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Relaxation in the Glassy State: Volume, Enthalpy, and Thermal Density Fluctuations

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ABSTRACT: The theory of thermal density fluctuations in the glassy state is employed to explore their relaxation toward the thermodynamic equilibrium state and to compare the rate with those of enthalpy and volume. The experimental basis for this comparison is Kovacs' volume relaxation data for poly(vinyl acetate) at 30 and 25 °C. With the aid of the theory, the departures from the equilibrium values are computed as a function of time. From these results, the two other functions are derived. Whereas volume and enthalpy relax at comparable rates, the density fluctuations remain practically constant over the identical time interval. This is in qualitative accord with observations on other polymers. Thus no special and distinct mechanism need be invoked in an interpretation of this result. It could be a consequence of the changes in the distribution of the free volume cluster sizes during the aging process. This affects volume and enthalpy more than the relative density fluctuations.

Introduction

The physical properties of a glassy system change with time due to its nonequilibrium character. However, when the rate of change is small compared with the rate of experimentation, a quasi-equilibrium state for a specified formation history, e.g., pressure and/or cooling rate, can be defined.

We have recently pursued two directions pertinent to the present purpose. Both of these are based on a statistical thermodynamics of the equilibrium melt, as modified for the quasi-equilibrium glass (see, for example, ref 1). A characteristic structure function represented by a hole or free volume fraction h appears in the theory. From a consideration of the quasi-equilibrium state, we turned to a discussion of time processes, i.e., of the relaxation of the volume toward the equilibrium state below T_g.[2,3] The time dependence of the h function, as extracted from isothermal annealing experiments, was introduced into a Doolittle expression to predict the variation in time of the shift factor, obtained from stress relaxation experiments. Continuing this line of investigation, a kinetic theory for hole diffusion in the glass was formulated, subject to confrontation with aging experiments in terms of the h function.[4] The other direction is the computation of mean square density fluctuations in the quasi-equilibrium glass. General relationships were derived based on the equation-of-state theory[5] and compared with experimental results at high and low temperatures below T_g.[6]

The purpose of this paper is to compare with each other the relaxation rates of three quantities, namely, volume V, enthalpy H, and relative density fluctuations $\langle \delta\rho^2 \rangle/\rho^2$, where the latter two are derived from information about the first. The experimental starting points are the detailed investigations of Kovacs on poly(vinyl acetate) (PVAc) glass.[7,8] These were recently analyzed in terms of the theory.[3] Based on the evaluation of our free volume function by means of these experiments, the other two relaxing functions can be predicted. We are particularly motivated by the observation that relaxation of $\langle \delta\rho^2 \rangle/\rho^2$ is, to say the least, extremely slow in a temperature range where a time dependence of V and H is observable.[9,10] Is this observation indicative of differences in mechanism, e.g., frozen inhomogeneities vs. thermal fluctuations, or can it be interpreted in terms of a universal theoretical description of thermal density fluctuations?

Theory

The scaled equation of state is

$$\tilde{P}\tilde{V}/\tilde{T} = (1-\eta)^{-1} + (2y/\tilde{T})(y\tilde{V})^{-2}[1.0110(y\tilde{V})^{-2} - 1.2045] \quad (1)$$

where $\eta = 2^{-1/6}y(y\tilde{V})^{-1/3}$ and $y = 1 - h$. At atmospheric pressure we have $\tilde{P} \simeq 0$. Equation 1 serves to transform an observed time-dependent V into a time-dependent h. Moreover, it provides the equilibrium volume $V_e \equiv V(t = \infty)$ at any temperature above or below T_g. Here, the hole fraction is determined by the minimization of the free energy, which implies the relation[11]

$$(s/3c)[(s-1)/s + y^{-1}\ln(1-y)] = (\eta - 1/3)(1-\eta)^{-1} + (y/6\tilde{T})(y\tilde{V})^{-2}[2.409 - 3.033(y\tilde{V})^{-2}] \quad (2)$$

We define, as previously, the equivalent s-mer by equating the flexibility parameter $3c/s$ with unity and taking $s = \infty$.

For the configurational enthalpy we have[12]

$$H = \{(y/2)(y\tilde{V})^{-2}[1.0110(y\tilde{V})^{-2} - 2.409] + (3/2)\tilde{T}\}P^*V^* \quad (3)$$

where P^* and V^* are the characteristic pressure and volume scaling parameters, respectively. Again, both equilibrium (employing eq 2) and nonequilibrium values are predicted, once the time dependence of h is known from eq 1.

