$$\text{for} \quad B\Gamma + (1-\Gamma)\left[\mu + \frac{\Gamma}{1-\Gamma}\right]^{1/2} < H < B\Gamma + (1-\Gamma B/n^{1/2})\left[\mu + \frac{\Gamma}{1-\Gamma B/n^{1/2}}\right]^{1/2}$$

$$\frac{\partial}{\partial H}\frac{\Delta F_{CD}^*}{^3/_2 kT} = \frac{1}{\Gamma}\left[2\left(\frac{H}{\Gamma} - B\right)\frac{\Gamma}{1-\Gamma} - q\right] + \frac{\partial C}{\partial H} \qquad \text{(B.2b)}$$

$$\text{for} \quad H < B\Gamma + (1-\Gamma)[\mu + \Gamma/(1-\Gamma)]^{1/2}$$

and

$$\frac{\partial}{\partial H}\frac{\Delta F_{BC}^*}{^3/_2 kT} = \frac{\partial C}{\partial H} \qquad \text{(B.3a)}$$

$$\text{for} \quad \Gamma B + q(1-\Gamma)/2 < H < \Gamma n^{1/2} + q(1-\Gamma)/2$$

$$\frac{\partial}{\partial H}\frac{\Delta F_{BC}^*}{^3/_2 kT} = \frac{1}{\Gamma}\left[2\left(\frac{H}{\Gamma} - B\right)\frac{\Gamma}{1-\Gamma} - q\right] + \frac{\partial C}{\partial H} \qquad \text{(B.3b)}$$

$$\text{for} \quad H < B\Gamma + q(1-\Gamma)/2$$

where

$$\partial C/\partial H = -2H/\Gamma + q/\Gamma \qquad \text{(B.4a)}$$

$$\partial C'/\partial H = -2H/\Gamma \qquad \text{(B.4b)}$$

The choice of the deepest free energy minimum (ΔF_{AB}^*, ΔF_{BC}^*, ΔF_{CD}^*) is based on the comparison of numerical results. This choice determines also which one of the free energy derivatives $\partial\Delta F_{AB}^*/\partial H$, $\partial\Delta F_{BC}^*/\partial H$, or $\partial\Delta F_{CD}^*/\partial H$ has to be inserted into eq 38 to yield the change in normal stress difference caused by equilibrium crystallization.

References and Notes

(1) Hoffman, J. D.; Davies, G. T.; Lauritzen, J. T., Jr. *Treatise Solid State Chem.* **1976**, *3*.
(2) Flory, P. J. *J. Chem. Phys.* **1947**, *15* (6).
(3) Smith, K. J. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1975**, *16* (2), 337.
(4) Wu, W. L. *J. Polym. Sci.* **1978**, *16*, 1671–1683.
(5) Roe, R.-J.; Smith, K. J., Jr.; Krigbaum, W. R. *J. Chem. Phys.* **1961**, *35* (4).
(6) Baranov, V. G.; Elyashevich, G. K. *Vysokomol. Soedin., Ser. B* **1974**, *16*.
(7) Gaylord, R. J. *J. Polym. Sci.* **1976**, *14*, 1827–1837.
(8) Jarecki, L.; Ziabicki, A. *Polymer* **1979**, *20*, 411. It has been brought to the authors' attention that the question of junction mobility has been recently addressed also by Smith (182nd National Meeting of the American Chemical Society, New York, Aug 23–28, 1981).
(9) Allegra, G. *Makromol. Chem.* **1980**, *181*, 1127–1141.
(10) James, H. M.; Guth, E. *J. Chem. Phys.* **1947**, *15* (9).
(11) Ronca, G.; Allegra, G. *J. Chem. Phys.* **1975**, *63*, 4104.
(12) Astarita, G.; Marrucci, G. "Principles of Non-Newtonian Fluid Mechanics"; McGraw-Hill: New York, 1974.
(13) Judge, J. T.; Stein, R. S. *J. Appl. Phys.* **1961**, *32*, 2357.
(14) Krigbaum, W. R.; Roe, R.-J. *J. Polym. Sci., Part A* **1964**, *2*, 4391.
(15) Yeh, G. S. Y. *Polym. Eng. Sci.* **1976**, *16* (3), 138.
(16) Kawai, H.; Iguchi, M.; Tanami, H. *Kolloid Z.* **1968**, *221*, 28.

