



Amplitude of spatial density fluctuations in glassy propylene carbonate probed by oxygen diffusion

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ABSTRACT

Oxygen translational mobility is very sensitive to structural heterogeneities in molecular glass formers. The heterogeneities manifest themselves as the regions, within which the oxygen jump rates have either the same or similar values. The length of spatial correlation for the oxygen jump rates in glassy propylene carbonate has been determined to be about 1.5 nm [Syutkin et al., *J. Chem. Phys.* 133 (2010) 074501]. The heterogeneities detected by oxygen diffusion are likely the static density fluctuations associated with a spatially nonuniform distribution of free volume. In the present paper the isothermal dependence of oxygen diffusion coefficient on glass density was measured in propylene carbonate using the technique of phenanthrene phosphorescence quenching by oxygen molecules. Glasses of different densities were produced by annealing samples to the equilibrium state at various temperatures. The amplitude of spatial density fluctuations was calculated assuming that (i) a heterogeneous diffusion is due to density fluctuations, and (ii) the dependence of jump rates on region density is the same as that of oxygen diffusion coefficient on the average glass density. The value for $\sqrt{(\Delta\rho)^2}/\rho^2$ was found to be 0.008 ± 0.003 .

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1. Introduction

The dynamics in deeply supercooled liquids is spatially heterogeneous on nanometer length scale [1,2]. The times of molecular motions in different regions of a matrix can differ by several order of magnitude. This phenomenon is often considered to be the consequence of density fluctuations [3,4]. The density fluctuations are detected in silica and other covalent glass formers [3–6]. In molecular glass formers however the density fluctuations are not observed in the static structure factor [7–9]. One of the possible reasons is that the magnitude of nanometer density fluctuations in these matrixes is too small to detect via neutron and X-ray scattering.

The structural heterogeneity of glasses can manifest itself in the dynamic properties of probe molecules [10–13]. It has been recently shown that in glassy propylene carbonate (PC) the jump rates of oxygen molecules are spatially correlated [14]. The size of the regions, within which the jump rates have either the same or similar values, is about 1.5 nm. The regions of this size consist of about 30 molecules. In the present work, we have estimated the magnitude of density fluctuation in this glass.

The length of spatial correlation for the oxygen jump rates can be considered as the characteristic size of structural heterogeneities.

Indeed, a free volume in supercooled liquids and glasses is distributed over a sample in the form of numerous irregularly shaped cavities of atomic length scale [15–17]. Below the glass transition temperature T_g , the times of molecular rearrangements become very long [18]. Therefore, one can consider that the cavities are fixed in space. However, small molecules, such as oxygen, preserve high translational mobility in molecular glasses [19–22]. The diffusion of these particles is decoupled from the rearrangement of the matrix. The molecules diffuse due to thermoactivated jumps from one cavity to another [17,23,24]. The height of potential barrier for a jump depends on both the energy required to pass a neck between the neighboring cavities and the energy required for expanding the cavity into which a particle jumps [25]. Both of the energies depend on the local density of medium (local molecular structure). It is reasonable to suggest that the difference in oxygen jump rates in various regions of glassy PC is due to their different density. Therefore the regions detected by oxygen diffusion are the static density fluctuations associated with a spatially nonuniform distribution of free volume.

PC is one of the most fragile low molecular weight glass formers. Its steepness index, m is equal to 100 [26,27]. The goal of this work is to estimate the amplitude of density fluctuations in glassy PC. Our approach consists in the following.

We assume that the heights of potential barriers in various regions are determined by the density of these regions. We also suggest that the dependence of the barrier height on the density of the region is the same as the dependence of the average barrier height on the average

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density of glass [28]. In this case the height of the barriers ε in the regions with density ρ obeys the equation

$$\varepsilon = \langle \varepsilon \rangle + (\rho - \langle \rho \rangle) \left[\frac{d\langle \varepsilon \rangle}{d\rho} \right]_T, \quad (1)$$

where $\langle \varepsilon \rangle$ and $\langle \rho \rangle$ are the average height of the barriers and the average glass density, respectively. From Eq. (1) we obtain the expression for the mean-square density fluctuations

$$\langle (\Delta\rho)^2 \rangle = \langle (\Delta\varepsilon)^2 \rangle \left[\frac{d\langle \varepsilon \rangle}{d\rho} \right]_T^{-2}. \quad (2)$$