Finally, the expression for the mean square thermal density fluctuations reads[13]

$$\langle \delta\rho^2 \rangle/\rho^2 = (kT/N^2)(\partial\mu/\partial N)^{-1}_{T,V,A\neq 0} \quad (4)$$

where μ is the chemical potential, k the Boltzmann constant, N the number of particles in the volume V, ρ the average number density, and A the chemical affinity defined explicitly here as[5,6]

$$A = -(\partial F/\partial h)_{T,V}$$

with F the Helmholtz free energy. The explicit evaluation of eq 4 yields[5,6]

$$(\partial\mu/\partial N)_{T,V,A} = -(V^2/N^2)\{(\partial P/\partial V)_{T,N,h} + (\partial h/\partial V)_{T,N,A}[(1/V)(\partial F/\partial h)_{T,V,N} + (\partial P/\partial h)_{T,V,N}]\} \quad (5)$$

where

$$(\partial\tilde{P}/\partial\tilde{V})_{\tilde{T},N,h} = (V^*/P^*)(\partial P/\partial V)_{T,N,h} = 2y^3R^2(3\lambda - 5\mu R) - (\tilde{T}/\tilde{V}^2)\{1 - (2/3)\eta\}/(1-\eta)^2 + \{DR^2/\tilde{V} - (2/3)\tilde{T}\eta R^{1/2}/(1-\eta)^2\}(\partial h/\partial\tilde{V})_{\tilde{T}} + [(3\tilde{T}/y)\{1 + y^{-1}\ln(1-y) - (\eta - 1/3)/(1-\eta)\} + R\{(3/2)\xi R - \lambda\}](\partial^2 h/\partial\tilde{V}^2)_{\tilde{T}} \quad (5a)$$

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Table I
Dependence of the Relative Deviations of Volume, Enthalpy, and Thermal Density Fluctuations on Annealing Time for PVAc

t, min	V, cm^3/g	$h \times 10^2$	$-H$, J/g	$\langle \delta \rho^2 \rangle / \rho^2 \times 10^{24}$	$\frac{\Delta V}{V(\infty)} \times 10^3$	$-\frac{\Delta H}{H(\infty)} \times 10^3$	$\frac{\Delta \langle \delta \rho^2 \rangle / \rho^2}{(\langle \delta \rho^2 \rangle / \rho^2)(\infty)}$
			T = 303 K				
50	0.84263	7.7825	465.30	2.443	1.7073	1.652	0.3911
100	0.84245	7.7586	465.43	2.437	1.4889	1.373	0.3877
200	0.84227	7.7347	465.56	2.431	1.2712	1.094	0.3843
400	0.84209	7.7200	465.68	2.425	1.0560	0.837	0.3809
∞	0.84120	7.6503	466.07	1.7561	0.0	0.0	0.0
			T = 298 K				
50	0.84148	7.7104	466.39	2.412	3.7007	4.142	0.4316
100	0.84127	7.6824	466.54	2.405	3.4401	3.822	0.4275
200	0.84107	7.6558	466.68	2.399	3.2007	3.523	0.4236
400	0.84086	7.6278	466.81	2.392	2.9705	3.246	0.4195
1370	0.84052	7.5824	467.04	2.381	2.5712	2.754	0.4128
∞	0.83837	7.3507	468.33	1.685	0.0	0.0	0.0

$$(\partial h/\partial \tilde{V})_{\tilde{T},N,\tilde{A}} = V^*(\partial h/\partial V)_{T,N,A} = [DR^2\tilde{V}^{-1} - (2/3)\tilde{T}\eta R^{1/2}/(1-\eta)^2]/[(3\tilde{T}/y^2)\{(2-y)/(1-y) + (2/y)\ln(1-y)\} + \tilde{T}y^{-2}(1-\eta)^{-2}\{3\eta^2 - (8/3)\eta + 1\} + DR^2/y] \quad (5b)$$

$$(\partial \tilde{F}/\partial h)_{\tilde{T},\tilde{V},N} = (P^*V^*)^{-1}(\partial F/\partial h)_{T,V,N} = (3\tilde{T}/y)\{1 + y^{-1}\ln(1-y) - (\eta - 1/3)/(1-\eta)\} + R\{(3/2)\xi R - \lambda\} \quad (5c)$$

$$(\partial \tilde{P}/\partial h)_{\tilde{T},\tilde{V},N} = (1/P^*)(\partial P/\partial h)_{T,V,N} = DR^2\tilde{V}^{-1} - (2/3)\tilde{T}R^{1/2}\eta/(1-\eta)^2 + (\partial h/\partial \tilde{V})_{\tilde{T}}[\{(2-y)/(1-y) + (2/y)\ln(1-y)\}(3\tilde{T}/y^2) + (\tilde{T}/y^2)/(1-\eta)^2\{1 - (8/3)\eta + 3\eta^2\} + DR^2/y] \quad (5d)$$

with $R = (y\tilde{V})^{-2}$, $\xi = 1.0110$, $\lambda = 1.2045$, and $D = (6\xi - 2\lambda/R)R^{5/2}$. Note the structures of eq 1, 3, and 5. Whereas the former two depend directly on the magnitude of h, the latter is determined by derivatives, which are functions of h or y.

