Sorption and permeation of gaseous molecules in amorphous and crystalline PPX C membranes: molecular dynamics and grand canonical Monte Carlo simulation studies*

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Amorphous and crystalline poly (chloro-p-xylylene) (PPX C) membranes are constructed by using a novel computational technique, that is, a combined method of NVT+NPT-molecular dynamics (MD) and gradually reducing the size (GRS) methods. The related free volumes are defined as homology clusters. Then the sorption and the permeation of gases in PPX C polymers are studied using grand canonical Monte Carlo (GCMC) and NVT-MD methods. The results show that the crystalline PPX C membranes provide smaller free volumes for absorbing or transferring gases relative to the amorphous PPX C area. The gas sorption in PPX C membranes mainly belongs to the physical one, and H bonds can appear obviously in the amorphous area. By cluster analyzing on the mean square displacement of gases, we find that gases walk along the x axis in the crystalline area and walk randomly in the amorphous area. The calculated permeability coefficients are close to the experimental data.

Keywords: cluster analysis, parylene C, grand canonical Monte Carlo method, molecular dynamics

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1. Introduction

Poly (chloro-p-xylylene) (PPX C) membranes are good gas barrier materials applied for the prevention of gas walking.[1,2] Demirels reported[3] that there are two types of layers, including the amorphous (high energy part) and the crystalline (low energy part) areas.[4] However, the study lacked a theoretical method for building amorphous and crystalline membranes. In 2010, Smalara *et al.*[5] carried out AM1, PM6, and B3LYP-DFT calculations to study p-xylylene based polymers to evaluate the surface electronic structures. The authors concluded that the binding sites of polymer chain units exist at the π bonds of the benzene ring. This motivates us to determine the different areas in PPX C membranes from a chain units' review. In this work, a novel method based on molecular dynamics (MD)[6] and gradually reducing the size (GRS)[7] methods is used to construct and describe the high and low energy areas of PPX C membranes.

Permeation properties of gases in PPX C are strongly influenced by the relative diffusion and sorption parameters.[8] At present, the existing methods are very desirable to use grand canonical Monte Carlo (GCMC) and MD methods to understand and predict the transport properties of gas molecules through membranes.[9,10] For example, Lu *et al.*[11] reported the sorption quantities of gases by simulating the solubility in PPX C. This technique not only determines the sites and the quantities of gases, but also reduces the calculating time for further MD simulations. The diffusion coefficients of gases were calculated using the Einstein fluid equation. However, the Einstein fluid equation just fits for calculating gases' jump diffusing through the connected walking paths. Fox and Flory[12] predicated that the small gases can first vibrate and then jump back through cut-off walking paths in PPX C membranes. This diffusion process belongs to a non-normal one that may lead to errors in using the Einstein fluid equation at the molecular level.[13,14] This work describes the diffusion behaviors of gases in PPX C by cluster analyzing gases' trajectories.[15,16] We intend to construct and describe

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the amorphous and the crystalline PPX C membranes, and to investigate the related sorption and diffusion properties.

2. Computational details

All simulations were implemented on SGI workstations at the China Academy of Engineering Physics with Materials Studio and self-programming software. The parameters of the force field for the PPX C were described as bonded angle-bending, torsional and out-of-plane interactions arising from the near-neighbor connections in the structure.[10,11] The so-called non-bonded excluded-volume and electrostatic potentials were applied to all atom pairs separated by more than two bonds in the same or different molecules. The non-bonded interactions in the gas permeation study of PPX C membranes were described by the Weeks–Chandler–Anderson (WCA) potential,[6] which is close to the realistic excluded-volume Lennard–Jones (LJ) and electrostatic forms. The low computational consumption of the WCA form allowed a steady-state uptake of gases to be completed in the MD simulations. But PPX C membranes had to be constrained into rigid walls to maintain the density. LJ ($U_{\rm LJ}$) and electrostatic ($U_{\rm Coul}$) terms of non-bonded potentials were calculated using the following equations,[6] which can remove the walls and allow the membranes to be relaxed in a realistic way,

$$U_{\rm LJ}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right], \qquad (1)$$

$$U_{\rm Coul}(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}, \qquad (2)$$

where $U_{\rm LJ}(r_{ij})$ and $U_{\rm Coul}(r_{ij})$ denote the Lennard–Jones and the electrostatic potentials, respectively, r_{ij} is the distance between atoms i and j, the well depth ε and the distance σ at the LJ potentials tend to zero, ε_0 is the vacuum permittivity, and q_i (q_j) is the partial charge on atom i (j).

