Density Fluctuations and Structure of Amorphous Polymers

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A comparison of density fluctuation, estimated from the different equations, has been done. It was shown that density fluctuation can be calculated from the values of the volume of a fluctuational free volume minimum hole. The concentration fluctuation can be calculated from the structural characteristics of amorphous polymers. This parameter serves as the characteristic of the degree of the nonuniformity of a structure in the amorphous state of polymers.

Keywords: Amorphous polymers; density; fluctuations; structure

The study of thermal density fluctuation for liquids and amorphous polymers is of a primary interest because of correlation with the structure these states [1, 2]. In the paper [3] density fluctuation are generally believed to be characteristic of the degree disorder of system. In the papers [4, 5] the value of density fluctuation in glass-forming systems $\langle \Delta\rho/\rho \rangle_g^2$ is associated with fractional fluctuational free volume f_g and can be estimated as

$$\langle \Delta\rho/\rho \rangle_g^2 = f_g \left(V_h / V_a \, t \right) \tag{1}$$

where V_h is the volume of minimum fluctuational microvoid and $V_a \, t$ is the atomic volume.

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Equation (1) allows the direct evaluation of $\langle \Delta\rho/\rho \rangle_g^2$ using the data from mechanical tests in tension and comparison with the literature values, as reported in the papers [1–6]. The Poisson's ratio μ can be determined from the well-known equation [5]:

$$\frac{\sigma_y}{E} = \frac{(1 - 2\mu)}{6(1 + \mu)} \tag{2}$$

where σ_y is the yield stress and E is the elastic modulus.

The f_g is in turn found from the formula [7]:

$$f_g \simeq 0.017\left(\frac{1 + \mu}{1 - 2\mu}\right). \tag{3}$$

The volume of the minimum hole V_h can be estimated [7]:

$$V_h = \frac{3(1 - 2\mu)\, kT_g}{f_g\, E} \tag{4}$$

where k is the Boltzmann constant, T_g is the glass temperature.

Thus, the Eqs. (2)–(4) allow to estimate the values f_g and V_h. For the polymer the atomic volume may be treated as the volume of monomeric unit, which is the basic fractional unit of the chain [8].

Temperature dependencies of $\langle \Delta\rho/\rho \rangle_g^2$ for glassy polycarbonate (PC) and polyarilate (PAr) are shown in Figure 1. It is not difficult to see that, a quite adequate, both in the trend of the temperature dependence and in absolute $\langle \Delta\rho/\rho \rangle_g^2$ values agreement of functions $\langle \Delta\rho/\rho \rangle_g^2 (T)$ with the literature data [1, 6] has been obtained.

The authors of papers [5, 9] have proposed a equation that allows to consider $\langle \Delta\rho/\rho \rangle_g^2$ for volume $V_0 = N_A\, r_0^3$ (where N_A is the Avogadro number, r_0 is the equilibrium distance between atoms) only a function of the Poisson's ratio:

$$\langle \Delta\rho/\rho \rangle_g^2 = \frac{(1 - 2\mu)^3}{6(1 - \mu)^2} \tag{5}$$

The V_0 is in turn found from the formula [9]:

$$V_0 \simeq 18\left(\frac{1 + \mu}{1 - 2\mu}\right)^2 \frac{RT_g}{E} \tag{6}$$

where R is the universal gas constant.
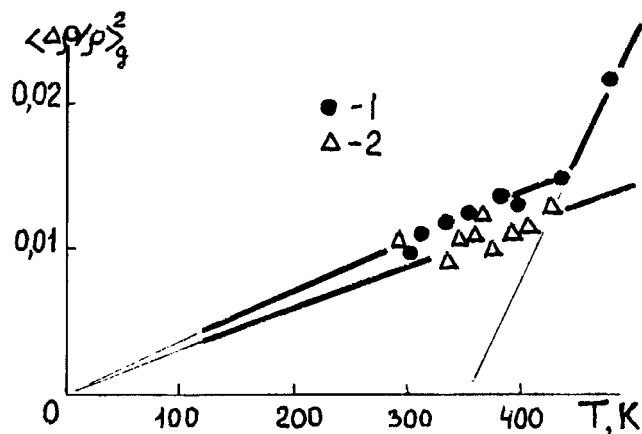
FIGURE 1   Temperature dependencies of density fluctuation $\langle \Delta \rho / \rho \rangle_g^2$ for polyarylate (1) and polycarbonate (2).