Theory of Density Fluctuations in the Glassy State: High and Low Temperatures

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ABSTRACT: A formal extension of the classical equilibrium theory of thermal density fluctuations to systems with nonvanishing chemical affinity has been given by Wendorff and Fischer. It has been evaluated explicitly by us earlier with the aid of our equation-of-state theory of the glassy state. The same methods are now applied to a polystyrene and a poly(methyl methacrylate) glass. In the range between $T_g - 50$ and T_g good agreement between theoretical prediction and measurements of Ruland and Wiegand ensues. These results once more demonstrate the only *partial* freeze-in of the theoretical free volume function in the glass transition. By means of the low-temperature equation of state, the approach of the thermal density fluctuation to the zero limit at $T = 0$ is derived. Experiment, however, indicates the onset of departures from theory in the region of the β process, which ultimately results in substantial residual contributions at $T = 0$. An analysis in terms of essentially temperature-independent inhomogeneities is given. The results indicate that these cannot be associated with the free volume quantity introduced in connection with the configurational thermodynamics of the glass. Instead, more numerous and smaller inhomogeneities must be invoked.

Introduction

We have recently derived expressions for the mean square thermal density fluctuations,[1] based on equation-of-state theory for the glassy state. The important structure parameter in this theory is a hole or free volume fraction h. In the equilibrium melt it is uniquely determined by the minimization of a configurational free energy. At the glass transition, a partial freeze-in process starts, which so far has been evaluated by a combination of equation-of-state measurements for glasses of specified formation history with theoretical expressions. Two alternative procedures have been employed. One involves the numerical solution of a partial differential equation derived from the free energy expression.[2] The other and approximate procedure requires the numerical solution of an algebraic equation.[3,4] For several polymers, the latter procedure only has been applied. For two poly(vinyl acetate) (PVAc) glasses on the other hand, a comparison of the two solutions shows numerically small differences in absolute values, albeit larger differences in the temperature coefficients of h. The results of the elaborate treatment were employed to compute the density fluctuations of PVAc in the range $T_g - 60 < T < T_g - 10$.[1] The limits are imposed by the range of validity of the numerical solutions of the differential equation. The results are consistent in the neighborhood of T_g with the approximation of Wendorff and Fischer[3] and derived from their general theory,[5] which forms also the basis for our theory. Their approximation involves the compressibility of the melt at T_g and should not be valid at lower temperatures.

For purposes of comparison, total intensity measurements for PVAc have only recently become available.[6] On

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the other hand, X-ray data for polystyrene (PS) and poly(methyl methacrylate) (PMMA) have been obtained.[7,8] These extend far beyond the glass transition region into the cryogenic range. It becomes desirable then to test theoretical predictions for these two systems with their comparatively elevated T_g's. However, the computations of the h function have not been performed by the elaborate methods described above. Thus it becomes necessary to start with a comparison of the density fluctuations for a PVAc glass, computed in two ways.

Dilatometric investigations, such as those described in ref 3, clearly reveal the onset of the β process, conventionally examined by means of dynamic measurements. Hence a second decrease in the temperature coefficients of h follows. We note that concomitant changes in the pressure coefficients derive from the compressibility changes in the β region. Finally, in the range 50–70 K, dilatometric observations are consistent with the assumption of a practically completely frozen structure as expressed by the h parameter.[10] These results may then be used to compute the thermal density fluctuations at cryogenic temperatures.

Ruland and Wiegand's measurements of several amorphous and semicrystalline polymers[7,8] yield finite intercepts at $T = 0$, with a flattening out of the curves considerably above this limit. This indicates a nonthermal origin of the fluctuations and a contribution by a frozen structural disorder. A typical magnitude of this contribution is about 50–60% of the value at T_g. Thus this effect becomes already important at higher temperatures in comparison with the thermal contributions.

In the next section we recapitulate the general expressions for the mean square density fluctuations and the comparative evaluations for the PVAc glass discussed earlier.[1] The following section contains the application to high-temperature glasses of PS and PMMA. Next, low-temperature fluctuations are evaluated. We conclude with a discussion of frozen inhomogeneities.

Theory

The basic relation for the mean square thermal density fluctuations $\langle\delta\rho^2\rangle$ for N molecules in a volume V at a temperature T reads[5]

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

with μ the chemical potential and A the affinity, defined explicitly in our theory as[1]

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

with F the Helmholtz free energy. The equation of state yields

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

In the limit $A \to 0$, eq 2 reduces to the familiar result involving the isothermal compressibility. On the other hand, if the hole fraction h is frozen at some constant level, only the first term on the right-hand side of eq 2 survives and a compressibility quantity is the sole determining factor.