2.1. Construction of PPX C membranes

Chain units of PPX C were constructed by using the forcefield method,[5,11] that is, molecular mechanics (MM) minimization after 200 ps NPT+NVT molecular dynamics. The errors of calculated bond lengths and angles of polymers chain units were less than 0.72% with respect to the literature data.[9]

The binding sites of polymer chain units should be confirmed before the PPX C areas are built. The electronic distributions of PPX C chain units were calculated using the B3LYP-DFT method.[17,18] As illustrated in Fig. 1, the high energy parts of the chain units are the most probable binding sites, combining randomly with adjacent chain units. This binding energy increases the total energy, which leads polymers to be in the amorphous phase. Whereas the low binding energy of the system leads to the π stacking of benzene rings, where PPX C chain units tend to be regularly arranged. The corresponding polymers belong to the crystalline phase, see Fig. 1(c).

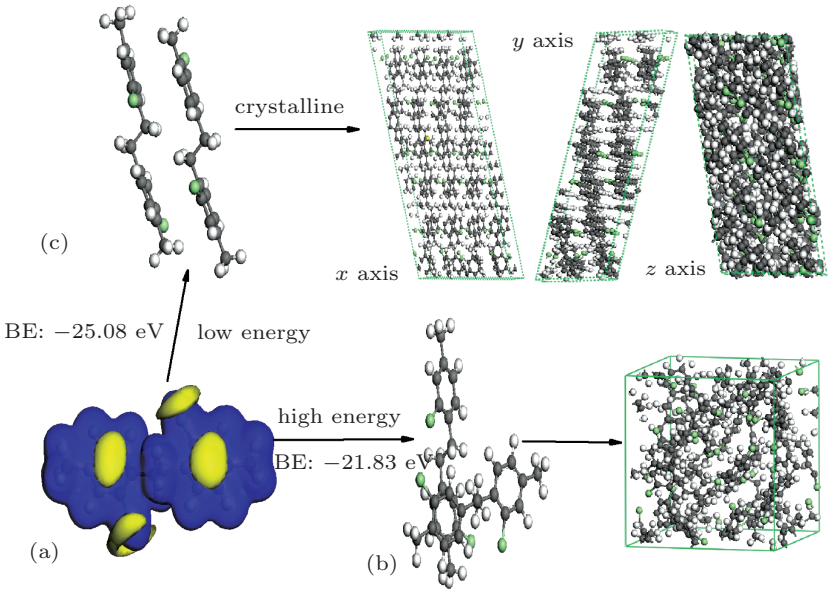


Fig. 1. (colour online) (a) Surface electrostatic energy of PPX C chain units, (b) amorphous and (c) crystalline areas of PPX C membranes. The binding energy (BE) of PPX C chain units is −25.08 eV. The colour code is as follows: grey, C; green, Cl; white, H; blue, low energy area; and yellow, high energy area.

After arranging the PPX C chain units, we constructed the high energy and the low energy PPX C membranes via 200 ps annealing-MD[5] and GRS[7] methods. There were 784 atoms in the cell of PPX C polymers. The calculated density, glass transition temperatures (T_g), and crystal parameters of PPX C membranes are shown in Table 1. These calculated results are close to the experimental data,[9,12,19] the errors of T_g of the amorphous and the crystalline states are 0.84% and 4.44%, respectively. The density of crystalline PPX C membranes approaches to the experimental data too. It indicates that the crystalline area has a high ratio in PPX C membranes. Besides, the chain-end area, found near the boundary layers, is considered to be crystalline PPX C polymers.

Table 1. Calculated structures, densities, and T_g of amorphous and crystalline PPX C membranes.

