



# Heterogeneity length scale for oxygen diffusion in glassy squalane

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## ABSTRACT

The kinetics of phenanthrene phosphorescence quenching by mobile oxygen molecules was used to study characteristics of oxygen diffusion on a nanometer length scale in glassy squalane. The phosphorescence decay was described using a model of glassy matrix with spatially correlated oxygen jump rates. The correlation length was determined to be 2.5 nm. The dispersion of barrier energy for oxygen jumps is 1.8 kJ/mol and the average barrier energy is 32 kJ/mol. The structural heterogeneities are deduced to be fluctuations in structure frozen in from the supercooled liquid.

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## 1. Introduction

In organic glasses, the diffusion of small molecules, such as oxygen, is decoupled from cooperative matrix rearrangements. The molecules are believed to diffuse due to thermally activated jumps from one cavity of atomic length scale to another [1–3]. The cavities are fixed in space. The jump length depends on the sizes of matrix molecules. The jump activation energy corresponds mainly to the energy required for creating a channel between neighboring cavities for the jump to occur [4–7]. The activation energy varies in space due to disordered matrix structure [6].

Oxygen diffusion has been recently studied in glassy propylene carbonate (PC) [8]. It was shown that the heights of barriers between neighboring cavities are spatially correlated. The correlation length  $\xi$  ( $\approx 1.5$  nm) exceeds the average distance between the neighboring matrix molecules by a factor of three. It follows that in the regions, consisting of about 30 PC molecules, the jump rates of oxygen molecules vary moderately, whereas between the neighboring regions, these may differ by two orders of magnitude.

The correlation length,  $\xi$ , is the characteristic size of the structural heterogeneities that can be represented by e.g., the density or the configurational entropy fluctuations frozen at the glass transition temperature from the liquid state [9–12]. Alternatively, the heterogeneities may arise from the glass structural units of various origin [15–18], such as nanometer structures with the energetically preferred configurations of molecules.

PC molecule has only one conformation (its chemical structure is shown in Fig. 1). The heterogeneities in glassy PC may be caused by both the fluctuations in structure and the structural units. For molecules with

a great number of conformations, the entropy factor will retard the formation of nanostructures. Squalane exemplifies such molecules. Its chemical structure is shown in Fig. 1. Squalane is a branched alkane with 24 carbon atoms in its backbone and 6 methyl side groups placed along the backbone. Rotation around carbon-carbon bonds leads to a variety of molecule conformations in the liquid state [19]. Both liquid and glass (matrix structure remains the same at the liquid-glass transition [13,14]) contain the tangled molecular chains [20]. Because of this, it is unlikely that glassy squalane consists of certain structural units. Most likely, the nanometer heterogeneities in this matrix are due to fluctuations in structure.

The goal of this work is both to determine the correlation length  $\xi$  and the dispersion of barriers for oxygen molecule jumps  $\sigma$  in glassy squalane and to discuss the origin of glass heterogeneities.

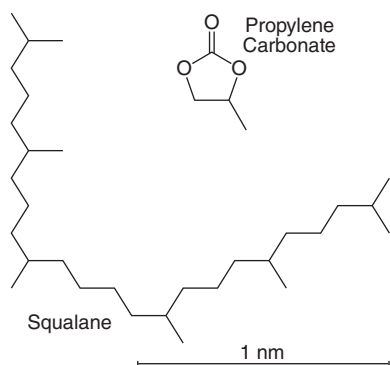
The kinetics of phenanthrene phosphorescence quenching by mobile oxygen molecules is an appropriate tool for studying oxygen diffusion on the nanometer scale [8]. In the present paper, the phenanthrene phosphorescence quenching was used to estimate the characteristics of oxygen diffusion in glassy squalane. The experimental data on this matrix have been obtained earlier by one of us [24].