The evaluation of eq 2 makes use of the equation of state and resulting evaluation of the function $h(V,T)$. The solutions to two PVAc glasses have been given in polynomial form and used in ref 1. Approximations to these are based on the equation of state, $P = P[V,T;h(V,T)]$, as derived for thermodynamic equilibrium, but disregard the equilibrium restraint $(\partial F/\partial h)_{T,V} = 0$. Instead, h is obtained by solution of the above equation for specified experimental P, V, and T values. In Figure 1 the two modes of evaluating eq 2 are exhibited. The approximation yields consistently lower values with a maximum difference at the lowest temperature of $T_g - 60$ of 12% at atmospheric pressure, increasing to 16% at 800 bar.

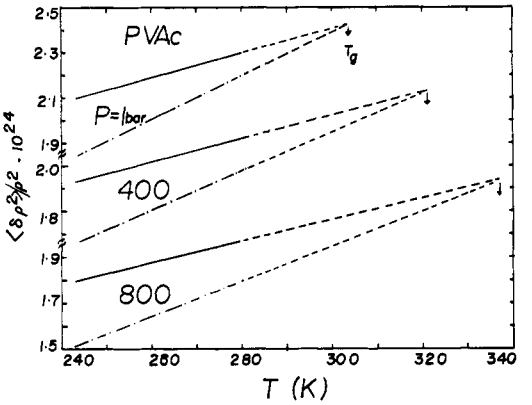

Figure 1. Relative density fluctuations $\langle\delta\rho^2\rangle/\rho^2$ as a function of temperature for poly(vinyl acetate): solid curves, exact; dotted, approximate theory; dashed lines, extrapolated. For explanation, see text.

At sufficiently low temperatures, h may be considered as a constant and its numerical value absorbed in the definition of the scaling parameters. An expansion of the Lennard-Jones–Devonshire cell potential to the quasi-harmonic term then yields the reduced equation of state as follows:[10]

$$\tilde{P}\tilde{V} = 2\tilde{V}^{-2}(C\tilde{V}^{-2} - D) + 3G\tilde{\Theta}\{\tfrac{1}{2} + [\exp(\tilde{\Theta}/\tilde{T}) - 1]^{-1}\} \qquad (3)$$

with $C = 1.0110$, $D = 1.2045$, and $\tilde{\Theta}(\tilde{T}) = h\nu/(kT^*)$, where T^* is the scaling temperature and ν the characteristic volume-dependent frequency. From this dependence there follows

$$\tilde{\Theta}(\tilde{T}) = \tilde{\Theta}(0)(V_0/V)^{4/3}[(\gamma\tilde{V}^{-2} - \delta)/(\gamma\tilde{V}_0^{-2} - \delta)]^{1/2} \qquad (4)$$

with $\gamma = 11.0530$, $\delta = 5.2797$, and $\tilde{V}_0$ the reduced volume at $T = 0$. A universal value of 5×10^{-3} could be assigned to the reduced quantum temperature $\tilde{\Theta}(0)$,[10] which results in the effective validity of a principle of corresponding states for polymer glasses at low temperatures. Finally, the intermolecular Grüneisen parameter G is given by the relation

$$3G = (7\gamma\tilde{V}^{-2} - 4\delta)/(\gamma\tilde{V}^{-2} - \delta) \qquad (5)$$

At atmospheric pressure, $\tilde{P} \simeq 0$, and eq 3 reduces to

$$\xi = \tilde{\Theta}/\tilde{T} = \ln\{1 + 3G/[2\tilde{V}^{-2}(D - C\tilde{V}^{-2})/\tilde{\Theta} - 3G/2]\} \qquad (3a)$$

For $T = 0$, there follows $\tilde{V}_0 = 0.9199$.

From eq 3 the reduced isothermal compressibility for fixed free volume, $\tilde{\kappa}_h = -(1/\tilde{V})(\partial\tilde{V}/\partial\tilde{P})_{\tilde{T}}$, is obtained, viz.