	Amorphous	Crystalline
a/nm	1.78	0.95
b/nm	1.87	2.15
c/nm	1.97	4.21
Density/g·cm^{-3}	1.27	1.29
T_g/K	320.67	332.13

2.2. Free volumes of PPX C membranes

Based on the density of PPX C polymers, this work confirmed the volumes of PPX C membranes by using the pressure mercury principle, including the occupied volumes (V_o), hole sizes (free volume V_f), and specific surface areas. The total volumes (V_t) were made up of V_o and V_f. Therein, the free volumes in a cell were related to the sorption sites or the diffusion paths of gas molecules,[20] and the cut-off by uniform chain units of PPX C polymers.[11] The free volume theory[12] shows that the free volumes can be influenced effectively by pressure or temperature. In order to obtain the reasonable free volume distribution, this work relaxed amorphous and crystalline PPX C membranes using 110 ps NPT-annealing methods.[21] Then the free volumes in a cell were uniform and calculated using Eq. (3). The standard combination rules were used for all cross terms, except for gas–gas interaction parameters, which were set to zero to represent the ideal gas. It was found that $\langle p_{ip} \rangle$ could be changed with the cell of gases and membranes. It was set as a function of z for bin widths of 0.1 nm. While P was 100 kPa, $n_g + n_p = 5613$, and 7572 gases probes were inserted into membranes in amorphous and crystalline PPX C membranes for absorbing or transferring studies. Here

$$\begin{aligned} P &\approx (n_p k_B T)/(p_{ip} V_p) \\ &\approx [(n_g + n_p) k_B T]/(V_g + p_{ip} V_p), \end{aligned} \tag{3}$$

where P is the pressure, T is the temperature, p_{ip} shows the probability of insertion for probes into PPX C membranes, n_p is the number of probes inserted into PPX C membranes, n_g is the number of probes in gases, V_p shows the volume of PPX C membranes, and V_g is the free volume.

This work cluster-analyzed the free volumes of PPX C membranes as the homology free volumes by determining the energy minimum sites of gas sorption. As shown in Fig. 2(a), the polymer chain units in amorphous PPX C membranes are staggered to form large and connect-free volumes for gas walking. However, the chain units of crystalline PPX C membranes are regularly arranged. The corresponding free volumes just exist at the chain-end area. Their total volumes are less than those of amorphous PPX C membranes. There is no favorable free volume in the inner part of crystalline PPX C membranes. We have

$$\chi_\alpha \chi_\beta g_{\alpha\beta}(r) = \sum_{i=1}^{N\alpha} \sum_{j=1}^{N\beta} \delta(r - r_i - r_j), \tag{4}$$

where $g(r)$ is the radial distribution function, χ is the molar fraction of atoms, $\delta(r - r_i - r_j)$ is the setting distance difference, and N denotes the number of molecules.

The radial distribution functions show the atomic distances of gas and polymers. According to Eq. (4), the molar action ($\chi_\alpha \chi_\beta$) term is the inverse ratio to $g(r)$, and the abscissa of $g(r)$ showes the intramolecular lengths. Figure 2(b) shows that $g(r)$ in amorphous PPX C membranes is about 9 times to that in crystalline PPX C membranes. The related minimum H–H bond length is 0.15 nm, which is easy to form continuum free volumes or new H bonds. It also proves that amorphous PPX C membranes have high free volumes and provide more H bonds for absorbing or transferring gas.