Let us consider temperature dependence of the Poisson's ratio. As above noted, Poisson's ratio μ is determined from Eq. (2). Consider the interpretation of the temperature effect on the value μ of amorphous polymers within the scope of the cluster model of structure of amorphous state polymers [10]. In the glassy state, segments in a cluster may be treated as linear defects, similar to dislocations in crystals [11]. Therefore the yield stress σ_y is determined by Eq. (11):

$$\sigma_y = \frac{\sqrt{3}\, Eb\, \sqrt{\rho_d}}{4\pi(1 - 2\mu)} \qquad (7)$$

where b is the Burgers vector, ρ_d is the density of dislocation.

The length of the segment in a cluster is taken equal to the statistical segment length l_s. The l_s is in turn found from the formula [12]:

$$l_s = \sqrt{3/2}\, l_M\, C_\infty \qquad (8)$$

where l_M is the length of a monomeric unit along the chain, C_∞ is the characteristic ratio [13].

The Burgers vector b is calculated by the Sinani and Stepanov method [14]:

$$b = \frac{4}{3\pi}\left(r_{\mathrm{c}} + l_{\mathrm{M}}\right) \qquad (9)$$

where r_{c} is the one-half of the distance between chains.

Every contact of pair of parallel segments in a cluster forms a physical cross-link of the fluctuational network, whose density V_{e} is estimated by method [15]. The parameter ρ_{d} can be determined as a total length of defects in unit volume of a polymer, which does estimate from the equation:

$$\rho_{\mathrm{d}} = V_{\mathrm{e}}\, l_{\mathrm{s}} \approx 1.22\, V_{\mathrm{e}}\, l_{\mathrm{M}}\, C_{\infty} \qquad (10)$$

The Eqs. (2), (7) and (10) allow to estimate the direct dependence of the Poisson's ratio from the structural (V_{e}) and molecular (b, l_{M}, C_{∞}) characteristics:

$$\mu = 0.5 - \frac{3\sqrt{3}}{4\pi}\, b\, \sqrt{1.22\, V_{\mathrm{e}}\, l_{\mathrm{M}}\, C_{\infty}} \qquad (11)$$

The comparison temperature dependencies of Poisson's ratio calculated with the aid of Eqs. (2) and (11) is shown in Figure 2 for

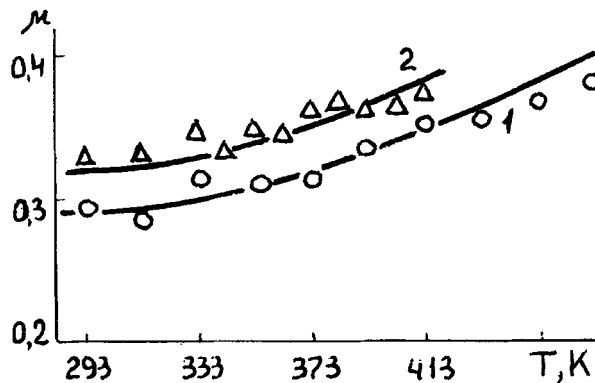FIGURE 2   Temperature dependencies of Poisson's ratio μ for polyarylate(1) and polycarbonate (2); calculations from Eqs. (2)–(1, 2) and (10)– (1′, 2′).

PC and PAr. As can be seen, there exist a good agreement of functions $\mu(t)$, estimated from these equations. As would be expected [16], the μ increase with increasing temperature. Turn now to the application of the Eq. (5). Since with increasing temperature the Poisson's ratio increased, this means value $\langle \Delta\rho/\rho \rangle_g^2$ to decrease, in accordance with the Eq. (5). Thus, disagreement of functions $\langle \Delta\rho/\rho \rangle_g^2$ both estimated from the Eq. (1) and taken to literature data [1–3, 6], has been obtained.

