependence of bond relaxation depends on the instantaneous density. A nonlinear integral equation for the time-dependent density is found and compared to experiment for PVAc by using relaxation parameters from dielectric loss data above T_g. The τ_{eff} "paradox" is only apparent. For all initial density deviations, δ_0, one eventually has $\tau_{\text{eff}} \rightarrow \infty$ at $\delta_\infty \rightarrow 0$. For finite times, samples which begin at higher initial temperatures stay ahead of those which start at lower temperatures. The final drop of $\tau_{\text{eff}} \rightarrow \infty$ occurs quite close to $\delta_t = 0$, so that samples with positive temperature steps show different, seemingly finite, intercepts. The proposed density behavior of the dispersion exponent implies pressure-sensitive loss peaks and activation volumes for PVAc near T_g.

Introduction

Volume recovery of amorphous polymers near the glass transition exhibits complicated time and rate dependencies, pronounced asymmetry, nonlinearity, and memory effects. These phenomena, well documented in the pioneering temperature-jump studies of Kovacs[1] on volume recovery of poly(vinyl/acetate) (PVAc), are extremely demanding of a theoretical model put forward to describe them. For example, a single parameter free-volume model accounts for the asymmetry and nonlinearity, but Kovacs and co-workers[2] demonstrate that a distribution of relaxation times, hypothesized to arise from multiple ordering parameters, is required to explain the memory effects. Robertson[3] suggested that a relaxation time distribution results from thermal fluctuations that cause environments of different free volume to coexist. From a computation of transition probabilities using a chain model, he is able to calculate the rate of volume relaxation, and recent results suggest a close mathematical, if not physical, correspondence to the Kovacs theory.[4,5] Moynihan et al.,[6,7] in an approach based on the earlier work of Narayanaswamy,[8] described the recovery behavior of glasses in terms of a fractional exponential relaxation function. The time dependence obtained by using the multiparameter model of Kovacs is similar to that found by Moynihan, pointing to an overall descriptive unity of theories which began from different physical models. In spite of the progress achieved, a number of issues remain to be clarified. In particular they are as follows:

1. Why does the effective relaxation time τ_{eff} not approach a unique value (as all theories predict it should) as volume equilibrium is approached following a positive temperature jump?
2. What is the connection between the relaxation function for volume response and that for other macroscopic variables such as the electric or elastic displacements?
3. What is the physical origin of the distribution of relaxation times or, alternatively, the nonexponential molecular kinetics?

In this paper we present another microscopic model of volume recovery in polymer glasses.[9] The theoretical basis is also a fractional exponential decay function—identical in form to that used by Moynihan,[6,7] Narayanaswamy,[8] and others[10,11]—derived previously[12,13] on the basis of a dynamical competition between the rate of particle relaxation and the rate of excitation of correlated states (CS) in the surroundings of the particle.[23] A new element of the present theory is an explicit dependence of the fractional exponent on the thermodynamic state. The origin of this dependence is the change in dynamic perturbation following changes in the surroundings.

The main result is a bond hopping rate which depends both on time and on the instantaneous density of the polymer. A nonlinear integral equation for the density deviation δ_t at time t is derived in terms of the density and hopping rates at all earlier times. The integral equation is involved numerically by successive approximations.

To illustrate the theory, relaxation parameters for PVAc are evaluated from the dielectric data of Sasabe and Moynihan[14] and a power-series representation of the density dependence of the exponent n is adopted to calculate the volume recovery. An explanation of the τ_{eff} paradox is presented and implications for pressure-dependent dielectric dispersion and activation volumes near T_g are mentioned.

Theory

The model applies a relaxation theory recently proposed by one of us (K.L.N.)[12,13] to describe low-frequency dynamic responses in condensed matter. The theory is reviewed briefly to highlight the physical assumptions, establish notation for the polymer problem, and make the presentation self-contained. The original papers are referred to for motivation and background, as well as nonpolymeric applications.

The theory considers the dynamics of a single degree of freedom (called a "bond" for convenience) governed by a potential surface with minima separated by activation barriers. In polymers, "bonds" are backbone degrees of freedom undergoing conformational transitions (e.g., via dihedral angles with some bending and stretching[3,4]). We assume a symmetrical two-state potential with a single energy barrier E_a as a crude model of a local mode or "flexed bond". (Equating energies simplifies the analysis and is not an important approximation. More doubtful is the restriction to two states. Many vinyl polymers exhibit several isomerization mechanisms, often between more than two states.)