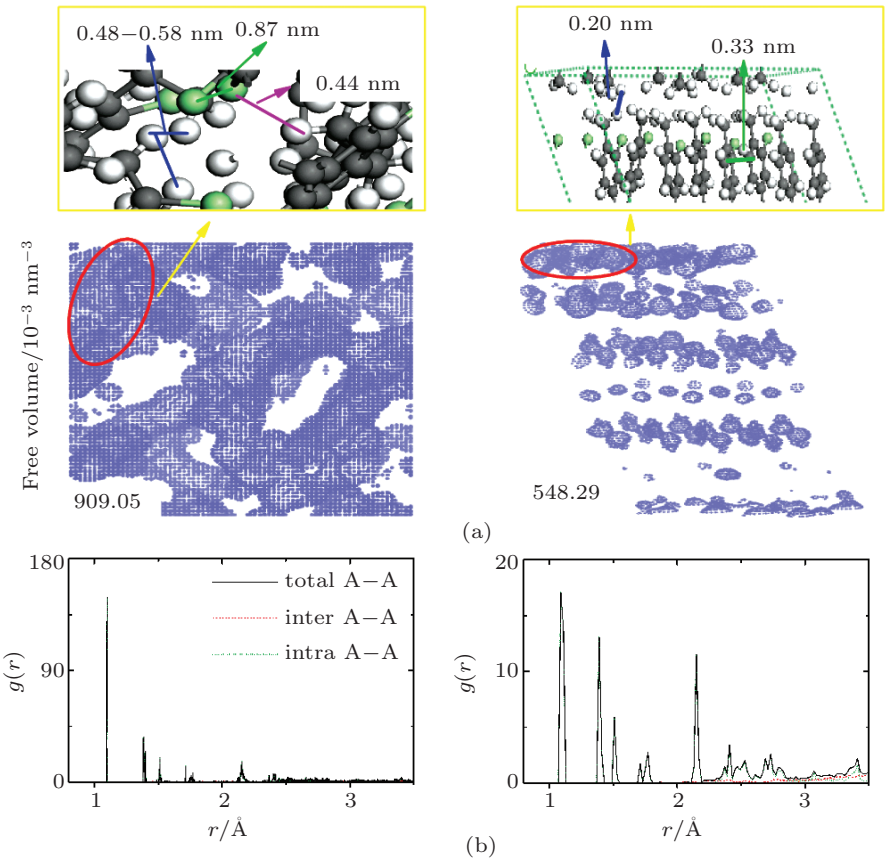


Fig. 2. (colour online) (a) Free volumes and (b) $g(r)$ of amorphous (left) and crystalline (right) PPX C membranes. The purple code shows the free volumes, the part in red line means the most probable sorption sites and diffusion paths of gas.

2.3. Simulations on the sorption and diffusion properties of gas molecules in PPX C membranes

Figure 3 shows the sorption and diffusion properties of gas in the free volumes. All the interatomic interactions followed the COMPASS force field. The short-range van der Waals term was calculated using the atom based method. The Ewald + group summation method was used for the long-range electrostatic interaction.[22] The temperature was controlled by using an Andersen caldarium, and the integration of motion equation was done using the verlet algorithm. The time step was 1 fs, and the cut-off distance was 0.95 nm. The representative decomposed product gases of CHNO energetic materials were selected, including He, N_2, H_2O, NH_3, NO, NO_2, CH_4, CO, and CO_2.[13,14] Molecular diameters of gases are the major factors influencing sorption and diffusion properties of gases.[5] The molecular diameters and the basic jump energy barriers of gases were calculated using Eq. (5), as shown in Table 2. In the connected walking paths, large molecular diameter gases should overcome the high energy barriers (ΔE) to diffuse

$$\Delta E = \pi d^2 \lambda / 4, \tag{5}$$

where d is the diameter of a gas molecule, λ is the diffusion step and increases with time increasing.

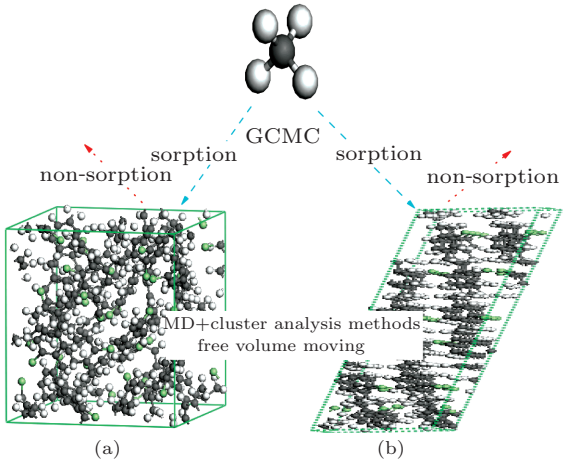


Fig. 3. (colour online) Illustration of sorption and diffusion simulations on gas molecules in the free volumes.

Table 2. Molecular diameters, covalent bonds, and ΔE of gas molecules. The λ term was 0.1 nm.

