

# Diffusion of Gas Molecules in the Polystyrene Matrix

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## Abstract

We have studied the diffusion of gas molecules inside an amorphous polystyrene matrix. The diffusion constant of several gases at  $T = 450\text{ K}$  in the polystyrene was computed. Particular attention was given  $CO_2$  for temperatures between 300 and 800 K. Analyzed were the temperature dependence of diffusion constant and the relationship between the diffusion constant and the gas diameter. The results correlate well with experimental data.

We further examined the motion of the gas molecules on the short time scale not readily accessible to experimental observation. Here we used the cage overlap function which gives information on the typical cage sizes and distribution times. On the short time scale the gas molecules show a hopping behaviour. Calculated were the distribution of the time period between hopping events, the distance between the cages and the size of the cages in the polystyrene matrix in the presence of guest molecules.

## 1 Introduction

The knowledge of the diffusion coefficient of gases in polymer melts is very important in many industrial processes. The most striking example is the production of polymer foams by mixing of a blowing agent like  $CO_2$  into the molten polymer under high pressure followed by sudden expansion to the atmosphere [1]. The diffusion of gases in the amorphous polymer matrix is a complicate process

which can be observed directly only by few experiments, for example by neutron scattering [2]. Most experiments measure the diffusion constant of gas molecules in the polymer matrix (for example, the *time-lag* method from Barrer [3]) below the glass transition temperature of polymer ( $T_g$ ). In some cases, like the above mentioned production process of polymer foams, it is indispensable to know the diffusion constant of gas in the polymer above the glassy state. But the measuring of the diffusion constant of the gases in such states is very difficult because it is difficult to prepare the sample of polymer melts which the gas molecules should penetrate through, especially for the case  $T \gg T_g$ . Since the diffusion is an activated process, the diffusion coefficient has a strong dependency on temperature and on the polymer matrix. It is also impossible to extrapolate the coefficient from the results obtained by experiments at lower temperatures. Computer simulations can overcome this difficulty and “observe” the diffusion process by analyzing the motion of gas molecules in the matrix directly [4, 5, 6, 7] especially at high temperatures.

The motion of a gas molecule in the amorphous polymer matrix without external force field can be described by a *random walk* with the *Einstein's relation* on a long time scale (longer than a few hundred *ps*). For equilibrium processes this is the time scale one needs to consider. In non-equilibrium situation like the above quoted expansion this is not the case. On a small time scale within a range of about a few *ps*, a gas molecule shows two different types of motion: local movements inside small areas (*trapping*) and sudden jumps between these local areas

(*hopping*). Such a behavior can be explained by the *hopping-mechanism* [4, 5, 6, 7, 8, 9, 10]. In the amorphous polymer matrix one assumes that there are volumes available to the guest atoms. If this volumes are large enough, they can trap the gas molecules and behave like a cage. In the cage the gas molecules can move only locally. An opening can be formed through the thermal fluctuation of the matrix such that to such volumes overlap. If a gas molecule meets the opening and has enough kinetic energy, it can escape from the cage and be trapped directly by another cage which overlaps the original one. It should be emphasized here that the *overlap of the volumes* is one of the most important factors for the non-local jumps of the gas molecules.

Appealing as this picture may be, we need a measure to observe the *trapping* and *hopping* precisely. The hopping appears normally within a short period (smaller than pico-second). By means of the *cage overlap function* [9, 10] we can analyze the hopping-behavior of gas molecules. Then, from the analysis we are able to give a measure for the motion of the gas and the accessible-volume in the matrix.

The outline of this paper is like follows: In section II. we introduced the method and parameters of the simulation. Then we presented in section III section the results of the diffusion of gas molecules in the polystyrene matrix on the large time scale. In the section IV, the hopping-process is analyzed.