In addition to the effects of the potential, a bond receives impulses from neighboring chains and from nonbonded groups in the same chain. The correlated states (CS) theory distinguishes between fluctuating forces which are higher in frequency than bond transition rates and those of comparable or lower frequencies. Kramers' Brownian motion model[15] describes the consequences of large, high-frequency random forces on the long-time dynamics of a bond in a symmetric double well; jumps between energy minima occur with an escape time τ_0

$$\tau_0 = \tau_\infty e^{E_a/RT} \tag{2.1}$$

where τ_∞ depends on the friction constant, the moment of inertia of the bond, and the curvature of the potential,[15] R is the gas constant, and T is the absolute temperature. The CS theory assumes that at low temperatures in the melt or solid, low-frequency random forces arise from a coupling of the bond motion to the surroundings and that these low-frequency "correlated states" alter the character of the rotational hopping.

The dipole moment autocorrelation function $G(t)$ is related to dielectric loss arising from single bond reorientations.[16] If $\mu_z{}^j(t)$ is the z component of the electric moment of the jth bond, then

$$G(t) = \langle \mu_z{}^j(0)\mu_z{}^j(t)\rangle \tag{2.2}$$

where brackets denote an equilibrium ensemble average. (All bonds are assumed to be equivalent and the index j is dropped.) The normalized correlation function $g(t) = G(t)/G(0)$ is the probability of finding at time t that value of the component which existed at time zero. We assume that $g(t)$ also describes the time evolution of the bond probability.

Glass transition kinetics are distinguished by long relaxation times. From the molecular viewpoint, this means that many bond vibrations occur in an individual well between hops. The time variable t is expressed as a multiple of τ the vibration period in a well. The kinetics are known if the probability of hopping during each vibration period τ_i is calculable. This is accomplished (formally) by introducing a time-dependent transition rate $W(t)$[13] so defined that the definite integral

$$\int_{\tau_{i-1}}^{\tau_i} W(t)\,\mathrm{d}t \tag{2.3}$$

equals the probability of a hop in the period from τ_{i-1} to τ_i. The probability $p(i)$ of remaining fixed during the ith period is

$$p(i) = 1 - \int_{\tau_{i-1}}^{\tau_i} W(t)\,\mathrm{d}t \tag{2.4}$$

and transition probabilities for different periods are independent. The probability $g(t)$ of remaining fixed for a time $t = K\tau$ equal to K vibration periods is the product

$$g(t) = p(1)p(2)p(3)...p(K) \tag{2.5}$$

If t is large compared to τ, an equation of motion for $g(t)$ is obtained by expanding $g(t + \tau) - g(t)$:

$$(\mathrm{d}/\mathrm{d}t)g(t) = -W(t)g(t) \tag{2.6}$$

Progress requires an expression for the time-dependent transition rate $W(t)$. From quantum mechanical perturbation theory plus a model for the bath density of states, the CS theory yields the two-parameter form[12,13]

$$W(t) = At^{-n} \tag{2.7}$$

with $0 < n \leq 1$ and $A = [(e^\gamma \nu_c)^n \tau_0]^{-1}$, where $\gamma = 0.5772156$ is Euler's constant, ν_c is the cutoff frequency of the density of states, and τ_0 is Kramers' hopping time[15] of eq 2.1. With eq 2.7, the correlation function $g(t)$ is

$$g(t) = e^{-(t/\tau_p)^{1-n}} \tag{2.8}$$

where

$$\tau_p = ((1 - n)(e^\gamma \nu_c)^n \tau_0)^{(1/1-n)} \tag{2.9}$$

For the case $n = 0$, $g(t) = e^{-t/\tau_0}$. If $n \neq 0$, $g(t)$ is a fractional exponential relaxation function related to empirical functions suggested by Kohlrausch, Pierce, and others[11] for mechanical relaxation and to the empirical Williams and Watts dielectric relaxation function.[10,11] The success of the latter has led to attempts to derive it by using chain models, frequently concluding $n = {}^1/_2$.[17,18] In addition to the dispersion result $0 < n \leq 1$, the CS theory leads to a novel temperature behavior for the relaxation rate. In eq 2.1, τ_0 has the activation energy E_a, whereas eq 2.8 and 2.9 imply loss peaks shifting as $e^{-E_{\mathrm{app}}/RT}$, where the apparent activation energy E_{app} is