Gas	Molecular diameter/ nm	Covalent bond	ΔE/eV
He	0.08	non-polar	0.02
N_2	0.20	non-polar	0.13
H_2O	0.37	polar	0.43
CH_4	0.35	non-polar	0.38
CO	0.31	polar	0.30
CO_2	0.39	non-polar	0.48
NH_3	0.29	polar	0.26
NO	0.23	polar	0.17
NO_2	0.28	polar	0.25

The sorption sites and quantities of gas molecules in PPX C membranes were confirmed by grand canonical Monte Carlo (GCMC) calculations with the Metropolis methods.[23] The step numbers of equilibrium and statistic stages were 10000 and 500000 steps, respectively. Gas molecules were randomly embedded in the cells of amorphous and crystalline PPX C membranes. Their sorption sites and ratios depend on the total sorption energy (E) of the system

$$E = E^{\mathrm{SS}} + E^{\mathrm{SF}} + U^{\mathrm{S}}, \tag{6}$$

where E is the total energy, E^{SS} is the intermolecular energy between absorbed molecules, E^{SF} is the interaction energy between gas molecules and the framework, and U^{S} is the total intramolecular energy between all absorbed molecules. The total sorption energies of gas molecules in PPX C membranes include the short-range van der Waals energy and the long-range electrostatic interaction energy.[24] The minimum energy principle[20] shows that the average sorption quantities of gas molecules can be influenced by the impact factors, including the temperature (β term) and the pressure (F term) in the following equations:

$$F = [(\beta f V)^N / N!] \exp[-\beta N u_{\mathrm{intra}}], \tag{7}$$

$$\rho_m = C \exp(-\beta E_m), \tag{8}$$

where ρ_m is the density of the m structure, C is the normalization constant, β is the reciprocal temperature, and E_m is the total energy of the m structure. The F shows the total fugacity, V is the volume of the m structure, f is the relative fugacity, u_{intra} is the intramolecular chemical potential, and N is the loading quantity. With β and F increasing, the loading quantity (N) of gases increased until E_m data had the minimum value. The average sorption quantities of gases were obtained by averaging N. The data in this paper were cited from Ref. [2].

After defining the sorption properties of gases in polymers, we chose the possible gas molecules in the membrane cells for exploring the gas molecule walking. The corresponding stable structure was obtained by 500 ps NVT-MD.[11] Then the mean square displacement (MSD) of gases was obtained by analyzing the MD trajectories. The diffusion behaviors of gases were clustered into vibration and diffusion terms. Therein, the vibration term of gases showed that the diffusion frequencies could be considered as the micro diffusion term of gases. This was solved by fitting the slope of the MSD data of gases. The related accuracy of linear regression line depended on the measure of linear correlation R, as illustrated in Fig. 4. Considering the effective of gas vibrations, we found that the R data must be not far away from 1. With R decreasing, the accuracy of the gas's trajectory decreased, while the diffusion behaviors of gas molecules changed to the jump diffusion. The auto correlation function of the system was close to the zero point.[15] By trial calculation, the vibrating term of gas molecules was considered completely as the jump diffusing term when R was close to 0.95. Then the jump diffusion directions of gases were unique errors for their diffusion coefficients, see Fig. 4(b). They were divided into two directions, i.e., positive and negative directions. Finally, we calculated the diffusion coefficients (D_0) of gas molecules by solving Eq. (9). The corresponding permeability coefficients were obtained from the solubility and the diffusion coefficients

$$D_0 = \lim_{\mathrm{t}\to 0} \mathrm{d} \sum_{i=1}^{N} \langle |r_{(t)} - r_{(0)}|^2 \rangle / (6N\,\mathrm{d}t), \tag{9}$$

where D_0 is the diffusion coefficient, $r_{(t)}$ and $r_{(0)}$ are the diffusion lengths at t and zero points.