The approach to equilibrium will be defined for any quantity Q by the ratio

$$\Delta Q(t)/Q(\infty) = [Q(t) - Q(\infty)]/Q(\infty) \quad (6)$$

The rates will be expressed by the ratio

$$R_Q(t) = \Delta Q(t)/\Delta Q(t_1) \quad (7)$$

where t_1 signifies the minimum time considered.

Results and Discussion

Kovacs[7,8] measured the time-dependent volume during annealing of PVAc and plotted it in terms of the dimensionless departure from the equilibrium volume $V(\infty)$:

$$d(t) = [V(t) - V(\infty)]/V(\infty) = \Delta V/V(\infty) \quad (8)$$

At 30 °C, d(t) is represented by an empirical relation[3]

$$d(t) = b \log [(t + t_m)/(t + t_0)] \quad (9)$$

where $b = 7.36 \times 10^{-4}$, $t_0 = 0.53$ min, and $t_m = 10\,500$ min. However, at 25 °C, d(t) is read from Table II in ref 3. The evaluation of eq 8 for $V(t)$ requires the computation of the equilibrium volume $V(\infty)$. We employ the theoretical interpolation expression[14]

$$\ln \tilde{V}(\infty) = -0.10335 + 23.8345\tilde{T}^{3/2}; \quad 1.65 < \tilde{T} \times 10^2 < 7.03 \quad (10)$$

with reducing parameters $V^* = 0.81386$ cm^3/g and $T^* = 9471$ K.[3] The values of d(t) and resulting $V(t)$ are given in columns 6 and 2 of Table I. In the third column appear the h values, derived from the V values by means of eq 1.

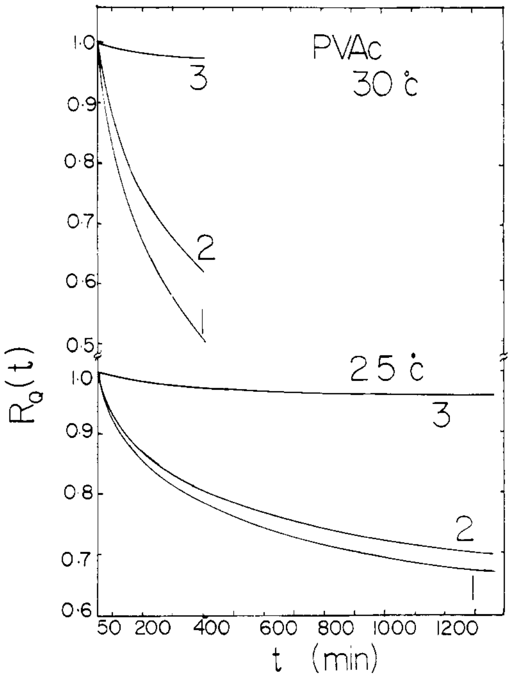

Figure 1. Computed relaxations $R_Q(t)$ for poly(vinyl acetate), eq 7, as a function of time. Lines 1 and 3, enthalpy and relative thermal density fluctuations, eq 3 and 5. Line 2, volume relaxation, data from ref 3 and eq 10.

The values of enthalpy H at atmospheric pressure under isothermal conditions are predicted with eq 3 and exhibited in column 4 of Table I. The relative thermal density fluctuations $\langle \delta\rho^2 \rangle/\rho^2$ are computed from eq 1, 4, 5, and 8–10. For the evaluation of $(\partial h/\partial V)_T$ and $(\partial^2 h/\partial V^2)_T$, h is expressed in the form

$$h = \sum_{i=0}^{1} a_i(T)\tilde{V}^i \quad (11)$$

with the following a_i values:

T, K	a_0	a_1
303	−1.000 447	1.041 436
298	−1.065 922	1.105 522

The maximum deviations between values obtained directly from eq 1 and computed from eq 11 are about 0.01%. The relative thermal density fluctuations are listed in column