In a heterogeneous medium the real diffusion pathways pass over low barriers. The temperature dependence of the diffusion coefficient D is determined by the highest barrier ε_c which should be overcome by particles to walk randomly through the sample [31]. $\ln D \sim -\varepsilon_c/RT$, where R is a universal gas constant. In glassy PC the distribution of ε is well described by the Gaussian distribution function [14]. The percolation level in the three-dimensional random Gaussian potential $\varepsilon_c \approx \langle \varepsilon \rangle - 0.95 \sqrt{\langle (\Delta\varepsilon)^2 \rangle}$ [32]. If $\langle (\Delta\varepsilon)^2 \rangle$ does not vary with density, $[d\langle \varepsilon \rangle/d\rho]_T = [d\varepsilon_c/d\rho]_T$. From Eq. (2) we obtain the equation connecting the mean-square density fluctuations and the oxygen diffusion coefficient

$$\langle (\Delta\rho)^2 \rangle = \frac{\langle (\Delta\varepsilon)^2 \rangle}{(RT)^2} \left[\frac{d \ln D}{d\rho} \right]_T^{-2}. \quad (3)$$

In glassy PC the dispersion of the barrier energies $[\langle (\Delta\varepsilon)^2 \rangle]^{1/2}$ is 4 kJ/mol [14]. In this work we have determined the oxygen diffusion coefficient D in glassy PC as a function of sample density in isothermal conditions and calculated $[d \ln D/d\rho]_T$. The amplitude of the density fluctuations of glassy PC was calculated from Eq. (3). The diffusion characteristics of oxygen were measured using the technique of phenanthrene phosphorescence quenching by molecular oxygen [14].

2. Experimental

2.1. Materials

Propylene carbonate ($C_4H_6O_3$, Fluka, >99%) and phenanthrene (Aldrich, $\geq 99.5\%$) were used as received. The glass transition temperature of PC is 158 K based on differential scanning calorimetry at a 10 K/min heating rate after quenching from a liquid state [9].

2.2. Samples

The samples were prepared from phenanthrene solution in PC with a concentration of 0.01 mol/l in quartz ampoules 3 mm in inner diameter and 20 cm in height. A solution was saturated with oxygen at room temperature. Oxygen solubility in PC obeys the Henry law with constant $(1.74 \pm 0.03) \times 10^{19} \text{ m}^{-3} \text{ Pa}^{-1}$ [14]. The procedure of sample saturation with oxygen at a saturation pressure of 0.5, 1.5 and 3.3 MPa as well as the procedure of sample deoxygenation has been described in detail in [14]. To saturate PC with oxygen at a pressure of 20 kPa, the dry air has been bubbled through a solution for 4 h. The gas-saturated liquid was poured into an ampoule. After that the ampoule was sealed. A free part of the ampoule was filled with air.

2.2.1. Freezing of samples

In all cases the sample height was 6 cm. The oxygen-saturated solution was frozen in two steps. First, the lower part of the ampoule, 3 cm in height, was immersed in liquid nitrogen. The remaining part of the sample was frozen 40 s later. In the first step, the upper liquid part of the sample served as a plug to prevent oxygen exchange

between the lower part of the sample and the gas phase. The rate of sample cooling in liquid nitrogen was about 200 K/min through the glass transition. The glass appeared to be transparent with a small number of cracks.

2.2.2. Preparation of samples with different density

We have used three series of samples with different density at the same temperature. The most dense glass was produced by annealing samples at 152 K for 2×10^5 s. The physical aging of glassy PC at 152 K has been studied in [33]. The annealing performed during 2×10^5 s leads to the almost equilibrium glass state. The glass of mean density was produced by annealing samples at 156 K for 10^4 s. The time of molecule rearrangements in the equilibrium samples at this temperature is 200 s [34]. Thus, 10^4 s annealing results in the equilibrium glass state. To preserve glass structure, the annealed samples were cooled at the rate of about 3 K/s by inserting ampoules into liquid nitrogen. So we produced glasses whose structure corresponds to the equilibrium glass structure at temperatures $T_f = 152$ and 156 K, respectively. The temperature T_f is called the fictive temperature of the glass (see, e.g., [35]).