## 2. The model of phenanthrene phosphorescence quenching by mobile oxygen molecules in glassy matrix

A simple cubic lattice with the potential barriers of different height between the neighboring sites was used as a model of the heterogeneous matrix. The energy barriers  $\varepsilon_{ij}$  between the sites  $i$  and  $j$  are the random values from the distribution described by the Gaussian function

$$G(\varepsilon_{ij}) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\varepsilon_{ij}^2}{2\sigma^2}\right), -\infty < \varepsilon_{ij} < \infty$$

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**Fig. 1.** Chemical structure of squalane (2,6,10,15,19,23-hexamethyltetracosane,  $C_{30}H_{62}$ ; the glass transition temperature  $T_g = 167$  K [21,22]) and propylene carbonate (4-methyl-1,3-dioxolan-2-one,  $C_4O_3H_6$ ;  $T_g = 158$  K [23]).

with zero mean ( $\langle \varepsilon_{ij} \rangle = 0$ ) and dispersion  $\sigma$ . The barriers heights are spatially correlated. A correlation function for  $\varepsilon_{ij}$  decays with increasing distance  $r$  between the barriers  $\varepsilon_{ij}$  and  $\varepsilon_{nm}$  as

$$C(r) = \frac{\langle \varepsilon_{ij} \varepsilon_{nm} \rangle}{\sigma^2} = \exp(-2r^2 / \xi^2).$$

Here, the brackets  $\langle \dots \rangle$  mean averaging over all the pairs of lattice barriers.

The lattice sites are considered to be the cavities for oxygen molecules. The molecules diffuse due to thermally activated jumps from one site to another. The particles can jump only into one of six nearest sites. The probability of a transition from the site  $i$  to the site  $j$  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,  $R$  is the universal gas constant, and  $T$  is temperature. In the model the mean height of the barriers is  $\langle \varepsilon_{ij} \rangle = 0$ . The dependence of  $P_{ij}$  on the average energy of the real barriers  $E$  is included in  $P_0$  as  $\exp(-E/RT)$ .

The free parameters of the model are: (i) the correlation length  $\xi$  (the characteristic size of structural heterogeneities), (ii) the dispersion of barrier energy for oxygen jumps  $\sigma$ , and (iii) the factor  $P_0$ .

Oxygen is known to be an effective quencher of triplet states [25]. It is usually assumed that the rate constant of phenanthrene deactivation has the form [26,24]

$$K(r) = K_0 \exp[-2(r-R_0)/L],$$

where  $r$  is the distance between phenanthrene and oxygen molecules,  $R_0$  is the minimal distance between these molecules,  $K_0$  is the rate constant at  $r=R_0$ , and  $L$  is the exchange interaction length. Based on the size of phenanthrene and oxygen molecules, the value of  $R_0$  is 0.65 nm [26]. The characteristics of exchange interaction in glassy squalane are the following:  $K_0 = (5.0 \pm 0.6) \times 10^7 \text{ s}^{-1}$  and  $L = 0.064 \pm 0.005 \text{ nm}$  [24]. In our model, the phenanthrene molecules are embedded at the centers of the interstitial lattice spaces.

The kinetics of phenanthrene deactivation depends on both  $\xi$  and  $\sigma$ . This dependence varies with oxygen concentration in the matrix [8]. A simultaneous successful fitting of the deactivation curves obtained at high and low oxygen concentrations unambiguously gives the correlation length  $\xi$  and the dispersion of barrier energy for oxygen jumps  $\sigma$ . The calculation procedures of the lattice with a spatial correlation of barrier heights and the kinetics of phenanthrene deactivation are described in detail in Ref. [8].

### 3. Results

The kinetics of phenanthrene phosphorescence quenching by mobile oxygen molecules was studied in glasses prepared by immersing of the samples in liquid nitrogen [24]. The structure of these glasses is similar to the equilibrium structure of supercooled liquid near  $T_g$  [27].