$$1/\tilde{\kappa}_h = \tilde{P} + 4\tilde{V}^{-3}(2C\tilde{V}^{-2} - D) - 3\tilde{\Theta}(\tfrac{1}{2} + \eta)(\partial G/\partial\tilde{V})_{\tilde{T}} - 3G\{\tfrac{1}{2} + \eta[1 - (1 + \eta)\xi]\}(\partial\tilde{\Theta}/\partial\tilde{V})_{\tilde{T}} \qquad (6)$$

with the abbreviation

$$\eta = (e^{\xi} - 1)^{-1}$$

Moreover, $(\partial G/\partial\tilde{V})_{\tilde{T}} = 2\gamma\delta\tilde{V}^{-3}/(\gamma\tilde{V}^{-2} - \delta)^2$ and $(\partial\tilde{\Theta}/\partial\tilde{V})_{\tilde{T}} = -(G/\tilde{V})\tilde{\Theta}(\tilde{T})$. Finally, eq 2 can be cast at low temperatures in the reduced form

$$\tilde{V}\langle\delta\tilde{p}^2\rangle(P^*V^*/T^*) = k\tilde{T}\tilde{p}^2\tilde{\kappa}_h = V\langle\delta\rho^2\rangle(P^*V^{*2}/T^*) \qquad (2a)$$

and $(\langle\delta\rho^2\rangle/\rho^2)(P^*V^*/kT^*) = (\tilde{T}/\tilde{V})\tilde{\kappa}_h$ with the asterisks

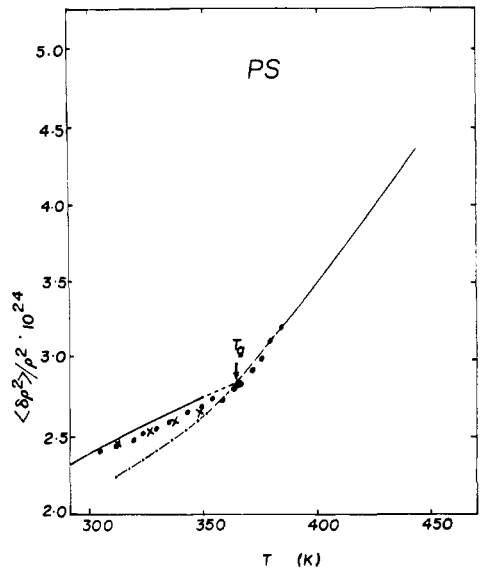

Figure 2. Relative density fluctuation $\langle\delta\rho^2\rangle/\rho^2$ in polystyrene melt and glass as a function of temperature: (●) measurements of Ruland and Wiegand;[7,8] dotted line, approximation; (×) corrected theory (see text); solid line, eq 2b.

indicating scaling parameters.

We consider next the pressure dependence of the fluctuations, at least for low-pressure glasses, generated by cooling under atmospheric pressure, since no *PVT* measurements on high-pressure glasses seem to have been pusblished. The pressure dependence at elevated temperatures is small. This will hold at low temperatures also, and linear approximations should be adequate. That is, instead of reconsidering explicitly eq 3 for finite $\tilde{P}$, we write

$$\tilde{V}(\tilde{P},\tilde{T}) = \tilde{V}(0,\tilde{T})[1 - \tilde{\kappa}_h(0,\tilde{T})\tilde{P} + \mathcal{O}(\tilde{P}^2)]$$

From the definition of $\tilde{\Theta}$, one obtains for the change in the characteristic value of $\tilde{\Theta}_0(\tilde{P} = 0) = 5 \times 10^{-3}$

$$\tilde{\Theta}_0(\tilde{P}) = \tilde{\Theta}_0(0)[1 + G\tilde{\kappa}_h\tilde{V}_0\tilde{P} + \mathcal{O}(\tilde{P}^2)]$$

where the coefficient of $\tilde{P}$ is to be taken at $\tilde{P} = 0$. The numerical adequacy of these approximations will be gaged below.

Applications: Elevated Temperatures

In Figure 1 the differences in the thermal density fluctuations have been illustrated, which result from the two alternative procedures of extracting the h function by means of experimental *PVT* data. Such a comparison has been possible so far for PVAc only. In the analysis of the scattering experiments on PS and PMMA to follow, we do not propose to pursue the more exact, but involved route. Instead, it will be assumed that a correction to the approximate computation of the scattering function can be made by adopting what amounts to a correspondence principle. That is, equality of the ratio of the two fluctuation values for different polymer glasses with *similar* formation histories at equal relative distances $(T_g - T)/T_g$ from the glass temperature and hence use of Figure 1 will be accepted. The numerical evaluation of eq 2 requires a series of expressions, stated in ref 1 as eq 6 and 18–20. Some modifications result from h now being a quadratic rather than a linear function in $\tilde{V}$. The working equations and numerical results are stated in the Appendix for the reader's convenience.