The least dense glasses were prepared by fast cooling of the samples in liquid nitrogen. The fictive temperature of these glasses was estimated as follows. The rapidly cooling samples have been annealed for 10^3 s at various temperatures ≥ 158 K. In all cases the annealing results in the equilibrium liquid state. We have compared the kinetics of phenanthrene phosphorescence quenching by molecular oxygen in the equilibrium samples with the quenching kinetics in the unannealed samples prepared by fast cooling. The quenching kinetics was measured at 145 K. A measurement time was short so that the glass structure (fictive temperature) had no time to change during this period. We have established that in the samples annealed at temperatures ≥ 160 K, the oxygen mobility coincides within experimental error with that in the samples prepared by fast cooling. At the same time, annealing of samples at temperatures ≤ 159 K slows down oxygen diffusion. Thus, the samples prepared by fast cooling are less dense than the equilibrium ones at 159 K and below. The density of the samples prepared by fast cooling is most close to that of the samples that are equilibrium at about 160 K.

We assume that the fictive temperature of the samples prepared by fast cooling is (160 ± 0.5) K which is in agreement with the data on structural relaxation. When the samples are cooled at the rate of 3 K/s, the frozen structure is the structure with times of molecular rearrangements of about 1 s. The time of structural relaxation in the equilibrium samples at 160 K is 1.5 s [34].

In the nonequilibrium glasses the phenanthrene phosphorescence quenching at temperature T has been studied just after the heating of samples to this temperature. The glass structure remained unchanged in the course of measurements. The oxygen concentration, C , in samples with different fictive temperature is given in Table 1. The oxygen concentration was calculated, taking into account the thermal expansion of PC.

Table 1

Values of T_f and C for different samples. The last column shows the temperature of measurements for each type of the samples.

T_f /K	C/cm^{-3}	T /K
152	9.6×10^{18}	145, 150, 152
152	2.9×10^{19}	140, 143, 145, 148, 150, 152
156	9.6×10^{18}	140, 144, 148, 152, 156
160	3.8×10^{17}	160
160	6.4×10^{19}	138, 140, 142

2.3. Phosphorescence measurement

After the transfer from the Dewar flask with liquid nitrogen into an experimental cell, the heat-up time of the sample up to a cell temperature was 3 min. The cell temperature was kept to within 0.1 K using gaseous nitrogen flow. The absolute temperature scale was determined to be accurate within ± 0.5 K.

Phenanthrene was excited by the light of a pulsed nitrogen laser with a wave length of 337 nm, a pulse duration of 15 ns and an average energy per pulse of 30 μ J. The height of illuminated sample area was about 5 mm. This area was 1 cm above the ampoule bottom. The laser pulse excites about 0.01% of phenanthrene molecules. Phenanthrene phosphorescence was measured at wavelength of 500 nm with a 30 ms delay after a laser flash using the photomultiplier FEU-119 and the digital oscilloscope ISA BUS CompuScope (Gage Applied Science Inc.).

2.4. Density measurement

The temperature dependence of the PC density over the range of 158–300 K was measured using a calibrated glass pycnometer of a volume of 1 cm³ upon sample cooling at the average rate of 0.3 K/min.

3. Determination of the oxygen diffusion coefficient

Oxygen is an effective quencher of triplet states [36]. The presence of mobile oxygen molecules in organic molecular glass containing small concentration of phenanthrene causes a substantial decrease in the intensity of phenanthrene phosphorescence due to the deactivation of phenanthrene by molecular oxygen [20,37]. It has been recently shown that the kinetics of phenanthrene deactivation can be used to determine the diffusion characteristics of oxygen in a heterogeneous medium [14].

In glassy PC the kinetics of phenanthrene phosphorescence quenching by molecular oxygen is well described by the following model of the heterogeneous glass [14]. The sites of a simple cubic lattice are considered to be cavities for oxygen molecules. The molecules diffuse due to thermoactivated jumps from one cavity to another. The particles can jump into one of six nearest sites. The energy barriers ε_{ij} between the sites i and j are the random values from the distribution described by the Gauss function with a zero mean and a dispersion of 4 kJ/mole. The spatial correlation function for ε_{ij} decays with increasing distance r between the barriers as $\exp(-2r^2/\xi^2)$ with $\xi = 1.5$ nm. The probability of an oxygen molecule jump over the barrier ε_{ij} in a unit of time is defined by the equation

$$P_{ij} = P_0 \exp(-\varepsilon_{ij}/RT),$$

where the factor P_0 specifies the time scale for oxygen diffusion.