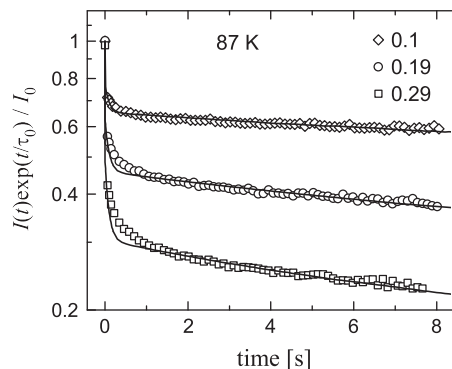
In oxygen-free samples, the phenanthrene phosphorescence decay obeys the exponential law. The time constant  $\tau_0$  (the intrinsic lifetime of phenanthrene triplet state) decreases monotonously with increasing temperature from 3.48 s at 77 K to 3.36 s at 160 K [24]. The standard error for  $\tau_0$  is 0.01 s. Oxygen accelerates the phosphorescence decay due to the deactivation of the excited triplet state of phenanthrene molecules. Hereinafter, to isolate the phosphorescence quenching caused by oxygen from the phosphorescence time profile, the data are plotted as  $I(t)\exp(t/\tau_0)$  vs.  $t$ , where  $I(t)$  is the phosphorescence intensity at a moment  $t$ .

Fig. 2 shows the kinetic curves of phenanthrene deactivation at 87 K. At this temperature, the oxygen molecules are considered to be immobile [24]. In this case, the deactivation kinetics depends on the positioning of cavities for oxygen about phenanthrene molecules. In our model, the location of cavities (lattice sites) depends on the lattice constant  $a$ . The lines in Fig. 2 represent the result of the best fitting of experimental curves. The obtained value of  $a$  is 0.44 nm. It is seen that the proposed model describes the experimental data. Consequently, the positions of the sites about phenanthrene at  $a=0.44$  nm is in fair agreement with the positions of the cavities for oxygen in glassy squalane.

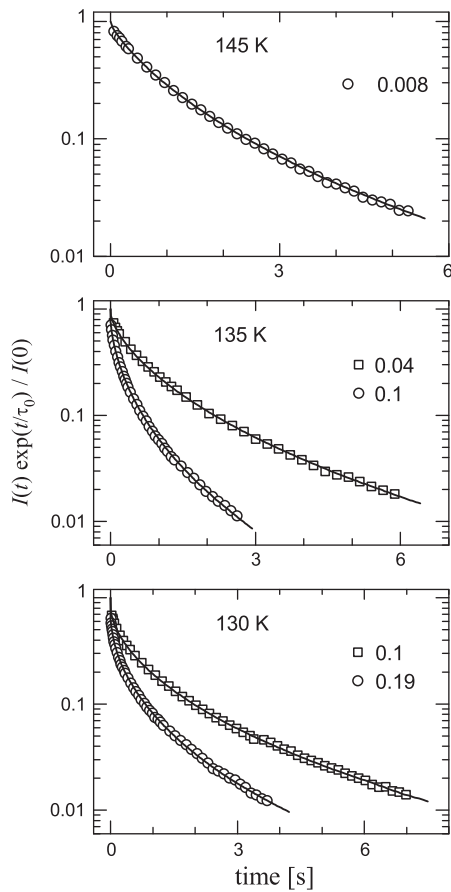
As follows from Fig. 2, some phenanthrene molecules are deactivated at very short times ( $<0.02$  s). We have found that the number of these molecules depends on the oxygen concentration  $C$  as  $\exp(-CV)$  with  $V = 4.0 \pm 0.5 \text{ nm}^3$ . The radius of the quenching sphere of volume  $V$  is 1 nm. Thus, the lifetime of the excited phenanthrene molecule does not exceed 0.02 s with the distance to oxygen molecule being less than 1 nm.

Phenanthrene deactivation is negligible at low temperatures and oxygen concentrations  $C \ll 1/V$ . Oxygen mobility increases with temperature and phenanthrene phosphorescence quenching occurs even with very little quantities of oxygen in the matrix. In this case, the deactivation kinetics is controlled by oxygen diffusion to the quenching sphere. The rate of oxygen molecules penetration into the phenanthrene quenching sphere is inherently the specific deactivation rate.