5 of Table I. Finally, the characteristic ratios $\Delta H/H(\infty)$ and $\Delta(\langle\delta\rho^2\rangle/\rho^2)/(\langle\delta\rho^2\rangle/\rho^2)(\infty)$ are exhibited in columns 6 and 7, respectively. As for the equilibrium values, they were derived for V and H from the theory of the equilibrium liquid and computed for the density fluctuations from an extrapolation of the experimental compressibility, described by a Tait equation.[1]

Before turning to the rates, it is of interest to examine the departures of the quasi-equilibrium values, $t = 0$, from the final equilibrium. At 30 °C we have from eq 8–10, $V(0) = 0.84394$ cm^3/g. Equation 3 yields $H = -464.42$ J/g and lastly from eq 4 and 5, $(\langle\delta\rho^2\rangle/\rho^2)(0) = 2.487 \times 10^{-24}$. By comparison with the last row of Table I it is seen that the fractional deviations from equilibrium are 0.33, 0.35, and 41.6%, respectively, a difference between the first two and the third by 2 orders of magnitude.

Consider next the rates $R_Q(t)$, displayed in Figure 1. The computed relaxation of enthalpy is more rapid than of volume. This is contrary to observations on identical samples of PVAc.[15] A discrepancy with respect to the quasi-equilibrium value of the change ΔC_p at T_g for PVAc has been noted previously.[1] That is, ΔC_p computed from a knowledge of the h function solely is too small.[1] This, of course, relates to the question of one vs. two or more parameters in the description of the glassy state.

Irrespective of the correctness of the H function computed, the quantitative difference between the behavior of the fluctuations from the other functions in Figure 1 is noteworthy. Between 50 and 400 min volume and enthalpy cover 38 and 84%, respectively, of the total relaxation distance to be traversed at 30 °C, and between 50 and 1370 min, 31 and 34% at 25 °C. For the fluctuation quantity on the other hand, the numbers are 3 and 4%, respectively. Thus it appears that V and, at least, the computed H are more sensitive to a reduction in temperature than the thermal density fluctuations. In any case, the differences in the absolute magnitudes are striking.

Enthalpy and volume are directly related to each other through the hole fraction h; see eq 1 and 3. The connection with the relative density fluctuations is less direct and transparent, since it involves the affinity A and other h- and A-dependent partial derivatives of complicated structure. The much slower decay of the fluctuation rate $R_{\langle\delta\rho^2\rangle/\rho^2}$, observed experimentally for other polymers, is now confirmed also by theory, at least for a system for which the requisite volume recovery data have been obtained. This somewhat surprising outcome suggests an examination of the individual terms in eq 5 and their time patterns. Could the result possibly be the mere consequence of opposite changes with t? Also, may the relative magnitudes of the individual terms permit a simplification of eq 5? In Table II this breakdown is exhibited for both temperatures. What emerges is that two contributions vay considerably over the time period examined, as seen in columns I and V. The remainders change but slowly. However, it is just the latter that determine the final outcome by virtue of their magnitudes. Thus eq 5 reduces in good approximation to

$$(\partial\mu/\partial N)_{T,V,A} = -(V^2/N^2)(\partial h/\partial V)_{T,N,A}(\partial P/\partial h)_{T,V,N} \quad (5A)$$

The involved character of these derivatives (see eq 5b,d) makes a simple interpretation difficult, to say the least. Column I contains the affinity A. Relatively small numerical departures from the ultimate value of zero have been shown to be indicative of significant departures from the equilibrium state.[5] One may expect the restraint of constant T and A to yield an enhanced sensitivity of the

Table II
Change of Individual Terms in Eq 5 with Time

t, min	I $\frac{1}{\tilde V}\left(\frac{\partial \tilde F}{\partial h}\right)_{\tilde T,\tilde V,N} \times 10^3$	II $-\left(\frac{\partial \tilde P}{\partial h}\right)_{\tilde T,\tilde V,N}$	III $\left(\frac{\partial h}{\partial \tilde V}\right)_{\tilde T,N,\tilde A}$	IV -III(I + II)	V $-\left(\frac{\partial \tilde P}{\partial \tilde V}\right)_{\tilde T,N,h} \times 10^2$	VI -(IV + V)	$\frac{\langle\delta\rho^2\rangle/\rho^2}{\rho^2} \times 10^{24}$, g^{-2} cm^6
				$T = 303$ K			
50	4.59	3.9144	0.5325	2.0819	1.068	2.0926	1.7345
100	3.75	3.9182	0.5319	2.0821	1.639	2.0985	1.7295
200	2.90	3.9228	0.5314	2.0830	2.171	2.1047	1.7245
400	2.06	3.9275	0.5308	2.0837	2.705	2.1108	1.7196
∞							1.2426
				$T = 298$ K			
50	12.81	4.3536	0.5358	2.3259	-23.61	2.0899	1.7081
100	11.83	4.3595	0.5352	2.3268	-22.98	2.0970	1.7023
200	10.90	4.3637	0.5346	2.3268	-22.31	2.1037	1.6968
400	9.91	4.3698	0.5340	2.3278	-21.69	2.1109	1.6911
1370	8.31	4.3793	0.5328	2.3290	-20.64	2.1226	1.6818
∞							1.1843

