

# Molecular Simulation of Oxygen Diffusion in Polymers

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**Abstract:** Oxygen diffusion in polymer membranes has great significances on the choice of packaging materials. In this work, molecular dynamics simulations and Grand canonical Monte Carlo were used to study the diffusion of oxygen in polymer membranes. It is found that the diffusion coefficient of oxygen in polymer membranes increases as the temperature increases. And the diffusion coefficient of oxygen in polymer membranes increases slowly as the pressure increases. In this paper has studied tentatively influences of nitrogen on the diffusion coefficient of oxygen in Polyethylene (PE). It shows that nitrogen makes the diffusion coefficient of oxygen in PE increasing greatly. In general, simulation results indicate that polymer membranes used at low temperatures and all-oxygen environment should be preferred in food preservation.

**Keywords:** diffusion coefficient; polymer membranes; molecular dynamics; oxygen; Monte Carlo

## 1. Introduction

Researches on diffusion of small molecule of gases such as oxygen in polymer membranes have been interested in scholars. In recent years, a powerful new research tool has been become available in this field, namely, the computer simulation of polymer microstructures. This has made possible the estimation of diffusion coefficients of gases in polymer membranes via molecular dynamics (MD) simulation techniques<sup>1-3</sup>. In food preservation, the oxygen barrier property of packaging films is one of the decisive factors, and hence of oxygen diffusion in polymer membranes has important significances. In life, packaging is exposed to the air, mainly oxygen and nitrogen. However oxygen diffusion in polymer membranes has been tested with all-oxygen in laboratory, and the effect of nitrogen for oxygen diffusion couldn't be estimated. The computer simulation has made possible the estimation of the effect nitrogen to oxygen diffusion in polymers. Polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC) have been widely used in food packaging with the advantages of rich sources and good composite performances. So in this work reported here, three structurally different and commercially important polymers, namely polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC) were selected as model polymers to compute diffusion coefficient of oxygen. In this paper, Grand canonical Monte Carlo and molecular dynamics simulations have been used to study the diffusion coefficient of oxygen in polymer membranes with Materials Studio software.

## 2. Model and Simulation Method

### 2.1. Simulation parameters

Selected simulation parameters are the most important actor to make computer simulation results accurate. In Materials Studio software, firstly, force field is selected. In the resent researches, it found that COMPASS (Con-

densed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field could predict the structure, conformation, vibration and thermal physical properties of various moleculars within the isolated or condensed systems in a large range of temperatures and pressures<sup>4</sup>. Therefore COMPASS force field was used in this paper. Secondly, cutoff radius and step length need to be selected because their sizes influence the length of computer simulation time and accuracy of simulation results. Through a lot of trial and error cutoff radius was set to 9.5 Å, and step length was set to 1 fs in this article.

### 2.2. Polymer models

The structures of three polymers differ with respect to the nature and size of their side chains. PE is the linear low density polyethylene, density of 0.92g/cm<sup>3</sup>. The PE model was a cell including 4 chains (degree of polymerization of 60) with three-dimensional periodic boundary conditions. PE chains were constructed based on the rotational isomeric state model. In unit cell, the initial configuration of PE was amorphous, short-range order and long-range disorder, with a total of 1448 atoms. The models of PP and PVC were similar to PE. The unit cell of PP was isotactic form including 4 chains, degree of polymerization of 60, density of 0.9g/cm<sup>3</sup> and the unit cell of PVC was amorphous including 4 chains, degree of polymerization 60, density of 1.4 g/cm<sup>3</sup>.