## 2 Simulation and Parameters

In this work we have simulated a system of amorphous polystyrene (PS) with small gas molecules (penetrants) using *molecular dynamics* (MD). Carbon-dioxide ( $CO_2$ ), methane ( $CH_4$ ),  $O_2$ ,  $H_2$  and helium ( $He$ ) were used as the penetrants.

The *united-atom model* was applied for the chains of polystyrene and all atomistic details were taken into account for the gas atoms. Clearly using the united-atom model will influence the measurement of the diffusion constant. The effect on the diffusion constant on large time scales is well understood. If there is an influence on the very short time scales we are considering is not yet clear.

The Hamiltonian of the system consists of 4 parts:

$$\mathcal{H} = \mathcal{H}_l + \mathcal{H}_\theta + \mathcal{H}_\phi + \mathcal{H}_{int}, \quad (1)$$

where  $\mathcal{H}_l = \sum_{bond} \frac{1}{2} \cdot k_l(l - l_0)^2$  and  $\mathcal{H}_\theta = \sum_{angle} \frac{1}{2} \cdot k_\theta(\theta - \theta_0)^2$  are the harmonic potentials for the bond length and bond angle of the molecules,  $\mathcal{H}_\phi = \sum_{torsion} (\sum_{n=1}^3 a_n(1 + \cos(n\phi - \phi_0(n))))$  denotes the potential of the dihedral (torsional) angle of the polymer chains and  $\mathcal{H}_{int} = \sum_{i<j} 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]$  represents the Lennard-Jones potential for the intermolecular interaction. The Lorentz-Berthelot combining rules [11]:

$$\sigma_{\alpha,\beta} = \frac{\sigma_\alpha + \sigma_\beta}{2}, \quad \epsilon_{\alpha,\beta} = \sqrt{\epsilon_\alpha \epsilon_\beta}, \quad (2)$$

were used for the calculation of interaction between different species  $\alpha, \beta$ . To accelerate the simulation, a cut-off radius for each atom was taken at ( $r_{cut-off} = 1.8\sigma$ ). The all force field parameters are adopted from AMBER.

Inside a cubic box the simulations were performed with 50 polystyrene chains. Each chain has 20 monomers. By taking different box-sizes (54.82 and 55.93 Å each side) the system density was adjusted between 0.81 and 1.05  $g/cm^3$ .

The polystyrene matrix was initialized to the bond lengths, bond angles and dihedral angles according to their equilibrated value. To avoid interaction between the gas molecules only 4 gas molecules were placed in the box at random positions. The system was equilibrated for 50  $ps$ . With a time step of only 0.05  $fs$  (for 1.05  $g/cm^3$ ) and 0.5  $fs$  (for 0.99  $g/cm^3$ ) the simulations were carried out with a temperature of 450 *Kelvin* ( $T_g$  of polystyrene is about 373 *K*) for about 5 (1.05  $g/cm^3$ ) and 1.5 millions (0.99  $g/cm^3$ ) MD-steps which corresponds to the real time of 0.25 and 0.75  $ns$ . Furthermore, simulations were carried out (with time step 1.0  $fs$ ) for the  $CO_2$ -polystyrene system with nine different temperatures 300, 323, 340, 353, 363, 373, 400, 600 and 800 *K*. The density of the system was adjusted for having the same system pressure (about 10 *MPa*) as the matrix of density 0.99  $g/cm^3$  at 450 *K*.

The Nosé-Hover algorithm [12] was applied to hold the temperature constant.

### 3 Diffusion of gas at long time scale

On a long time scale the motion of a gas molecule can be considered a random walk in the amorphous polymer matrix. This can be described by the Einstein relation [13]:

$$\langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle = 6Dt, \quad (3)$$

with  $t \rightarrow \infty$ , where  $\vec{r}(t)$  denotes the position of the center of mass of gas molecule at the time  $t$  and  $\langle \dots \rangle$  represents the average over all gas molecules.  $D$  is the diffusion constant of the gas.