Figure 2 deals with PS, and several results are displayed. The curves are normalized relative to T_g. First, we note the extent of agreement with experiment[7,8] above T_g when *PVT* data for the melt[9] are substituted into the classical

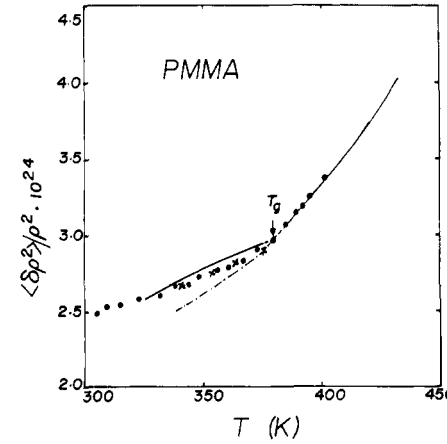

Figure 3. Relative density fluctuation $\langle\delta\rho^2\rangle/\rho^2$ in poly(methyl methacrylate) melt and glass as a function of temperature: (●) measurements of Ruland and Wiegand;[7,8] dotted line, approximation; (×) corrected theory (see text); solid line, eq 2b.

Einstein–Smoluchowski expression. In making such comparisons, one should keep in mind possible sample differences. Below T_g, the observations are displayed down to 300 K, sufficient for the present purpose. We note the result of the simplified h computation, followed by the corrected function. The latter satisfactorily reproduces the experimental data. For reasons of internal consistency and accuracy of the *PVT* data, the computations are not extended below 312 K. However, one may surmise from the published results[7,8] that below about 300 K the theoretical predictions will start to depart gradually from observation. Finally, we show the result of the approximation proposed by Wendorff and Fischer,[5] viz.

$$\langle\delta\rho^2\rangle/\langle\rho^2\rangle = (kT/V)\kappa_1(T = T_g) \qquad (2b)$$

where κ_1 represents the compressibility of the equilibrium melt. The curvature resulting from the thermal expansivity will be noted.

Analogous information for atactic PMMA is presented in Figure 3. Here, *PVT* data in ref 11 are employed in the computations, with an outcome essentially identical with that seen for PS. The lower temperature limit is dictated by the approach to the β relaxation.[3]

Applications: Low Temperatures

In light of the observations in the cryogenic temperature range,[7,8] this section is necessarily restricted to an exploration of the approach to $T = 0$ as predicted by the theory of *thermal* fluctuations, eq 2 and 3–6, and comparisons with the high-temperature values. Concerning the latter purpose, it must be recalled that the scaling parameters in the low- and high-temperature *PVT* theories are not identical. This arises from the approximation of the Lennard-Jones–Devonshire cell potential by a square well in the melt and high-temperature glass and by a quasi-harmonic potential at low temperatures. For PS, T^* and V^* are known under both conditions.[9,10] Studies at elevated pressures have not been undertaken at liquid He temperatures. Hence, P^* is unknown, but comparisons in terms of scaled variables can be made: see eq 2a. Where no experimental information is available, the requisite scaling temperature may at least be estimated by comparisons with other polymers; see below.

We begin with plots of the reduced ratio $(\langle\delta\rho^2\rangle/\rho^2)\cdot(P^*V^*/kT^*)$ as a function of $\tilde{T}$ for $\tilde{P} = 0$, 0.1, and 0.2 in Figure 4. Since P^* for polymer melts has been found to range from about 8×10^3 to 10^4 bar,[11] the reduced pressures chosen correspond maximally to ca. 2 kbar. The

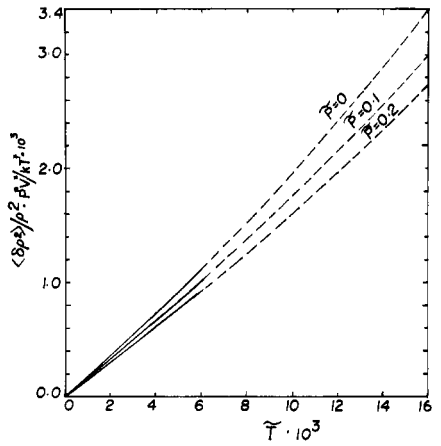

Figure 4. Theoretical scaled density fluctuation $\langle\delta\rho^2\rangle/\rho^2 \cdot (P^*V^*/kT^*)$ as a function of reduced temperature at several reduced pressures. Dashed portions, extrapolations.

average of the T^* found at low temperatures is about 1.4×10^4 K.[10] Thus the limits of 50–70 K for complete freeze-in of the h fraction correspond to $\tilde{T} \approx (4\text{–}5) \times 10^{-3}$. We observe a reasonable proportionality with $\tilde{T}$ up to approximately 6×10^{-3}. The graphs have been extended beyond the allowable range, as indicated by the dashed portions, to join up with the lower limit of the high-temperature theory.