$$E_{\mathrm{app}} = E_a/(1 - n) \tag{2.10}$$

The exponent n has a major effect on the relaxation. From the theory,[12,13] n is proportional to the interaction of a bond with its surroundings (i.e., CS). n and ν_c are material constants and depend on the polymer, state of aggregation (solution, liquid, rubber, glass, crystal), and thermodynamic variables such as temperature, density, stress, and strain. The memory effect described by the function $W(t)$ in eq 2.6 leads to transition probabilities (per vibration period) which diminish steadily. In the absence of CS, the transition rate $W(t)$ is independent of time, $n = 0$ and Kramers' result is found. As n increases, hops become more intermittent and dispersion increases. Physical conditions corresponding to weak interactions (eg., dilute solution and/or high temperatures) cause $n \rightarrow 0$. Conversely, as a melt or rubber is cooled, n usually increases because of the greater density and lower temperature. An increase in n with decreasing temperature near T_g, has two principal consequences:

A. The activation energy determined dielectrically (for example) from a plot of log $f_{\max}$ vs. $1/T$ increases with decreasing temperature (cf., eq 2.10) where $f_{\max}$ is the peak loss frequency at a given temperature. This behavior is reminiscent of the Williams–Landel–Ferry (WLF)[19] behavior for the shift factor a_T for relaxation of the Vogel relation for the viscosity η.

B. The relaxation spectrum obtained by Fourier transformation of the correlation function $g(t)$ in eq 2.8[23] becomes broader, suggesting a widening "distribution of relaxation times". Thermorheological simplicity fails to hold if n varies with temperature. The spectrum not only shifts but changes it shape as Kovacs, Stratton, and Ferry observed for PVAc.[20] (See also ref 14.)

The CS theory relates changes in dispersion to temperature-dependent activation energies since it suggests that they have the same cause, a temperature variation of n. The existence or nonexistence of one effect implies the existence or nonexistence of the other. This correlation has been examined by one of us (K.L.N.) for 20 glassy polymers[21] as well as for nonpolymeric glasses.

In this article, the theory is extended to include volume recovery near the glass transition by allowing n to depend on density and temperature. The density–n relation has the same origin as the temperature–n relation: variation in low-frequency bond hopping interactions (CS) with changes in state. In the next section, an equation of motion for a density deviation near T_g is derived and applied to the experimental results of Kovacs and co-workers for PVAc, using values of bond relaxation parameters E_a, ν_c, τ_∞, and $n(T)$ determined from dielectric data of Sasabe and Moynihan[14] above T_g.

Volume Recovery of PVAc

Following Robertson,[3,4] volume relaxation near T_g is attributed to backbone bond transitions, and this results from different packing arrangements available to trans and gauche bonds. The calculation begins by supposing that at time $t = 0$ a temperature jump (higher or lower) is made and that subsequent thermal equilibration occurs rapidly compared with volume V or structural recovery. Kovacs first introduced the fractional volumetric deviation δ_t at time t defined in terms of the instantaneous volumes V_t and the final equilibrium volume V_∞:

$$\delta_t = \frac{V_t - V_\infty}{V_\infty} \tag{3.1}$$

Since the origin of the deviation δ_t is a nonequilibrium bond population, the kinetics of δ_t parallels the bond relaxation (cf. eq 2.7)

$$(\mathrm{d}/\mathrm{d}t)\delta_t = -W(t)\delta_t \tag{3.2}$$

(once temperature has stopped changing). The transition rate $W(t)$ in eq 3.2 also depends on δ_t and we assume that the major contribution arises from the density dependence of n. Displaying the density dependence, the hopping rate is (cf. eq 2.8)

$$W(t) = \frac{W_0}{(e^{\gamma}\nu_c t)^{n(\delta_t)}} \tag{3.3}$$

Equation 3.2 is integrated

$$\delta_t = \delta_0 \exp\left[-\int_0^t \frac{W_0}{(e^{\gamma}\nu_c t)^{n(\delta_t)}}\,\mathrm{d}t\right] \tag{3.4}$$

where $W_0 = \tau_0^{-1}$.