In FIG. 1 we show the relation between the mean square displacement of the penetrants and the time  $t$  for the matrix density of  $0.99 \text{ g/cm}^3$ . The curves for large  $t$  present a linear relation between mean square displacement and  $t$ . This behavior corresponds to the Einstein relation. The values for the diffusion constants are tabulated in TAB. 1. The data indicates that the molecules with smaller diameter have a greater diffusibility as expected.

The diffusion is an activated process which obeys the Arrhenius-relationship [14]:

$$D = D_0 \exp\left(\frac{-E_a}{k_B T}\right), \quad (4)$$

where  $D_0$  is a pre-exponential factor,  $E_a$  is the activated energy and  $k_B$  is the Boltzmann constant. Both  $D_0$  and  $E_a$  depend not only on the properties of the matrix but also on the size of the penetrating gas [15, 16, 17].  $D_0$  is proportional to  $\lambda_D^2$  in the Barrer's *zone theory* [15], where  $\lambda_D$  denotes the step length of a jump during the diffusion. This step length is further proportional to the diameter of the gas molecule [17]. Therefore,  $D_0$  can be written as [18]:

$$D_0 = C_D \cdot d^2, \quad (5)$$

where  $d$  denotes the diameter of the gas molecule.

$E_a$  is the energy which gas molecules need to drive the polymer blocks away. It is determined by the gas diameter and can be formulated by the following equation [16]:

$$E_a = C_E \cdot (d - \phi^{0.5}/2). \quad (6)$$

Here  $\phi$  is the free volume per unit length of a monomer group measured along the chain axis and

$\phi^{0.5}/2$  corresponds to the mean unoccupied distance between two chains. The structure-factor of PS-matrix which we calculated from the simulation has a main-peak at about  $1.46 \text{ \AA}^{-1}$ , which corresponds the average distance between polystyrene chains of about  $4.3 \text{ \AA}$ . On the other hand, the polymer chain can be assumed to be a tube with a radius of about  $1.7 \text{ \AA}$  (exclude radius of the united-atom) and the space inside the tube is assumed to be occupied. The value of  $\phi^{0.5}/2$  is then estimated to be  $0.9 \text{ \AA}$ . With (4), (5) and (6) a new relation can be written as:

$$\frac{D}{d^2} = C_D \cdot \exp\left(-\frac{C_E (d - \phi^{0.5}/2)}{k_B T}\right), \quad (7)$$

where  $C_D$  and  $C_E$  are constants specified by the polymer matrix. Since only polystyrene was discussed in this study,  $C_D$  and  $C_E$  stayed unchanged at the same temperature.

Before we discuss further the relation between the diffusion constant and the size of gas molecules, it is necessary to estimate the diameter of gas molecules. In this work the diameter of molecules was computed by taking into account the Lennard-Jones radius  $\sigma$  and the geometric structure of gas with the assumption that  $He$  and  $CH_4$  have a spherical shape and  $H_2$ ,  $O_2$ ,  $CO_2$  are rotational Ellipsoids. The computed diameters are shown in TAB. 2 in comparison with the values used by Michaels and Bixler. Their values were determined from the viscosity-diameter with some corrections [17]. The difference between the values of our calculation and of Ref. [17] are small for most of the molecules. The deviation of about 8 % for the diameter of methane is probably caused by our assumption that methane has a spherical structure but actually, it is tetrahedral.

FIG. 2 shows the relation between the diffusion constant and the gas diameter. The simulation results reproduce the proposed relation (7).

FIG. 3 presents the simulation results for the diffusion constant of  $CO_2$  with different temperatures and one experimental point. The logarithmic plot of the diffusion constants reveals above  $350 \text{ K}$  a linear relationship with the inverse of the temperature. Below  $350 \text{ K}$  the points show a strong reduction in the diffusibility of  $CO_2$  in the matrix. The results of the simulation indicate a glass transition temperature of about  $350 \text{ K}$  for the short chains.