In the present work the oxygen diffusion coefficient was calculated from experimental data using the aforementioned model. The simulation of both the phenanthrene phosphorescence quenching by molecular oxygen $I(t)$ and the mean-square displacement of particles $\langle r^2(t) \rangle$ is described in detail in [14]. The factor P_0 is the only free parameter whose value was chosen so that the simulated kinetic curve of the phenanthrene phosphorescence quenching could be most close to the experimental one. In the model the mean height of the barriers $\langle \varepsilon_{ij} \rangle \equiv 0$. The dependences of the average energy of the real barriers $\langle \varepsilon \rangle$ on T_f and P_{ij} on $\langle \varepsilon \rangle$ are included in P_0 . The value $\langle r^2(t) \rangle$ was then calculated in the lattice with a fitted P_0 value. The diffusion coefficient was determined from the equation

$$D = \lim_{t \rightarrow \infty} \langle r^2(t) \rangle / 6t. \quad (4)$$

4. Results

In oxygen-free samples the phenanthrene phosphorescence decay kinetics is described by exponent [14]. A phosphorescence lifetime τ decreases monotonously with increasing temperature from 3.59 at 96 K to 3.48 s at 152 K and then decreases more sharply to 3.31 s at 161 K. The standard error for τ is 0.01 s.

In samples with oxygen the phenanthrene phosphorescence decays faster due to the deactivation of phenanthrene by molecular oxygen. Fig. 1 exemplifies the phosphorescence deactivation kinetics in equilibrium PC at 156 K. To show the contribution of phenanthrene deactivation caused by oxygen, the data are plotted as $I(t)\exp(t/\tau)$ vs t , where $I(t)$ is the phosphorescence intensity. It is seen that the process of deactivation cannot be described by exponent, because phenanthrene molecules differ in quenching rate constants as their environments differ in oxygen mobility [14]. The fitting kinetic curve is denoted by the solid line in Fig. 1. It is seen that the experimental data are well-described by the aforementioned model.

The inset in Fig. 1 shows the oxygen effective diffusivity [38] as a time function in the lattice for which the simulated kinetic curve is demonstrated in the main figure. At long times the oxygen diffusion is observed to be Fickian. The diffusion coefficient D was calculated from Eq. (4).

Satisfactory agreement between the model and the experiment is observed for all the samples at temperatures below T_g , where the structure is "frozen". Thus, the $\Delta\varepsilon$ value for various regions is independent of either T or T_f . In this case the activation energy of oxygen diffusion, ε_c , differs from $\langle \varepsilon \rangle$ by a constant only. Therefore, substituting $[d\langle \varepsilon \rangle / d\rho]_T$ by $[d\varepsilon_c / d\rho]_T$ in Eq. (2) is quite reasonable.

At 160 K the time of deactivation of 90% of phenanthrene molecules is about 6 s in the samples with an oxygen concentration of $\approx 4 \times 10^{17}$ cm⁻³. It exceeds the time of molecular rearrangements equal to about 1.5 s [34]. As a result, the environment of phenanthrene molecules changes in the course of experiment. The difference in quenching rate constants, observed below T_g , disappears and the quenching kinetics becomes close to the exponent. The phenanthrene phosphorescence quenching by molecular oxygen can be interpreted as a diffusion-controlled reaction with the radius of the quenching sphere $R_Q = 0.9$ nm [14]. At low oxygen concentration the rate constant is set by the expression $k_D = 4\pi R_Q D$ [39]. At 160 K the oxygen diffusion coefficient was calculated from the measured quenching rate constant k_D .