This evident disagreement makes necessary a more detailed analysis of the Eq. (5). Temperature dependencies $\langle \Delta\rho/\rho \rangle_g^2$ for PC and PAr, estimated from Eq. (5), are shown in Figure 3. As would be expected from the above, the $\langle \Delta\rho/\rho \rangle_g^2$ decrease with increasing temperature. Comparing the data of Figures 1 and 3 shows that the absolute values of density fluctuation, estimated from Eq. (5), some lower corresponding estimated from Eq. (1). It follows from Eqs. (5) and (11) that the density fluctuation is connected with a cluster model of structure of polymers. It was shown earlier [17] that the elastic modulus of the
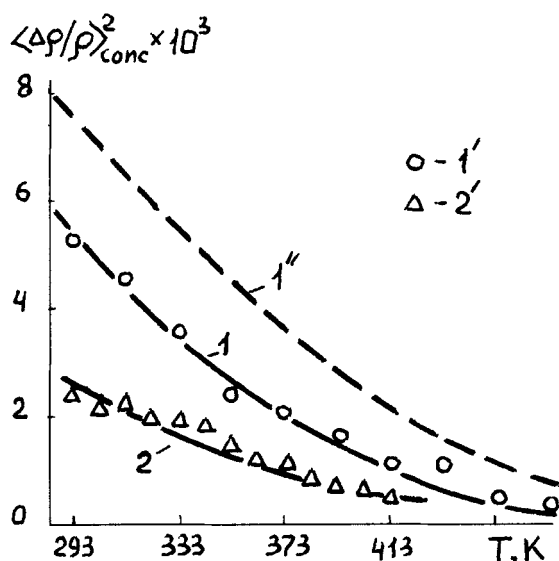

FIGURE 3 Temperature dependencies of concentration fluctuation $\langle \Delta\rho/\rho \rangle_{conc}^2$ for polyarylate (1, 1', 1'') and polycarbonate (2, 2'); calculations from Eqs. (5)–(1, 2), (11)– (1', 2') ($\Delta\rho = 0.122$ g/c.c.) and (11)–(1') ($\Delta\rho = 0.145$ g/c.c.).

glassy amorphous polymers in terms of the cluster model can be treated as a modulus of the two-phase composite. This observations allow to consider the values $\langle \Delta\rho/\rho \rangle_g^2$, estimated from the Eq. (5), as a concentration fluctuation [18], which reflects two factors: a difference in the density between clusters and loose matrix and the clusters fraction in polymer (must be noted that the cluster fraction decrease with increasing temperature [10]). Thus, the value of concentration fluctuation $\langle \Delta\rho/\rho \rangle_{\text{conc}}^2$ (Fig. 3) can be expressed to be the intuitive approximation:

$$\langle \Delta\rho/\rho \rangle_{\text{conc}}^2 = \left(\frac{\Delta\rho}{\rho} \right)^2 \varphi_{\text{cl}} \tag{12}$$

where $\Delta\rho$ is the difference in the density between clusters and loose matrix, ρ is the density of bulk polymer, φ_{cl} is the fraction of macromolecules in clusters.

The value of φ_{cl} can be estimated from the following considerations. The total length of macromolecules in unite volume of a polymer, L is the reciprocal of the macromolecule cross-section area S [19]:

$$L = \frac{1}{S} \tag{13}$$

The φ_{cl} is estimated from the relation:

$$\varphi_{\text{cl}} = \frac{\rho_d}{L} \tag{14}$$

Temperature dependence $\langle \Delta\rho/\rho \rangle_{\text{conc}}^2$ for PC and PAr, calculated from the Eq. (11), also is shown in Figure 3. As seen from Figure 3, this temperature dependence $\langle \Delta\rho/\rho \rangle_{\text{conc}}^2$ is similar to the one, estimated from the Eq. (5), although the absolute values of the first are some larger. Probably, this is due to the using as a $\Delta\rho$ the difference between the densities of the crystalline and amorphous phases for the polyethylene ($\Delta\rho = 0.145$ g/c.c. [20]).