In preliminary sorption experiments of  $CO_2$  in polystyrene (PS) by means of a *microbalance technique* [19] found at 353 K and 10 MPa a value of the diffusion coefficient of  $D_{exp} = 3.7 \pm 1.9 \cdot 10^{-9}$  m/s. This value correlates very well with the results presented by the simulations as can be seen from FIG. 3, though about twice lower at the same temperature. The reason for a lower  $D_{exp}$  can be searched in the fact that the simplification of the polymer by means of the *united-atom model* produces more unoccupied space in the matrix during the simulation. Moreover, short polymer chains of 20 monomer units were used in the simulation, whereas commercial PS has an average polymerization degree of about 1000 [21]. Around the end-group of polymer chains there is more free volume which can enhance the diffusibility of the penetrates in the matrix.

The glass transition temperature  $T_g$  of pure PS with polymerization degree of 1000 is about 363 K [21]. It is known that the incorporation of  $CO_2$  to a polymer melt results in a plasticization effect and, therefore, in a lowering of  $T_g$ , that can be expected to be of the order of magnitude up to 50 K [24]. Furthermore, simulations of Roe and Rigby presented a strong dependence of  $T_g$  with the chain length if the polymer chains are short and if the torsional forces of the chains are taken into account [22, 23]. The polymer system of shorter chains should have a lower  $T_g$ . Thus, the experiments and the simulations above 353 K were performed under the condition that they are above the glassy state. FIG 4 displays the self-diffusion constant of the polystyrene segments under different temperatures which is computed through the mean square displacement of the center of mass of the PS segments. The data reveals a clear Arrhenius behavior above the temperature of 350 K and an obvious lowering of  $T_g$ . The glass transition temperature here is around 350 K which corresponds with the  $T_g$  estimated from the diffusion constant of  $CO_2$  on different temperatures.

## 4 Motion of gas at the small time scale: the “hopping-process”

The motion of gas molecules on the short time scale can be explained by the *hopping-mechanism*. With MD simulation it is possible to study the hopping-mechanism and the properties of the cage (accessible- or free-volume) in the polystyrene matrix by analyzing the trajectory of gas molecules directly with the *cage overlap function*.

The cage overlap function gives a measure for the hopping behavior of the gas molecule by addressing the neighbor atoms around the molecule [9, 10]. At first, a neighbour-list  $l_i(t)$  at time  $t$  must be constructed:

$$l_i(t) = \begin{pmatrix} l_{i,1}(t) \\ l_{i,2}(t) \\ \dots \\ l_{i,N}(t) \end{pmatrix}, \quad (8)$$

where  $i$  denotes the index of a gas molecule and  $N$  the total number of the atoms of polystyrene matrix.  $l_{i,n}(t)$  are functions of value 0 or 1 under the following condition:

$$l_{i,n}(t) = \begin{cases} 1 & : \quad |\vec{r}_i(t) - \vec{R}_n(t)| \leq r_{cage} \\ 0 & : \quad otherwise \end{cases} \quad (9)$$

$\vec{r}_i(t)$  and  $\vec{R}_n(t)$  denote the position of gas molecule  $i$  and matrix atom  $n$  at time  $t$ .  $r_{cage}$  is the *cut-off* of the neighbour-list. In this work we used the first minimum of the *pair correlation function* of the system around the gas molecule as  $r_{cage}$ . This assumption is arbitrary but reasonable because most of the matrix-atoms that make up the boundary of the cage for a gas molecule should be nearest neighbours. The average distance between a gas molecule and its nearest neighbours is at the first maximum of the pair correlation function. By changing the cut-off for 10 % the analyses showed almost the same results.