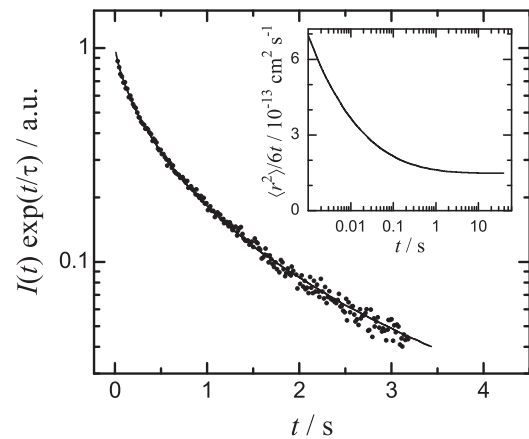


Fig. 1. Phenanthrene phosphorescence quenching by molecular oxygen in equilibrium PC at 156 K as a function of time (circles). The oxygen concentration is 9.6×10^{18} cm⁻³. The solid line is a fitting kinetic curve. The inset demonstrates that at $t > 1$ s the mean square displacement of oxygen grows linearly with time, which corresponds to Fickian diffusion.

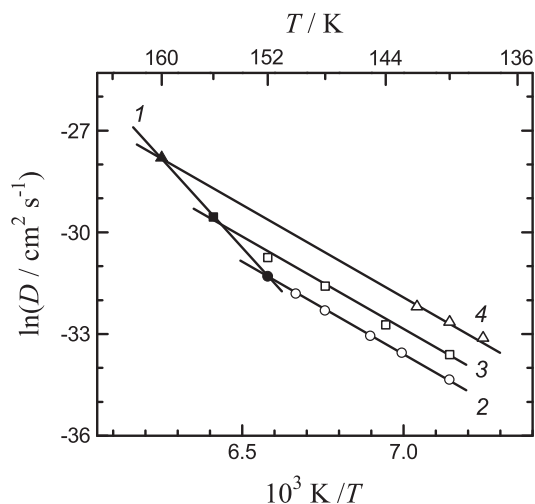


Fig. 2. Arrhenius plot of oxygen diffusion coefficients in glasses with different fictive temperature T_f : 152 (circles), 156 (squares), and 160 K (triangles). For equilibrium glasses ($T_f = T$) the symbols are filled. Standard errors for $\ln D$ are equal to the size of symbols. Lines 1, 2, 3, and 4 denote the linear fitting at $T_f = T$, 152, 156, and 160 K, respectively.

The dependence of the natural logarithm of oxygen diffusion coefficients on the temperature is shown in Fig. 2 for glasses with the different fictive temperature. For the nonequilibrium glasses with $T_f = 160$ K only the low-temperature results are available, as the structure of these glasses varies in the course of experiment at temperatures above 145 K due to the short times of structural relaxation [40]. The straight lines in Fig. 2 are obtained using the linear fitting of the dependence $\ln D$ vs $1/T$. The slopes of lines 2–4 are set by the oxygen diffusion activation energy. The difference in the activation energies for the glasses with the different fictive temperature lies to within the experimental error, $\varepsilon_c = 45 \pm 5$ kJ/mole.

The inset in Fig. 3 demonstrates the change in the density of supercooled liquid and glassy PC with temperatures. The density of the glassy PC was calculated by molecular-dynamics simulations in

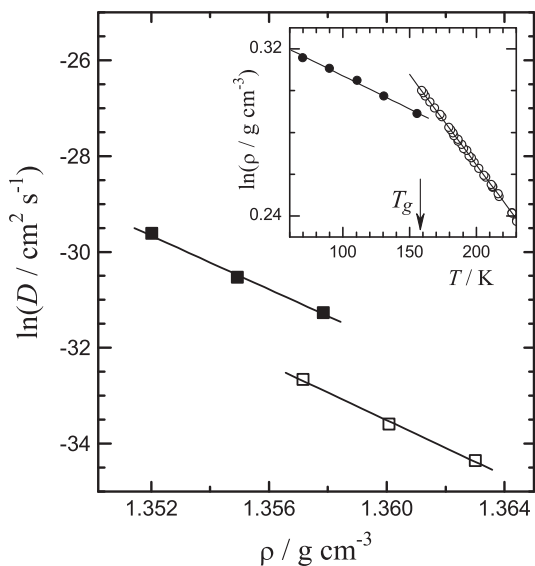


Fig. 3. The oxygen diffusion coefficient as a glass density function at 152 K (closed squares) and 140 K (open squares). Standard errors for $\ln D$ are equal to the size of symbols. The straight lines denote the linear fitting. The inset demonstrates the temperature dependence of the density of liquid (open circles) and glassy (closed circles) PC. The glass density reproduced from [9]. The straight lines denote the linear fitting.