As be note earlier [3], the value $\langle \Delta\rho/\rho \rangle_g^2$ serves a characteristic of the disorder for the amorphous polymer. Figure 4 shows dependencies of the values of $\langle \Delta\rho/\rho \rangle_g^2$ and $\langle \Delta\rho/\rho \rangle_{\text{conc}}^2$, estimated from the Eqs. (1) and (5), respectively, on the fraction of clusters φ_{cl} in the polymer. As would be expected from the above, the $\langle \Delta\rho/\rho \rangle_g^2$ decrease with
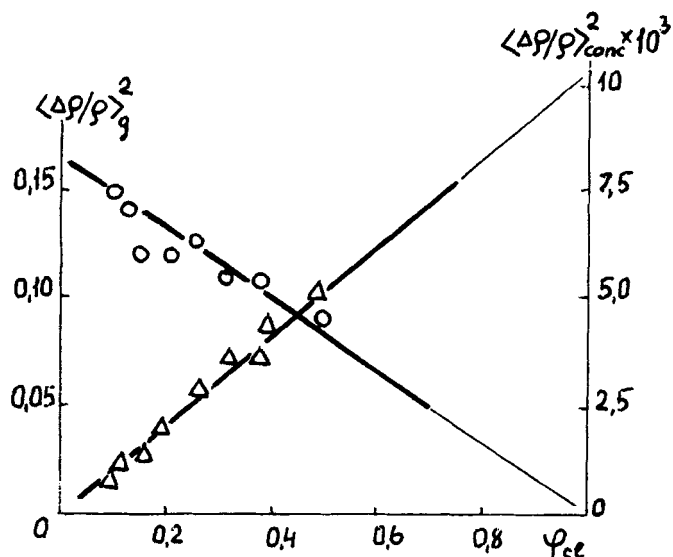
FIGURE 4   Density fluctuation $\langle \Delta\rho/\rho \rangle^2_g$ (1) and concentration fluctuation $\langle \Delta\rho/\rho \rangle^2_{conc}$ (2) as the function of the volume fraction of clusters ϕ_{cl} for polyarylate.

increasing φ_{cl}. These data in turn evidence the usefulness of application of the parameter $\langle \Delta\rho/\rho \rangle^2_g$ to description of a disorder, since φ_{cl} is a characteristic of the local ordering in the amorphous polymers [10]. Can be seen, this dependence appear to be linear and is extrapolated to the magnitude $\langle \Delta\rho/\rho \rangle^2_g = 0$ at $\varphi_{cl} = 1$. In accordance with Eq. (1), this means, that the density fluctuation is determined only to the existence of fluctuational free volume, but not taken into account the thermal oscillations of atoms. This would be expected, since even in the 100% crystalline polymers exist unavoidably a finite other than zero density fluctuation, determined by X-ray scattering [3].

The variation $\langle \Delta\rho/\rho \rangle^2_{conc}$ with φ_{cl} as well appear to be linear and is extrapolated to the magnitude $\langle \Delta\rho/\rho \rangle^2_{conc} = 0$ at $\varphi_{cl} = 1$. It is easy to make sure that this follow from absence of the base of density fluctuation – the quasi-two phase system – and from this standpoint polymer consist only of uniform loosely packed matrix. The dependence $\langle \Delta\rho/\rho \rangle^2_{conc} = f(\varphi_{cl})$ is extrapolated to the magnitude ~ 0.0103 at $\varphi_{cl} = 0$. In accordance with Eq. (11), now can be calculated the value $\Delta\rho(\rho \simeq 1.20\,\mathrm{g/c.c}$ and $\phi_{cl} = 0)$, which is equal to

TABLE I   The comparison of a volumes V_0 and V_{cl} for polyarylate

T, K	V_0, A^3	V_{cl}, A^3
293	1056	3312
313	2480	4610
333	1378	3534
353	1545	4025
373	2272	7730
393	3208	8183
413	3968	4879
433	4150	4688

~ 0.122 g/c.c. This value is a difference between the densities of the close and loosely packed regions of glassy polyarylate. Having using this value $\Delta\rho$ in Eq. (11), we can plot the curve, which is close to the curve $\langle \Delta\rho/\rho \rangle^2_{conc} = f(T)$, estimated from the Eq. (5) (Fig. 4).

Let us consider the variation of a volume V_0 (Eq. (6)) with temperature. It is evident, that the value V_0 may be varied, namely in accordance with an increase μ and a decrease E, would increases with increasing temperature. It is of interest of compare V_0 values with the volume V_{cl} per cluster in the amorphous polymer. It was shown earlier [21], functionality of cluster F is defined as the number of chains emerging from cross-link site; a cluster contains $N = F/2$ segments on the average. The number of clusters in unite volume of polymer, N_{cl}, is equal to $2V_e/F$. The value V_{cl} is the reciprocal of N_{cl}:

$$V_{cl} = \frac{F}{2V_e} \tag{15}$$

Table I present the comparison variations of values V_0 and V_{cl} with temperature. Despite of considerable disagreement of an absolute values of this volumes, coincidence by the order of magnitude and in the trend of the temperature dependencies has been obtained.

Thus, the calculation from Eq. (5) present a values of concentration fluctuation, since amorphous polymers are interpreted as quasi-twophase system. It is assumed that the close (clusters) and loosely (matrix) packed regions may be interpreted as two quasi-phases in terms of the cluster model of amorphous state of polymers.

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