The cage overlap function  $C_i(t, t_0)$  for gas molecule  $i$  at time  $t$  with respect to time  $t_0$  is defined as

$$C_i(t, t_0) = \frac{\sum_{n=1}^N l_{i,n}(t) \cdot l_{i,n}(t_0)}{\sum_{n=1}^N l_{i,n}(t_0) \cdot l_{i,n}(t_0)} \quad (10)$$

with  $t \geq t_0$ . A parameter  $C_r$  is defined as the *critical overlap*. It gives a measure to decide whether hopping has happened: There should be a hopping of one gas molecule if the cage overlap function of the gas molecule reaches a value smaller than  $C_r$ . Figure 5(a) shows the *mean cage overlap function*  $\langle C(t) \rangle = \langle C_i(t, t_0) \rangle_{i, t_0}$  of  $O_2$  in the polystyrene matrix at a density of  $1.05g/cm^3$ , where  $\langle \dots \rangle_{i, t_0}$  denotes the average over all gas molecules and all possible reference time  $t_0$ . This function shows an exponential decay with time and has a crossing with  $C_r = 0.5$  at about  $3 ps$ . This time defines the mean time period that the  $O_2$  molecule stayed in the cage.

To analyze the evolution of the cage overlap function for a single molecule, a modified overlap function  $C_i'(t)$  for a gas molecule  $i$  is defined with a slight alteration of  $C_i(t, t_0)$ :

$$C_i'(t) = C_i(t, \tau_{i,ref}(t)), \quad (11)$$

with

$$\tau_{i,ref}(t) := \max\{\hat{t}_{i,k} \leq t : k \in \{0, 1, 2, 3, \dots\}\} \quad (12)$$

and

$$\hat{t}_{i,k+1} := \min\{t > 0 : C_i(t, \hat{t}_{i,k}) < C_r\}. \quad (13)$$

$\hat{t}_{i,k}$  indicates the moment that the  $k$ -th hopping of molecule  $i$  happened and  $\hat{t}_{i,k=0}$  is set to be 0 for all  $i$ . FIG. 5(b) shows the evolution of  $C_i'(t)$  for a  $O_2$  molecule during a simulation of  $50 ps$  with a small  $C_r$  of value 0.1. The dot-dash curves are the fitting of the cage overlap function for each time segment. The cage overlap function shows an exponential decay which we have already seen in FIG 5(a). The change of  $C_i'(t)$  from 0.6 to 0.4 happened in very short period. Such a change indicates a sudden and evident movement of the  $O_2$  molecule in the PS-matrix and can be identified with the hopping. For the analyses for the rest of this work,  $C_r$  was chosen to be 0.5.

Another phenomenon that can be observed are *back-jumps* of  $O_2$ . During the hopping process, it is possible that the gas molecule jumps back to the cage it came from, before the opening between the cages closed. In FIG. 5 the overlap function increases from 0.4 to 0.7 between  $38.5$  and  $44.5 ps$  and shows such *back-jump*.

To analyze the hopping-process, the following parameters are defined:

$$\Delta t_{hopping,i,k} = \hat{t}_{i,k+1} - \hat{t}_{i,k} \quad (14)$$

$$\tilde{r}_{i,k} = \langle \vec{r}_i(t) \rangle_{\hat{t}_{i,k} \leq t < \hat{t}_{i,k+1}} \quad (15)$$

$$\Delta d_{i,k} = |\tilde{r}_{i,k+1} - \tilde{r}_{i,k}| \quad (16)$$

$$\Delta r_{i,k} = |\vec{r}_i(\hat{t}_{i,k} + \Delta t) - \vec{r}_i(\hat{t}_{i,k})| \quad (17)$$

$$R_{cav,i,k}^2 = \left\langle |\vec{r}_i(t) - \tilde{r}_{i,k}|^2 \right\rangle_{\hat{t}_{i,k} \leq t < \hat{t}_{i,k+1}} + 2\sigma_i \quad (18)$$

for gas molecule  $i$  after  $k$  hoppings. The parameter without index denotes the mean value over all the indices ( $A = \langle A \rangle_{i,k}$ ).