free volume to changes in volume. Moreover, the approximate constancy in column III is consistent with the observation that the isothermal–isoaffinity lines for different affinity values, as computed previously for the quasi-equilibrium glass,[5] show pronounced slopes but are nearly parallel. Furthermore, one can anticipate a small variation of free volume with increasing pressure under isochoric–isothermal restraints, at least at moderate pressures, and hence large values in column III. The minor variation in the time span considered here arises from the small variation in V seen in the second column of Table I.

A qualitative rationalization of the slow decay of $\langle \delta\rho^2 \rangle / \rho^2$ is suggested by Cowie. During the initial stages molecular motions should primarily annihilate the large vacancy clusters of the size distribution.[16] Correspondingly, the fraction of smaller multiplets is enhanced. This distortion of the distribution should primarily affect V and H, related to molecular packing, whereas density fluctuations depend on the existence of inhomogeneities. According to this argument, the differences in aging rates should be more pronounced in high- than in low-T_g systems, as a consequence of the differences in the width of the distribution.[16]

Thus we have been able to show that comparatively rapid rates of relaxation of V and H are consistent with a very low rate for thermal density fluctuations. The relations used for the computations of the latter were the very same employed successfully for the quasi-equilibrium glass at elevated temperatures.[6] As shown earlier for polystyrene and poly(methyl methacrylate),[6] below about $T_g - 50$, frozen inhomogeneities begin to play the dominant role, and the outcome of aging experiments at low temperatures can be expected, but for different reasons than closer to T_g.

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Origin of Logarithmic Factors in the Four-Dimensional Polymer Chain Expansion Factor

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ABSTRACT: Based on the cluster series for the mean-square end-to-end distance $\langle R^2 \rangle$ of a linear flexible polymer chain in d dimensions, it is shown that the logarithmic dependence of $\langle R^2 \rangle$ on the number of bonds N in four dimensions arises from the counterbalance between the long-range and short-range interactions along the chain contour. The free energy due to segment–segment interactions and the second virial coefficient are also computed and are found to depend on $\ln N$ at $d = 4$.

Recently, Chikahisa, Tanaka, Šolc, and Takahashi (CTST)[1] calculated the mean-square end-to-end distance $\langle R^2 \rangle$ of polymer chains in d-dimensional space on the basis of the perturbation theory.[2–4] According to these authors, the square expansion factor α^2 for a ratio of the mean-square end-to-end distance to its value in unperturbed chains without interactions is a function only of z

$$\alpha^2 = 1 + C_1^{(d)} z - C_2^{(d)} z^2 + \ldots \qquad (1)$$

where $C_k^{(d)}$ are numerical constants depending on the dimensionality and z are defined for each dimension as

$$z = (d/2\pi b^2)^{d/2} N^{2-(d/2)} \beta \qquad \text{for } d = 1, 2, 3 \qquad (2)$$

$$z = (2/\pi b^2)^2 (\ln N) \beta \qquad \text{for } d = 4 \qquad (3)$$

$$z = (d/2\pi b^2)^{d/2} \beta \qquad \text{for } d = 5, 6, \ldots \qquad (4)$$

Here N is the number of bonds in a polymer chain, b is the effective bond length, and β is the binary cluster integral for a pair of segments.

In 2- and 3-dimension studies[2,5] it is well-known that the power-law dependence of α on N comes from interactions between segments far apart from each other along the chain contour. The scaling theory[6] predicts that α is independent of N for dimensions higher than 4 because the interaction free energy in such cases is negligible compared to the entropic contribution to the free energy. For exactly $d = 4$, the question is less simple. It was considered by CTST[1] that the logarithmic dependence originates largely from the interaction of nearby segments, since $C_1^{(4)} z$ involves an integral

$$I = \int_{1/N}^{1} \mathrm{d}x/x \qquad (5\mathrm{A})$$

where x is a reduced (by N) contour length between two

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