### 2.3. Simulation details

Firstly construct the initial polymer model in 298K by means of the Amorphous Cell module in Materials Studio software. The atoms of the polymer model initially do not uniformly occupy the cubic unit cell. So the total energy of the initial microstructure must be minimized first. During the minimization procedure, kinetic energy is not assigned to atoms. With certain polymers, it is possible to approximate the non-bond parameters using "charge groups" of atoms rather than individual atoms. Here use

charge groups throughout this paper as they increase the speed of the calculation without compromising the accuracy for parameterized systems. The simulation program locates the local minimum of the potential energy surface of the polymer structure using smart minimization method. To ensure that polymer model's minimum total energy retains constant with respect to the simulation time employed, MD simulations need equilibrate the microstructure. Thus, for equilibration the cell, an MD run of 100 ps was sufficient with NVT ensemble, a simulation protocol in which number of atoms (N), volume (V) and temperature (T) of the system retain constant. To get more real polymer model, the polymer microstructure need to be annealed. The simulated annealing procedure starts from the initial temperature of 298K to the maximum temperature of 448K heating up every 50K, then heating down to the initial temperature every 50K with NPT ensemble, a simulation protocol in which number of atoms (N), pressure (P) and temperature (T) of the system retain constant. The whole process cycles 5 times. After simulated annealing procedure, the internal stress of the polymer model reduced and partial unreasonable structure produce in the construction almost eliminated.

To simulate the diffusion coefficient of oxygen in polymer membranes, the polymer unit cells need to mix into a certain amount of oxygen molecular. Thus Grand canonical Monte Carlo (GCMC) method was used to study the number of oxygen adsorbed in the polymer unit cell by the means of the Sorption module in Materials Studio software. The initial polymer unit cell used in the GCMC simulation procedure was the final stable configuration in the above MD simulation procedure. The cell used Ewald of electrostatic summation method and charge group cut-off radius of 12.5 Å with three-dimensional periodic boundary conditions. The step in this procedure consisted of 50ps equilibration steps and 150ps production steps.

When oxygen absorbed in the cell, it need to be equilibrated again by MD simulations to ensure its minimized total energy retains constant with respect to the simulation time used. The equilibration step consisted of 100ps NVT molecular dynamics simulation, 200ps NPT molecular dynamics simulation and 500ps NVE molecular dynamics simulation using a standard Verlet algorithm. The initial velocity of each atom was random from Boltzmann distribution. Simulation time step was 1fs and the conformation of the cell was saved every 1000fs.

### 3. Results and Discussions

#### 3.1. Influences of Temperature on Diffusion coefficient of oxygen in PE

Diffusion coefficient of oxygen was determined from

MD simulations. In such simulations, the successive positions of a oxygen molecular diffusing in the polymer microstructure are computed as a function of time by solving Newton's equations of motion for the molecular. The computational procedure determined the random walk trajectory of the oxygen molecular in a given polymer microstructure. Diffusion coefficient of oxygen was calculated from the mean-square displacement (MSD) of oxygen molecular by means of the equation (1)<sup>5</sup>

$$D = \frac{1}{6N_\alpha} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^{N_\alpha} \langle [r_i(t) - r_0(t)]^2 \rangle \quad (1)$$

Where  $r_0(t)$  is an initial position coordinate of the penetrant molecular in the selected polymer microstructure, and  $r_i(t)$  is the position coordinate of penetrant molecular after a time  $t$ ,  $[r_i(t) - r_0(t)]$  represents the displacement of oxygen molecular during time  $t$ . But differentiation in equation (1) was replaced by the rate of mean-square displacements versus time, namely the slop  $a$  of the curve, so equation (1) simplifies equation (2):

$$D = a/6 \quad (2)$$

To find the influences of temperature on oxygen diffusion, diffusion coefficient and absorption of oxygen in PE membrane were simulated in the pressure of