Fig. 3 shows the kinetic curves of phenanthrene deactivation at various oxygen concentrations. It is seen that the deactivation kinetics is not described by exponential function. The reason is that the oxygen jump rates vary in space and the value of the deactivation specific rate depends on a phenanthrene molecule location. In this case, the kinetics of phenanthrene deactivation depends on the correlation length  $\xi$  and the dispersion of barrier energy  $\sigma$  [8].



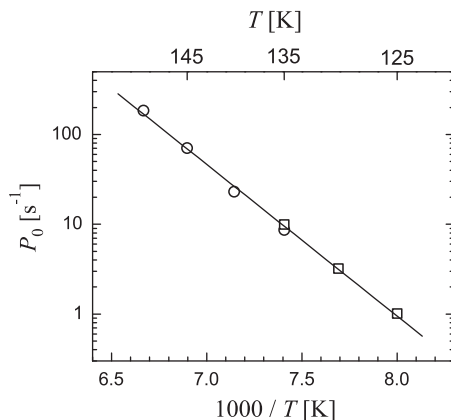
**Fig. 2.** The kinetics of phenanthrene deactivation by molecular oxygen in glassy squalane matrix at 87 K. The oxygen concentration in mol/l is shown in the legend. The lines were simulated using the lattice constant of 0.44 nm.



**Fig. 3.** The kinetics of phenanthrene deactivation by molecular oxygen in glassy squalane matrix at different temperatures. The oxygen concentration in mol/l is shown in the legends. The lines are the best fits, giving  $\xi = 2.5$  nm and  $\sigma = 1.8$  kJ/mol.

The lines in Fig. 3 represent the result of best fitting of all experimental data with the proposed model at  $a = 0.44$  nm. It is seen that the experimental data are well described by the model. The fitting parameter values are  $\xi = 2.5 \pm 0.7$  nm and  $\sigma = 1.8 \pm 0.4$  kJ/mol. A large uncertainty in the values of  $\xi$  and  $\sigma$  is due to a strong negative correlation of these parameters [8].

Fig. 4 shows the fitted values of  $P_0$  at different temperatures. The temperature dependence of  $P_0$  was found to obey the Arrhenius equation  $P_0(T) = A \exp(-E/RT)$  with  $A = (3 \pm 0.1) \times 10^{13} \text{ s}^{-1}$  and



**Fig. 4.** Arrhenius plot of factor  $P_0$  in glassy squalane at oxygen concentrations of 0.008 (circles) and 0.1 mol/l (squares). The straight line denotes the linear fitting.

$E = 32 \pm 2$  kJ/mol. The value of  $A$  is close to the characteristic vibrational frequency of molecules in the condensed phase. The structure of the glasses studied is temperature independent as no glass aging is observed during experiments (measurement temperature  $\leq T_g - 17$  K) [24]. It is assumed then that the average barrier height for the oxygen molecule jump is also temperature independent. In this case, the value of  $E$  corresponds to the average barrier height.

According to Ref. [8], an estimate of the values of  $\xi$  and  $\sigma$  does not depend on lattice constant at  $a < \xi/3$ . The factor  $P_0$  depends on  $a$  in such a way that the diffusion coefficient  $D \sim a^2 P_0$  remains constant, as it must be.

#### 4. Discussion

The reorientation dynamics of molecules in supercooled liquids and amorphous polymers in the rubbery state near  $T_g$  is spatially heterogeneous [28–30]. The size of regions  $\zeta$  with molecular reorientation times longer than the average time falls in the range from 1 to 3 nm for low-molecular-weight glass formers [31,10] and is about 4 nm for poly(vinyl acetate) [31]. The lifetime of these regions is on the same time scale as cooperative reorientation of molecules ( $\alpha$ -relaxation) [32–38]. Thus, the same matrix rearrangement leads to both the reorientation of molecules in the region of volume  $\sim \zeta^3$  and the change in reorientation times of these molecules. It is assumed then that the length scale of cooperativity is also the length scale of heterogeneity in molecular dynamics.