The accuracy of the expansion in $\tilde{P}$ may be judged from the following results: $\tilde{V}_0(0) = 0.9199$; $\tilde{V}_0(0.2) = 0.8899$; $\tilde{\Theta}_0(0) = 0.005$; $\tilde{\Theta}_0(0.2) = 0.00545$. A more accurate evaluation of $\tilde{\Theta}_0$ may be desirable but is unnecessary here.

Consider next the theoretical characteristic ratio $\langle\delta\rho^2\rangle/\rho^2$ for PS, which decreases from 2.85×10^{-24} to 2.45×10^{-24} between 89 and 39 °C. With the aid of the scaling quantities[9] $V^* = 0.9598$ cm^3/g, $T^* = 12680$ K, and $P^* = 7453$ bar, the scaled quantity $\langle\delta\rho^2\rangle/\rho^2(P^*V^*/kT^*)$ is seen to vary from 1.165×10^{-2} to 1.002×10^{-2} at atmospheric pressure. On the other hand, in the low-temperature relations we substitute[10] $V^* = 0.9947$ cm^3/g and $T^* = 13430$ K. The extrapolation to 39 °C then yields 5.4×10^{-3}, or 54% of the value given above. While part of this difference will arise from higher terms in the expansion of the cell potential, the more important contribution comes from the temperature dependence of the structure, expressed in our theoretical frame by the h function. It is instructive, furthermore, to compare the reduction in the thermal density fluctuations between T_g and 60 K, which represents the approximate temperature of practical freeze-in of free volume. The ratio is 0.81/11.65, or 7%.

Similar estimates may be made for the other two polymers considered here, although no dilatometric measurements at liquid He temperatures have been performed for either PMMA or PVAc. Between 67 and 105 °C and with $V^* = 0.8370$ cm^3/g, $T^* = 11920$ K, and $P^* = 9147$[11] for the former, one finds a variation from 1.174×10^{-2} to 1.384×10^{-2}, deriving from $10^{24}\langle\delta\rho^2\rangle/\rho^2 = 2.523$ and 2.975, respectively. With the above value of T^*, the extrapolation of the low-temperature equations to 340 K yields at atmospheric pressure 6.96×10^{-3}, i.e., 59% of the total. A correction with respect to the unknown value of T^* may be made by assuming the ratio of T^*'s in the two versions of the equation of state to be identical for PS and PMMA. This would increase T^* from 11920 to 12625 K. The ensuing change in $\tilde{T}$ by 6% is hardly significant. Further, the ratio of thermal fluctuations at 60 K and T_g is 6%. The analogous calculation for PVAc with the scaling parameters $V^* = 9.8141$ cm^3/g, $T^* = 9419$ K, and $P^* = 9380$ bar[4] yields at 250 K and atmospheric pressure 56% of the total. At 60 K, the computed thermal density fluctuations amount to 9% of the magnitude at T_g. This somewhat higher value may arise from the closer proximity of the glass temperature. In essence then, the results for the three polymers are identical, that is, a contribution of 40–50% by the temperature- (and pressure) dependent free volume fraction h to the relative density fluctuations some 50 to 40 K below T_g, with less than 10% of the value at T_g surviving at 60 K.

Frozen Inhomogeneities

We have so far confronted the theory with the observations of Ruland and Wiegand[7,8] at elevated temperatures, i.e., above $\simeq T_g - 50$. Moreover, we have computed the rate of decay of thermal fluctuations in the cryogenic temperature region. The flattening out of the experimental curves between the two temperature regimes cited above and the resulting finite intercept at $T = 0$ suggest a frozen structural disorder, which overshadows the thermal contributions.