Knowledge of the behavior of n with δ at different temperatures is needed to solve the self-consistent nonlinear integral equation (3.4). (If n were independent of δ_t, then the fractional-exponential behavior of eq 2.8 results and the asymmetry and nonlinearity is not explained.) A crude estimate of the n–δ dependence may be found by using available n–T and T–δ behavior, but the quality of such data is uncertain. Another procedure is to adopt a power series from

$$n(T,\delta) = n_0(T) + n_1(T)\delta + n_2(T)\delta^2 + \ldots \tag{3.5}$$

treating the coefficients as adjustable parameters. This is the method reported. When eq 3.5 is substituted in eq 3.4, the density δ_t reflects the entire history from $t = 0$. Though formidable in appearance, eq 3.4 is readily solved by successive approximations for δ_t. The results of the numerical work for PVAc are expressed in terms of τ_{eff} as defined by Kovacs:

$$\tau_{\mathrm{eff}} = -(\mathrm{d}\delta_t/\mathrm{d}t)\delta_t^{-1} \tag{3.6}$$

Application of eq 3.4 to volume recovery in PVAc requires relaxation parameters for the correlation function eq 2.8, plus estimates for the coefficients in eq 3.5. The glass transition kinetics of PVAc are well described by a fractional exponential, and several dielectric studies are available. The dielectric loss results of Sasabe and Moynihan[14] are consistent with the following values for PVAc:[22]

$$\tau_\infty = 3.8 \times 10^{-25}\ \mathrm{s} \tag{3.7a}$$

$$E_a = 28.4\ \mathrm{kcal/mol} \tag{3.7b}$$

$$\nu_c = 6.3 \times 10^{9}\ \mathrm{s}^{-1} \tag{3.7c}$$

$$n = 0.47 \text{ at } 44\ {}^\circ\mathrm{C} \tag{3.7d}$$

Sasabe and Moynihan report temperature-dependent dispersion, but their measurements do not go as near to T_g as the volume studies. Larger values of n (roughly extrapolated from ref 14) are used at 35 and 40 °C.

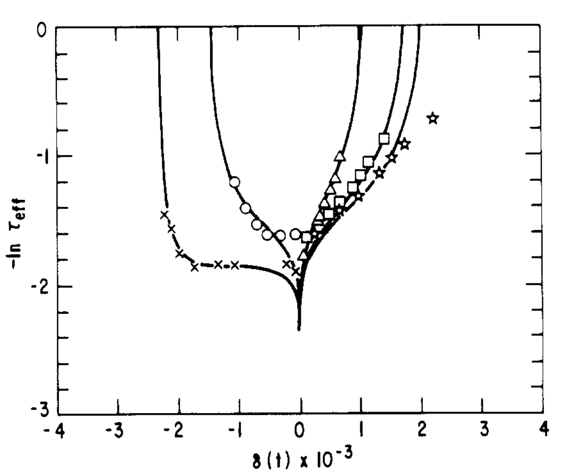

Figure 1. Negative of the natural logarithm of τ_{eff} plotted against log δ_t for PVAc from ref 1 and calculated from the integral equation of eq 3.4 by using the PVAc model parameters of eq 3.7 and n–δ relation eq 3.8, for a final temperature of 35 °C.

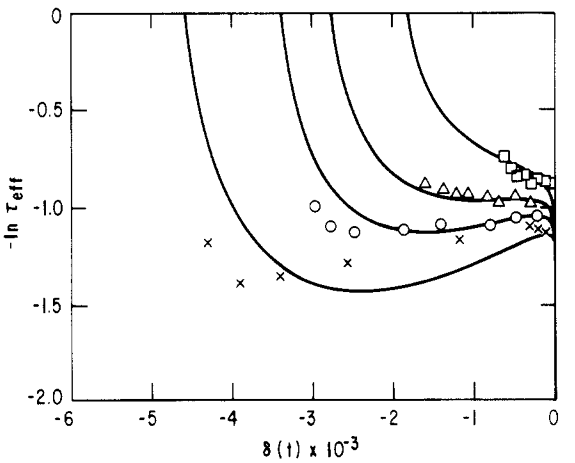

Figure 2. Same as Figure 1, for a final temperature of 40 °C.