Ref. [9] and the liquid density was measured. The slopes of the straight lines are equal to the thermal expansion coefficients, α_l and α_g , for liquid and glassy PC, respectively. They do not vary with temperature. $\alpha_l = (8.54 \pm 0.03) \times 10^{-4} \text{ K}^{-1}$ and $\alpha_g = (3.16 \pm 0.14) \times 10^{-4} \text{ K}^{-1}$. As follows from the figure, at T_g the calculated density is lower than the experimental one. However, it is of little significance, because the coefficients of the thermal expansion of glasses with the different fictive temperature (with different density) are, usually, equal and coincide with the coefficient of thermal crystal expansion [18]. The molecular structures of glass and crystal are different, but temperature independent. In both of the cases a change in sample volume with temperature is determined by the anharmonicity of intermolecular potential.

Let us take the density of equilibrium PC at the temperature $T_R = 160$ K as a reference point; $\rho_R = 1.3486 \text{ g/cm}^3$. The change in the density of the equilibrium glasses with temperature is determined by the coefficient α_l [18]. Thus, the density of the equilibrium glass at T_f is $\rho_R \exp[\alpha_l(T_R - T_f)]$. For the fixed structure, the coefficient of thermal expansion is equal to α_g . Thus, the sample density at the temperature T and at the fictive temperature T_f is assigned by the expression

$$\rho(T, T_f) = \rho_R \exp[\alpha_l(T_R - T_f) + \alpha_g(T_f - T)]. \quad (5)$$

Fig. 3 plots the oxygen diffusion coefficient as a function of glass density at 140 and 152 K. The glass density was calculated from Eq. (5). The experimental data at 140 K and the fitting values in Fig. 2 at 152 K are used in the plot. The slopes of both straight lines in Fig. 3 provide the value of $[d \ln D / d \rho]_T = 280 \pm 30 \text{ cm}^3/\text{g}$. In the glassy PC the dispersion of barrier heights is $(4 \pm 1) \text{ kJ/mole}$ [14]. From Eq. (3) the amplitude of PC density fluctuations at temperatures just below T_g is

$$\sqrt{(\Delta \rho)^2 / \rho^2} = 0.008 \pm 0.003.$$

5. Discussion

Sokolov and coworkers have suggested that the nanometer structural heterogeneities decreases with increasing fragility of the glass-forming liquid [41,42]. The density fluctuations are detected in silica and other covalent glass formers [3–6]. The length scale of density fluctuations is 2 nm and the magnitude $\sqrt{(\Delta \rho)^2}$ is a few per cent of the average density [3,4]. These materials are the most strong systems in Angell's classification scheme [43]. In the fragile glass formers the density fluctuations are not observed in the static structure factor [7–9]. PC is one of the most glass formers. Its steepness index, m is equal to 100 [26,27].

The kinetics of phenanthrene phosphorescence quenching by mobile oxygen molecules is a very sensitive tool for studying nanometer structural heterogeneities in molecular glass formers [14]. The heterogeneities manifest themselves as the regions, within which the oxygen jump rates vary moderately, while in neighboring regions they differ in the tens and hundreds of times. It is reasonable to suggest that the difference in oxygen jump rates in various regions is due to their different density. The magnitude of density fluctuations is found to be about 1%. This fact corresponds to the hypothesis that the structural heterogeneity decreases with increasing fragility of the glass-forming liquid [41,42]. Their magnitude in molecular glass formers is so much moderate that they are not observed in the static structure factor [7–9].

6. Conclusions

The method of phenanthrene phosphorescence quenching by molecular oxygen was used to study oxygen diffusion in glassy PC. The glasses of different density were produced by annealing samples to

the equilibrium state at temperatures from 152 to 160 K. Oxygen diffusion has been studied at temperatures from 138 to 160 K. We have established that below T_g in all the glasses the oxygen diffusion is spatially heterogeneous on a nanometer length scale [14]. We assume that (i) a heterogeneous oxygen diffusion is determined by density fluctuations, and (ii) the dependence of diffusion mobility on the local density is the same as that of oxygen diffusion coefficient on the average glass density. The amplitude of static density fluctuations was calculated with these assumptions. The nanometer glass regions were found to differ by 1% in the density. This minor difference can manifest itself only in the dynamic glass properties.

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