$\Delta t_{hopping}$ , the *hopping-time*, is equivalent to the period that a gas molecule stays in the cage. The distribution of the hopping-time of  $O_2$  in the PS matrix is shown in FIG 6. The curve can be fitted well with an analytical function:

$$P_1(t) = \lambda t \cdot \exp(-\lambda t). \quad (19)$$

This function indicates a *Poisson-process* which describes the distribution of time between events which happen independently (“1” means “one count after time  $t$ ”) [25].  $\lambda$  is called the *rate* of the Poisson-process and the inverse of  $\lambda$  denotes a measure of the average hopping-time. FIG. 6 shows also the distribution of the hopping-time of all the gas molecules we considered in the PS-matrix of  $1.05g/cm^3$  and the values for the inverse of  $\lambda$  are displayed in TAB. 3. The hopping-time is proportional to the size of molecule.

$\Delta d$  represents the distance between the center of the cages before and after one hopping event. The distributions of  $\Delta d$  is displayed in FIG. 7. The distributions show that the distance between the center of the cages is smaller for the matrix with larger molecules.

FIG. 8 shows the distribution of  $\Delta r$  — the displacement of the gas within  $\Delta t = 0.5ps$  during the hopping. In general, the smaller molecules like  $H_2$  and  $He$  jump much further than the larger ones.

The cage size  $R_{cav}$  can be estimated from the radius of gyration of the trajectory of the gas molecule during its local movement and the excluded volume radius of the gas molecule. The distributions of  $R_{cav}$  for different molecules are presented in FIG. 9. The distribution of the size shows three characteristics for the cages in the PS-matrix:

- (a) The average size of the cages of the PS-matrix with larger gas molecules is larger.
- (b) The distribution of the size is broader for system with smaller gas molecules.
- (c) The diameter of the cages in the PS-matrix is about a few angstroms and is not much larger than the size of the gas molecules!

The free-volume is formed by thermal fluctuation in the polystyrene matrix. The free-volume with a larger diameter than the gas molecule can trap the molecule form a cage. If we use the gas molecule as a kind of *detector* of the cage size, only the free-volumes which are larger than the gas molecule can be *seen*. It is quite clear that molecules like *He* can be trapped by more free-volumes (which have a smaller size) than *CH<sub>4</sub>*. Thus, it is obvious that the distribution of the cage size is broader for *He* than *CH<sub>4</sub>* and the mean value of the distribution is also smaller for *He*. On the other hand, we find that the largest cages in the polystyrene matrix have a radius from 4.5 to 5 Å. A *large* free-volume with more than 10 Å in the matrix is statistically possible but not realistic. The maximum of the cage size has about the same scale like the gas molecules. It indicates that most cages are forced to enlarge their size by trapping the gas molecule.

It was emphasized in Section I that the hopping event can be observed using the overlap between cages. If we consider the distribution of the free-volumes ( $R_{cav}$ ) and the distance between the center of two cages ( $\Delta d$ ) we can find the relation

$$\langle \Delta d \rangle \leq 2 \cdot \langle R_{cav} \rangle.$$

It indicates an overlap between two cages that caught a gas molecule before and after a hopping event. The larger the molecules the stronger is the overlap and thus we see that gas molecules do not travel a long distance after an escape from a cage.

## 5 Summary

In this work we have discussed the behavior of gas molecules in the amorphous polystyrene matrix for long and short time scales. The analysis for the gas behavior on short time scale can be summarized with the following points: First, the average cage size within the PS-system depends directly on the diameter of the guest molecule. The accessible volumes are not much larger than the size of molecules

itself. Second, in most cases the hopping event can happen only if there is an enough overlap between the cages. The gas molecules will be trapped directly by another cage after the escape. Third, the smaller molecules jump more frequently and with larger distances than the bigger molecules.