The dynamically heterogeneous regions can be considered as spatial fluctuations in the density or the configurational entropy [39–42,10]. In this case, the fluctuations at distance  $\zeta$  from each other are statistically independent and their amplitude in the volume  $\zeta^3$  is a characteristic of these heterogeneities. As the temperature decreases, the lifetimes of the fluctuations increase sharply (along with the times of  $\alpha$ -relaxation). It is often assumed that below  $T_g$  the fluctuations manifest themselves as the static heterogeneities in density [9] or in elastic constants [43,11].

Let the glass heterogeneities probed by oxygen diffusion be the fluctuations in structure frozen from the liquid state. Let us verify this hypothesis. Table 1 summarizes the characteristics of oxygen diffusion in glassy PC and squalane. The correlation length  $\xi$  in squalane exceeds more than one and a half times that in PC. At the same time, the  $\sigma/E$  value in squalane is almost one and a half times smaller than that in PC. The value of  $\xi$  is inherently the characteristic size of structural heterogeneities. A relative dispersion of the barrier energy  $\sigma/E$  is taken as an estimate of the amplitude of heterogeneities [27]. Thus, an increase in the size of heterogeneities leads to a decrease in their amplitude. This conclusion corresponds to the hypothesis that the heterogeneities arise from fluctuations because for any fluctuations an increase in their size is accompanied by the drop of the amplitude [44].

Syutkin and coworkers have recently suggested that in glassy PC (i) the nanometer heterogeneities for oxygen diffusion are the fluctuations in density, 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 [27]. The amplitude of static fluctuations in density was calculated with these assumptions. The heterogeneities were found to differ in density by 0.8%. The amplitude of density fluctuations in squalane is probably less than that in PC. The static fluctuations are most likely associated with spatially nonuniform distribution of free volume.

**Table 1**

Characteristics of oxygen diffusion in glassy PC [8] and squalane: the correlation length  $\xi$ , the dispersion of barrier energy  $\sigma$ , and the average energy of barriers  $E$ .

Matrix	$\xi/\text{nm}$	$\sigma/\text{kJ mol}^{-1}$	$E/\text{kJ mol}^{-1}$
PC	$1.5 \pm 0.5$	$4 \pm 1$	$50 \pm 5$
Squalane	$2.5 \pm 0.7$	$1.8 \pm 0.4$	$32 \pm 2$

As follows from Table 1, the average barrier height in squalane is one and a half times smaller than that in PC. Let us discuss this result. The barrier energy is the energy required to form a channel between the cavities for oxygen diffusion. The oxygen jump is a cooperative process. The cooperativity length scale is set by the size of the regions with the spatially correlated displacement of matrix molecules upon formation of the channel between the cavities. In squalane, due to the interpenetrating molecular chains the cooperativity length is likely to be larger than in PC (the length scales of cooperativity and heterogeneity may be quite different). The greater is the cooperativity length, the smaller is the change in the distance between the neighboring molecules required to form the channel suitable for the oxygen molecule jump. In the matrix with a small cooperativity length, the channel is formed after great local structure deformations. In this case, the barrier will be very high.

The dispersion of barrier energies in squalane is two times smaller than in PC, probably, due to both the larger heterogeneities and the greater cooperativity length for oxygen diffusion in squalane.

## 5. Conclusions

The kinetics of phenanthrene phosphorescence quenching by mobile oxygen molecules has been used to study the structural heterogeneity on the nanometer length scale in glassy squalane. The matrix with a typical size of heterogeneities of 2.5 nm provides a good description of the phenanthrene deactivation at all oxygen concentrations. The dispersion of barrier energy for oxygen jumps is estimated to be 1.8 kJ/mol. The average barrier energy is about 32 kJ/mol.

The squalane matrix consists of the tangled molecular chains. In the liquid state, this structure leads to a large cooperativity length in molecular motion. The cooperativity length scale sets the correlation length for fluctuations in density and configurational entropy. These fluctuations freeze at  $T_g$  in the form of structural heterogeneities of nanometer size. The heterogeneities are the characteristic feature of the glassy state.

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