**Table 1. Diffusion coefficient and number of absorbed oxygen molecular in PE at different temperatures**

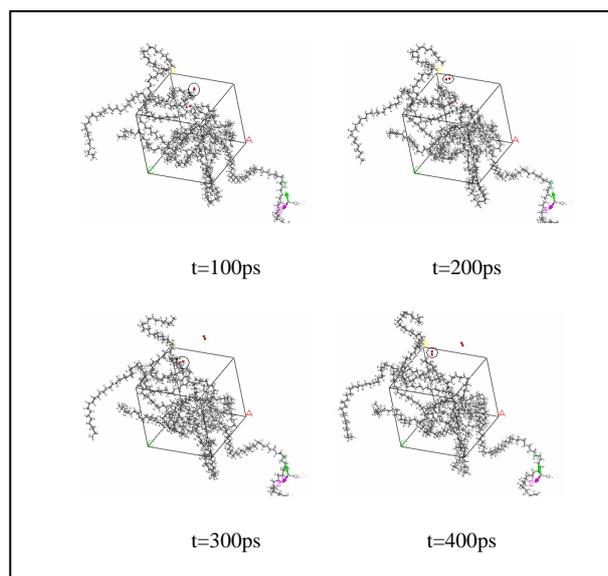
Temperature(K)	263	273	283	293	303
Number of absorbed oxygen	8	6	6	2	1
Diffusion coefficient, D (10 <sup>-6</sup> .cm <sup>2</sup> .s <sup>-1</sup> )	0.8487	1.096	1.958	5.689	8.112

101.325KPa at five different temperatures: 263K, 273K, 283K, 293K and 303K. Figure 1 showed diffusing procedure of oxygen molecular in PE cell at 293K and Figure 2 showed the trajectory of one oxygen molecular in PE at 293K and 101.325KPa.

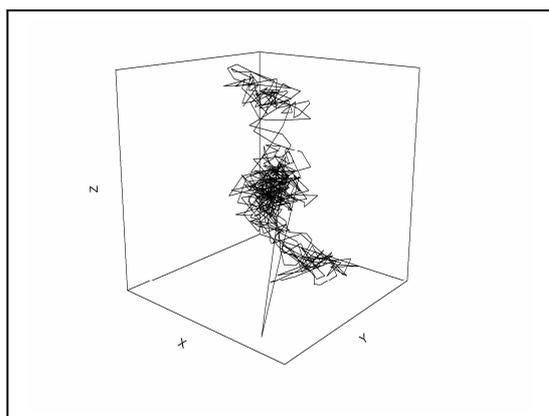
From Table 1, it is found that:

- 1) *The number of absorbed oxygen molecular in PE decreases as the temperature increases.* This indicates that the thermal motions of oxygen molecular become more and more tempestuous and the interaction force between oxygen molecular and PE molecular decreases as the temperature increases, so that the binding force of PE on oxygen reduces. Oxygen molecular overcomes the interaction force with PE to escape from cell, therefore the number of

absorbed oxygen molecular decreases.



**Figure 1. Diffusing procedure of oxygen molecular in PE cell at 293K.**



**Figure 2. Trajectory of one oxygen molecular in PE at 293K and 101.325KPa.**

- 2) Diffusion coefficient of oxygen in PE increases gradually as the temperature increases. It is related with the thermal motion. Oxygen energy increases with temperature increasing, which is helpful for the diffusing motion. Besides, according to the recent researches, the values of diffusion coefficient of oxygen coincide basically with the reported values. This proves MD simulations can be used in the study of diffusing procedure of oxygen in polymers.
- 3) Diffusion coefficient of oxygen in PE changes little at low temperature, but changes a lot at room or high temperature. This provides some guidance and basis for developments in selecting packing materials.

### 3.2 Influences of Pressure on Diffusion coefficient of oxygen in PE

Pressure is an important factor to the diffusion coefficient of oxygen in polymers. The properties of polymers are different at varying pressures, so that diffusion coefficients are different. In this work reported here, MD simulations about diffusion coefficient of oxygen in PE are processed in the temperature of 298K at four different pressures: 30KPa, 70KPa, 110KPa, 150KPa. Through MD simulations, diffusion coefficient of oxygen at different pressures was calculated, shown in Table 2.