A linear term is able to fit either the positive or negative temperature-jump experiment, but to fit both requires n_2. Figures 1 and 2 show the experimental data and calculated results by using eq 3.4 with the parameters of eq 3.7 and

$$n(35,\delta) = 0.508 - 3.4\delta + 7330\delta^2 + \ldots \tag{3.8a}$$

$$n(40,\delta) = 0.503 - 20\delta + 2635\delta^2 + \ldots \tag{3.8b}$$

Newton's method is used, and the coefficients in eq 3.5 are varied until reasonable results are found for a single initial condition. The shapes are sensitive to changes in all parameters. No effort to find "best fits" was made. The curves shown are calculated in 10 min on a VAX 11/782.

Discussion

From Figures 1 and 2 and inspection of eq 3.4, it is seen that for negative δ_0, nonlinearity dominates the relaxation over the whole course of the experiment. This arises from the circumstance that for negative δ_0, the polymer goes from a state of slow relaxation rates at $t = 0$ to relatively fast ones at $t = \infty$. The rate at any time t is dependent on the whole history up to that point, causing the more negative δ_0 jumps to continue to lag behind those that began at higher relaxation rates. Positive δ_0 jump samples start from fast rates and slow down. The rate of relaxation at any point in the experiment is much less dependent on the early history, since all of the early rates were very fast relative to the final "equilibrium" rate.

The theory concludes that all of the curves come together for $\delta_t \to 0$ at $\tau_{\text{eff}} = \infty$; the average waiting time from eq 2.7 is infinite. At small, finite δ_t, the calculated curves still appear separate with finite intercepts which are artifacts of the very sharp drop near $\delta_t \sim 0$.

The quality of the agreement with experiment is satisfactory, probably too good because of the latitude in choosing the coefficients of eq 3.5. This procedure may compensate for the many approximations: (a) a single backbone mode causing volume relaxation (cf. eq 2.8); (b) identification of the mode correlation function for dielectric and density relaxation; (c) assumption of thermal equilibrium in the equation of motion, eq 3.2; (d) two-state well with equal energies; etc. Most of these may be removed, though at the expense of introducing new parameters. Equation 3.5 implies a connection between dispersion and density (or pressure through the modulus). Dielectric or mechanical loss peaks in PVAc should become broader with increased pressure near T_g. At the same time, from eq 3.5 and 2.10, activation energies for dielectric or mechanical loss should increase with increasing pressure. In this way the coefficients could be found independently. (Note added in proof: The rough quality of the 40 °C fit of Figure 2 and the nonmonotonic behavior of n in eq 3.8 cannot be improved by any simple shift of the dielectric parameters of eq 3.7 and probably reflects a genuine shortcoming of the numerical calculation. The calculation assumes that the entire source of nonlinearity is the exponent n. Thus the only free parameters of the simulation are the coefficients n_1 and n_2 of eq 3.5. In retrospect, this may put too great a burden on the dispersion behavior, and one should also consider that the barrier height and volumetric relaxation strength are changing near T_g.)

An advantage of the model seems to be its economy of concepts and ability to relate dispersion to temperature and density behavior. Both temperature-dependent activation energies and changing "distribution of relaxation times", embodied in the exponent n, are related to the structure of the polymer near T_g. Thermorheological simplicity is not used nor is it obeyed by PVAc.[14,20] The calculation assumes a familiar molecular mechanism that may also be probed using NMR, dielectric, and mechanical relaxation.[23]

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Registry No. PVAc (homopolymer), 9003-20-7.

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(22) A reviewer noted that the Curie principle might seem to rule out a simple relationship between relaxation of vector (dielectric) and scalar (density) modes. In fact Curie's principle makes no statement about mechanisms but does limit the form of the kinetic coefficients relating macroscopic forces and fluxes. An analogue of the present theory is Onsager's treatment of elastic (tensor) and electric (vector) relaxation in ice—*J. Chem. Phys.*, **50**, 1089 (1969). Onsager could calculate the numerical factor relating the decay of the two correlations, since the structural details of ice are known. We avoid these important kinematic questions.

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