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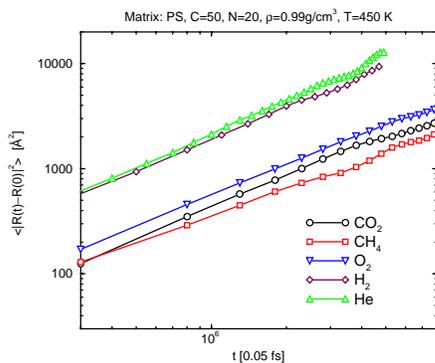


Figure 1: Mean square displacement of gas molecules in the polystyrene matrix with the density of  $0.99\text{g}/\text{cm}^3$ .

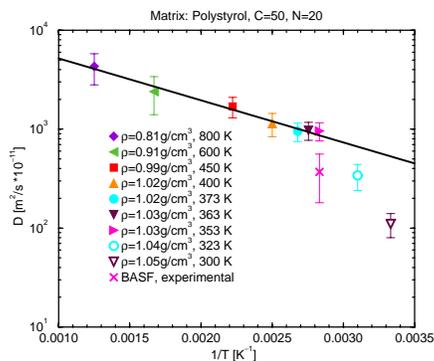


Figure 3: Arrhenius diagram of the diffusion coefficient of  $\text{CO}_2$  in polystyrene.

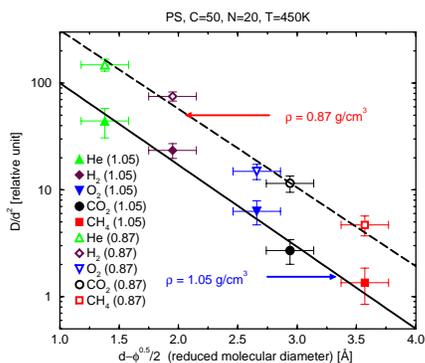


Figure 2: Relationship between the diffusion constant and the diameter of gas molecules.

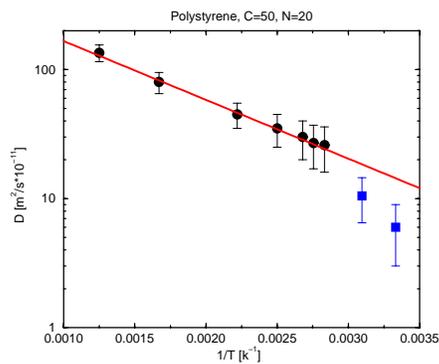
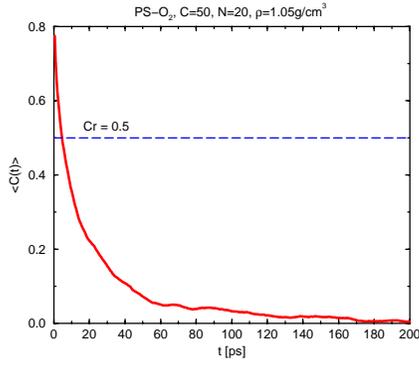
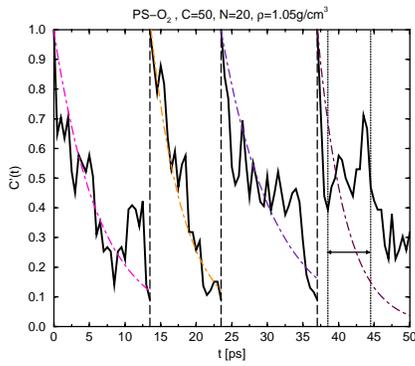


Figure 4: Arrhenius diagram of the self-diffusion coefficient of the polystyrene chains.



(a)



(b)

Figure 5: (a) Mean cage overlap function  $\langle C(t) \rangle$  of  $O_2$  with a critical overlap of 0.5 (b) Modified cage overlap function  $C'(t)$  of  $O_2$ , the dot-dash curves are the fitting of the exponential decay.