To pursue this subject, consider then density fluctuations arising from a *fixed* fraction h of empty sites, distributed at random in our quasi-lattice of L sites and volume V. The probability of finding a vacancy in a volume $v \ll V$ equals $v/V \ll 1$. The probability $W(i)$ of i such vacancies out of a total Lh occurring in v is given by a Poisson distribution, viz.

$$W(i) = (\lambda^i/i!)e^{-\lambda}$$

$$\lambda = Lhv/V$$

and

$$\langle i^2\rangle - \langle i\rangle^2 = \langle i\rangle^2/\lambda = (V/v)(1/Lh) \qquad (7)$$

Equation 7 is exactly analogous to the expression for the thermal density fluctuations in a perfect gas, resulting in the proportionality with the reciprocal number density. To evaluate this expression, consider N s-mers occupying Ns sites. Since $h = 1 - Ns/L$, the number N_h of vacancies in the sample is given by

$$N_h = Lh = Nsh/(1 - h) = N_A V/(V_{sp}M_s)h/(1 - h)$$

where V_{sp} is the specific volume, N_A is Avogadro's number, and $M_s = M/s$ is the segmental molecular weight. We can then finally write

$$V_{sp}\langle\delta\rho^2\rangle = \rho^2 V_{sp}(M_s/N_A)(1 - h)/h \qquad (8)$$

where the scattering volume v has been replaced by V_{sp}. Now taking as an average 50% of the value noted at T_g, an appropriate value for the right-hand side of eq 8 with $\rho \approx 1$ g/cm^3 would be 1.44×10^{-24}, or $M_s(1 - h)/h \simeq 0.87$. On the other hand, the hole fractions in the equation-of-state theory, which serve as a measure of structural disorder, have typical values at T_g from approximately 0.01 for the lowest to 0.09 for the highest T_g considered.[3] Correspondingly, the "frozen fractions" vary from ca. 0.9 to 0.5.[3] The segments defined by the requirement of the theory are constituted of about 2 CH_2 units for polyethylene and $^1/_2$ of the monomer unit in substituted vinyl polymers.[11] If these numbers with the underlying picture were to be retained in eq 8, the experimental result would be exceeded by an order of magnitude. Any reasonable, even if small, assignment to the segmental molecular weight requires a large value of h, exceeding at least $^2/_3$. Thus, it appears that the frozen-inhomogeneities to be invoked in the interpretation of low-temperature fluctuations cannot be identified with the free volume introduced in connection with the equation of state.

Table I
Coefficients in Eq 2A

	PS				PMMA			
	312.2 K	325.6 K	337.1 K	348.4 K	340.7 K	353.1 K	363.1 K	373.9 K
a_0	1.29213	1.28271	1.30046	1.30214	1.02656	0.98505	0.93787	0.95991
a_1	−2.48748	−2.48568	−2.53484	−2.54971	−2.12467	−2.05760	−1.97417	−2.02710
a_2	1.24807	1.25737	1.29029	1.30505	1.15997	1.13550	1.10015	1.13195

Ruland and Wiegand[7,8] sought to relate their observations to distance fluctuations between molecular units, choosing to define these by the statistical Kuhn segments of the chain. Adopting a lattice model, they derive root-mean-square fluctuations of about 0.25 Å. Regardless of the details of their model, a vacancy model would indeed require large values of h. The configurational thermodynamic properties, on the other hand, are determined at sufficiently low temperatures by the effective vibrational frequencies.

It is worth reiterating at this junction a comment by the above authors[7,8] on the approximation of Wendorff and Fischer (see above).[5] This approximation, applicable in the neighborhood of T_g, should be least appropriate for low-T_g systems, as is indeed the case.[7] This is in accord with the observation that the degree of freeze-in at T_g, as measured by the temperature coefficient of h, is most pronounced in polymers with low T_g[3] and so should therefore be the "frozen" contributions to the density fluctuations.

Conclusions and Outlook

There are two sources of density fluctuations in the glassy state. One arises from liquid-like thermal contributions. The equation-of-state theory has been successful in the range between about $T_g - 50$ and T_g. In this theory, it will be recalled, the difference between melt and glass is focussed on the free volume function h, and its dependence on temperature and pressure. The results once more demonstrate that this function does not reduce to a constant in the temperature range referred to above. Moreover, it is of interest to note that the lower limit of this range takes us to the neighborhood of the (broad) β process. The pressure and temperature coefficients of h have been shown to undergo a second change on passing through the β region,[3,9] but they do not vanish until 50–70 K. One may continue to employ the methods used at higher temperatures to compute the thermal contributions at lower temperatures. These tend, of course, to zero and represent in the above range but a small fraction of the value at T_g. In contrast, experiment at temperatures in the β range, at least for the polymers studied here, begins to depart from theoretical prediction, and at $T = 0$ about 50% of the effect seen at T_g remains, indicating as a second mechanism frozen, i.e., essentially temperature-independent inhomogeneities. We recall in this connection a similar nonthermal effect. Density fluctuations in pressurized polystyrene glass have been shown to be more intense after pressure release than in the unpressurized polymer.[12] A further exploration of the connection between β process and nonthermal contributions suggests the use of systems with intense sub-glass relaxations, e.g., polymers containing flexible side chains.