**Table 2. Diffusion coefficient and number of absorbed oxygen molecular in PE at different pressures**

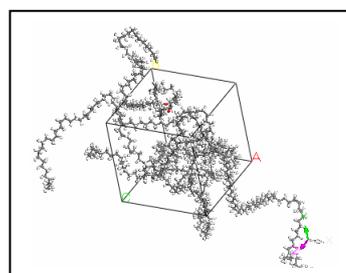
Pressure (KPa)	30	70	110	150
Number of absorbed oxygen	2	2	4	6
Diffusion coefficient, $D(10^{-6} \cdot \text{cm}^2 \cdot \text{s}^{-1})$	5.802	5.822	6.107	6.143

Table 2 shows that:

- 1) Diffusion coefficient of oxygen in PE is increasing slowly as the pressure increases. That is the reason of oxygen molecular's energies increasing. More energies lead to the thermal motions of oxygen molecular more intense, which are beneficial for the vibration and displacement of oxygen in PE cell. Hence, diffusing procedure is easier at high pressure.
- 2) As seen from the simulation results, diffusion coefficient of oxygen in PE as the pressure increases from 30KPa to 150KPa changes a little, increasing averagely about 1.4%. It indicates that low pressure has small influences on the oxygen diffusing procedure. So packing materials can be chosen without thinking of the pressure.

### 3.3 Diffusion coefficient of oxygen in different packaging materials

PE, PP, PVC are the most widely used packing materials.



PE

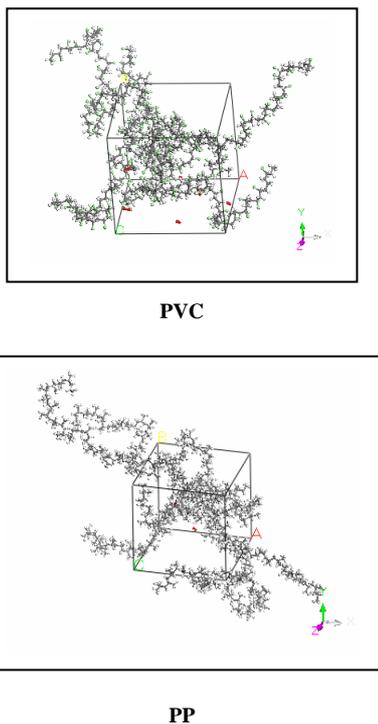


Figure 3. Models of oxygen diffusing in three polymers.

In order to better compare the differences of properties, diffusion coefficient of oxygen in three polymers was estimated by MD simulations at 298K and 101.325KPa. The simulated models of the above three polymers are shown in Figure 3.

The curves of the mean-square displacements versus time obtained from MD simulations, are shown in Figure 4. According to (2), the estimated diffusion coefficient of oxygen was respectively  $5.922 \times 10^{-6} \text{cm}^2/\text{s}$ ,  $3.688 \times 10^{-6} \text{cm}^2/\text{s}$  and  $4.424 \times 10^{-7} \text{cm}^2/\text{s}$ , decreasing in the polymer order  $\text{PE} > \text{PP} > \text{PVC}$ . This reduces, in turn, the diffusivity of oxygen in the polymers, because the rate of diffusion of oxygen molecular depends on the cooperative motion and mobility of the surrounding polymer chains.

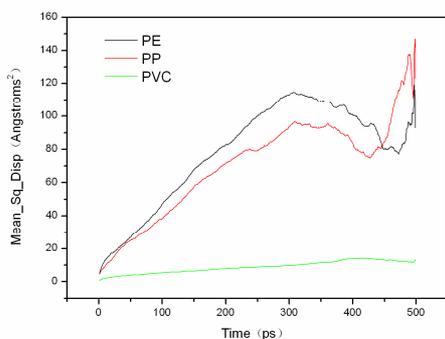


Figure 4. Mean square displacement of oxygen vs. time in PE, PP and PVC.