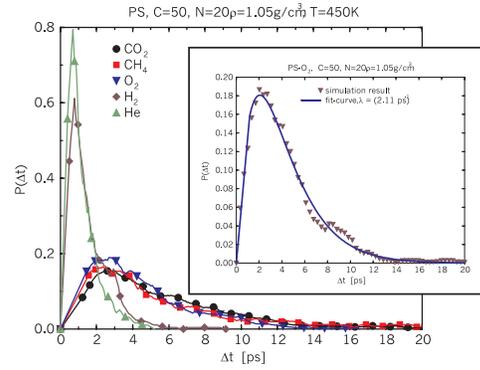


Figure 6: Distribution of the hopping-time of gas molecules.

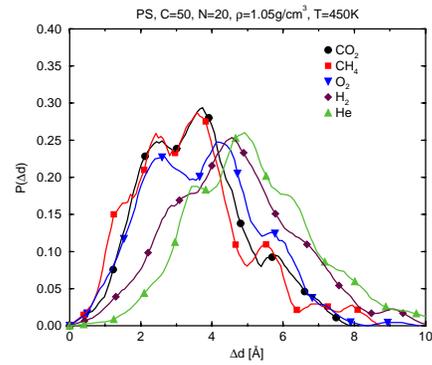


Figure 7: Distribution of the distance between the center of two cages in PS-matrix.

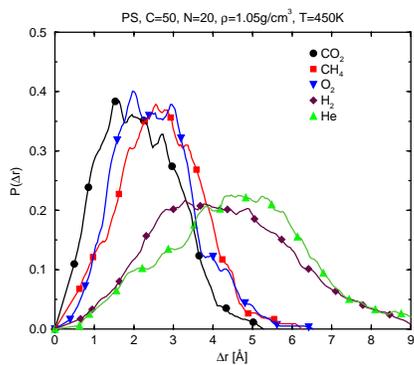


Figure 8: Distribution of the jump-distance of molecules during the hopping process in  $0.5 \text{ ps}$ .

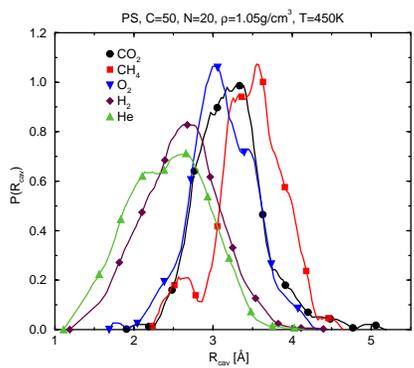


Figure 9: Distribution of the size from the free-volumes of systems with different gases.

gas	$\rho = 1.05g/cm^3$	$\rho = 0.99g/cm^3$
<i>He</i>	$23 \pm 7$	$77 \pm 10$
<i>H<sub>2</sub></i>	$19 \pm 5$	$61 \pm 6$
<i>O<sub>2</sub></i>	$8 \pm 2$	$17 \pm 3$
<i>CO<sub>2</sub></i>	$4 \pm 1$	$15 \pm 3$
<i>CH<sub>4</sub></i>	$3 \pm 1$	$10 \pm 2$

Table 1: Diffusion constant of gas molecules in the polystyrene matrix, unit:[ $10^{-9} \cdot m^2/sec$ ].

gas	d [ $\text{\AA}$ ] (a)	d [ $\text{\AA}$ ] (b)
<i>He</i>	2.28	2.2
<i>H<sub>2</sub></i>	2.85	2.7
<i>O<sub>2</sub></i>	3.57	3.5
<i>CO<sub>2</sub></i>	3.84	3.9
<i>CH<sub>4</sub></i>	4.47	4.1

Table 2: Diameter of gas molecules, (a): calculated in this work, (b): values from Ref.[17].

gas	$\lambda^{-1}$ [ps]
<i>He</i>	0.55
<i>H<sub>2</sub></i>	0.70
<i>O<sub>2</sub></i>	2.11
<i>CO<sub>2</sub></i>	2.68
<i>CH<sub>4</sub></i>	2.63

Table 3: Measure of the mean hopping-time ( $\lambda^{-1}$ ) of the gas molecules in the PS-matrix.