The current studies dealt with quasi-equilibrium conditions. It has been demonstrated recently that the equation-of-state theory, as applied here and previously,[1] can be extended to the kinetics of physical aging of volume through the h function.[13,14] This opens the way for a computation of the density fluctuations in annealing systems.

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Appendix

The equation of state is

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

where $\eta = 2^{-1/6}y(y\tilde{V})^{-1/3}$ and $y = 1 - h$. From eq 1A, h is derived for given P, V, T, and known scaling parameters. We obtain the following solutions:

$$h = \sum_{i=0}^{2} a_i(\tilde{T})\tilde{V}^i \quad (2A)$$

with the a_i's shown in Table I. The maximum deviation between values obtained directly from eq 1A and computed from eq 2A is about 0.01%.

Taking the derivatives appearing in eq 2 one by one, we have

$$\left(\frac{\partial\tilde{P}}{\partial\tilde{V}}\right)_{\tilde{T},N,h} = -\frac{\partial}{\partial\tilde{V}}\bigg|_{\tilde{T},N,h}\left(\frac{\partial\tilde{F}}{\partial\tilde{V}}\right)_{\tilde{T},h} - \frac{\partial}{\partial\tilde{V}}\bigg|_{\tilde{T},N,h}\left\{\left(\frac{\partial\tilde{F}}{\partial y}\right)_{\tilde{T},\tilde{V}}\left(\frac{\partial y}{\partial\tilde{V}}\right)_{\tilde{T}}\right\} \quad (3A)$$

The second derivatives of $\tilde{F}$ in eq 3A are obtained from eq 9;1 and 10;1 in ref 1. Equation 20;1 provides $(\partial h/\partial V)_{T,N,A}$ and eq 9;1 $(\partial F/\partial h)_{T,V,N}$. Finally, one has

$$\frac{1}{P^*}\left(\frac{\partial P}{\partial h}\right)_{T,V,N} = \frac{\partial}{\partial y}\bigg|_{\tilde{T},\tilde{V},N}\left(\frac{\partial\tilde{F}}{\partial\tilde{V}}\right)_{\tilde{T},h} + \left(\frac{\partial y}{\partial\tilde{V}}\right)_{\tilde{T}}\frac{\partial}{\partial y}\bigg|_{\tilde{T},\tilde{V},N}\left(\frac{\partial\tilde{F}}{\partial y}\right)_{\tilde{T},\tilde{V}} + \left(\frac{\partial\tilde{F}}{\partial y}\right)_{\tilde{T},\tilde{V}}\frac{\partial}{\partial y}\bigg|_{\tilde{T},\tilde{V},N}\left(\frac{\partial y}{\partial\tilde{V}}\right)_{\tilde{T}} \quad (4A)$$

References and Notes

(1) Balik, C. M.; Jamieson, A. M.; Simha, R. *Colloid Polym. Sci.* **1982**, *260*, 477.
(2) McKinney, J. E.; Simha, R. *Macromolecules* **1976**, *9*, 430.
(3) Simha, R.; Wilson, P. S. *Macromolecules* **1973**, *6*, 908.
(4) McKinney, J. E.; Simha, R. *Macromolecules* **1974**, *7*, 894.
(5) Wendorff, J. H.; Fischer, E. W. *Kolloid Z. Z. Polym.* **1973**, *251*, 876.
(6) Tribone, J.; Jamieson, A. M.; Simha, R., in preparation.
(7) Wiegand, W. Inaugural Dissertation, Marburg/Lahn, 1977.
(8) Ruland, W. *Pure Appl. Chem.* **1977**, *49*, 905.
(9) Quach, A.; Simha, R. *Macromolecules* **1971**, *4*, 268. *J. Appl. Phys.* **1971**, *42*, 4592.
(10) Simha, R.; Roe, J. M.; Nanda, V. S. *J. Appl. Phys.* **1972**, *43*, 4312.
(11) Olabisi, O.; Simha, R. *Macromolecules* **1975**, *8*, 211.
(12) Lee, H.; Jamieson, A. M.; Simha, R. *Colloid Polym. Sci.* **1980**, *258*, 545.
(13) Curro, J. G.; Lagasse, R. R.; Simha, R. *J. Appl. Phys.* **1981**, *52*, 5892. *Macromolecules* **1982**, *15*, 1621.
(14) Lagasse, R. R.; Curro, J. G. *Macromolecules* **1982**, *15*, 1559.