### 3.4 Influence of Nitrogen on Diffusion coefficient of oxygen in PE

The experiments of diffusion coefficient of oxygen in the lab are carried on in the all-oxygen environment while the packing materials are used in air, which leads to mistakes between experimental values and realistic values. Diffusion coefficient of gas in polymers could not test in the air limited to the experimental conditions, so computer simulation is used to study the differences. Air mainly consists of nitrogen and oxygen, so only the influence of nitrogen was studied in this paper.

Table 3. Diffusion coefficient of oxygen in PE with nitrogen or not

Temperature(K)	288	298	308
Diffusion coefficient without nitrogen, $D_1$ ( $10^{-6} \cdot \text{cm}^2 \cdot \text{s}^{-1}$ )	2.404	5.922	8.409
Diffusion coefficient with nitrogen, $D_2$ ( $10^{-6} \cdot \text{cm}^2 \cdot \text{s}^{-1}$ )	3.988	17.034	17.153
$D_2 / D_1$	1.66	2.88	2.04

The simulation was divided into two groups. One used the above simulation procedure to estimate the diffusion coefficient of oxygen in PE in the pressure of 101.325KPa at three temperatures: 288K, 298K and 388K. The other absorbed oxygen and nitrogen at the same time when calculating the equilibrated number of oxygen absorbed in cell by GCMC simulations to get the number of oxygen and nitrogen with nitrogen, other processes were the same to the former group6.

Simulation results are listed in Table 3. As seen from Table 3, diffusion coefficient of oxygen with nitrogen greatly increases, nearly double. Figure 5 and Figure 6

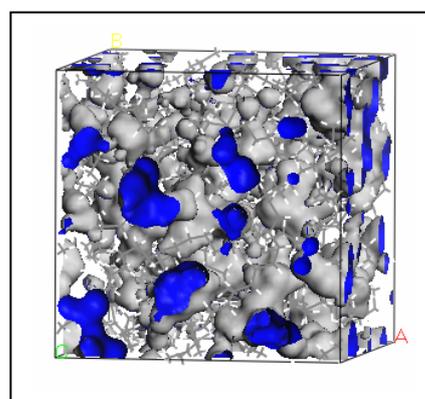
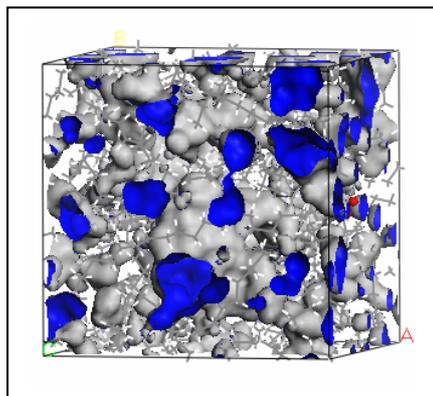


Figure 5. Snapshot of simulated oxygen absorption cell of PE without nitrogen. (Blue areas stands for the free volume  $V_f$ ,  $V_f = 2674.85 \text{ \AA}^3$ )



**Figure 6. Snapshot of simulated oxygen absorption cell of PE with nitrogen. (Blue areas stands for the free volume  $V_f$ ,  $V_f=2873.14 \text{ \AA}^3$ )**

shown the volume distribution of two groups. Compared them, it is shown that the free volume of PE increased 7.4% when nitrogen was absorbed. Hence, thinking of nitrogen, oxygen diffusivity improved largely, which did harm to food preservation. So the packing materials touching the air should choose the ones which have better barrier property to nitrogen in reality in order to avoiding economic losses.

#### 4. Conclusions

Diffusion coefficient of oxygen in polymers increases as the temperature increases, and oxygen diffusivity changes a little when pressure changes a lot. Compared

diffusion coefficients in three polymers, it is found PVC has the best barrier property to oxygen. Through the exploratory study of nitrogen influencing on diffusion coefficient of oxygen, it is shown that the free volume of PE increased 7.4% when nitrogen was absorbed, and diffusion coefficient of oxygen increases nearly double. In general, this work provides some guidance and basis for developments in food packing materials. More further study about the influence of nitrogen on oxygen diffusivity need to be carried out.

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