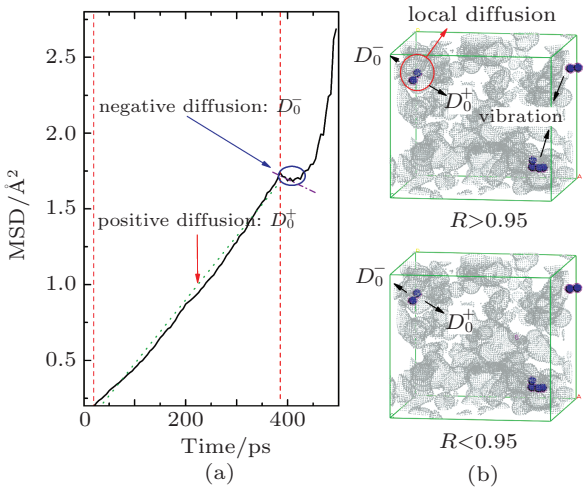


Fig. 4. (colour online) (a) Analysis on the MSD of gas molecules using the cluster analysis method, the corresponding diffusion behaviors of gases are shown in panel (b).

3. Results and discussion

3.1. Sorption properties of gases in PPX C membranes

Gas molecules are absorbed in the large free volumes of polymers,[9,21] and are physically but not chemically absorbed by PPX C membranes. Therein, the H-bonded sorption is determined by the electrostatic interaction energy. The Fermi energy is related to the pure physical sorption. The van der Waals energy is determined by having both roles. The total sorption energy of a system will be close to the Fermi point when the temperature increases, and the sorption ratios of gases tend to zero. As can be observed in Fig. 5, the sorption energy of gases is negative in amorphous PPX C membranes, however, is close to the Fermi point in crystalline PPX C membranes. This indicates that amorphous PPX C membranes absorb gases by both physical and H-bond forces. Gases are just physically absorbed in the chain-end area of crystalline PPX C membranes.

Sorption quantities of gases will have limited data, which can be defined by calculating the total energy of a system. The electronic layers of add-on gases overlap the surface electronic layers of PPX C polymers. This will enlarge the U^{S} term and cause the total energy of system to increase. But the related total energy will have a tendency to drop to the lowest points. Finally, the added-on gas molecules decrease the sorption probability of the other gases at stable sites. Figure 6 shows that, except He molecules, the average sorption quantities in amorphous PPX C membranes reduce with the temperature increasing and the pressure reducing, and then stabilize under 300 K and 100 kPa.[23] However, the sorption quantities do not change obviously in crystalline PPX C membranes. The related final sorption ratio of gases tends to 1. Typically, the inner part of crystalline PPX C membranes can not absorb gases.

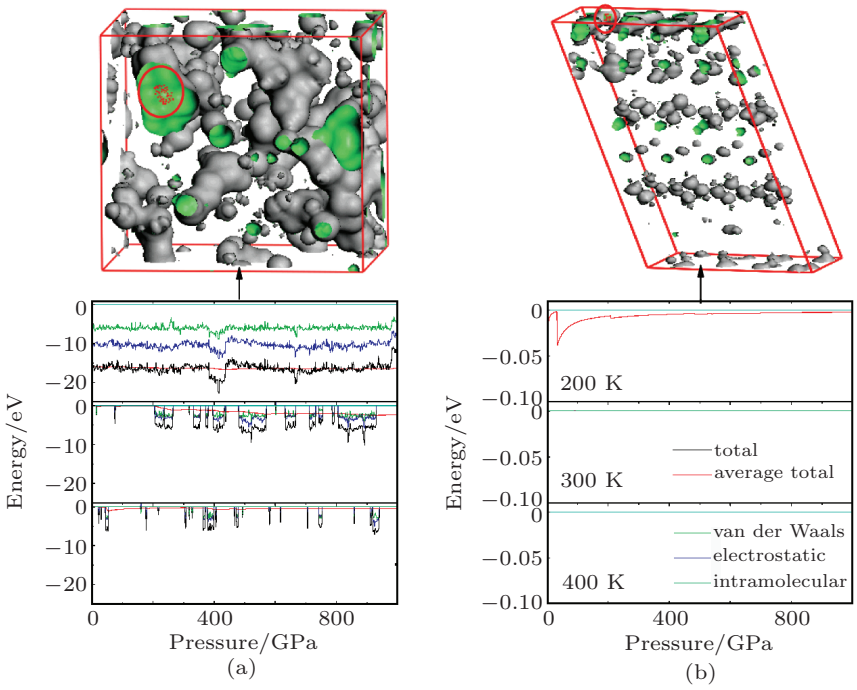


Fig. 5. (colour online) Sorption energies and sites of gases in (a) amorphous and (b) crystalline PPX C membranes.

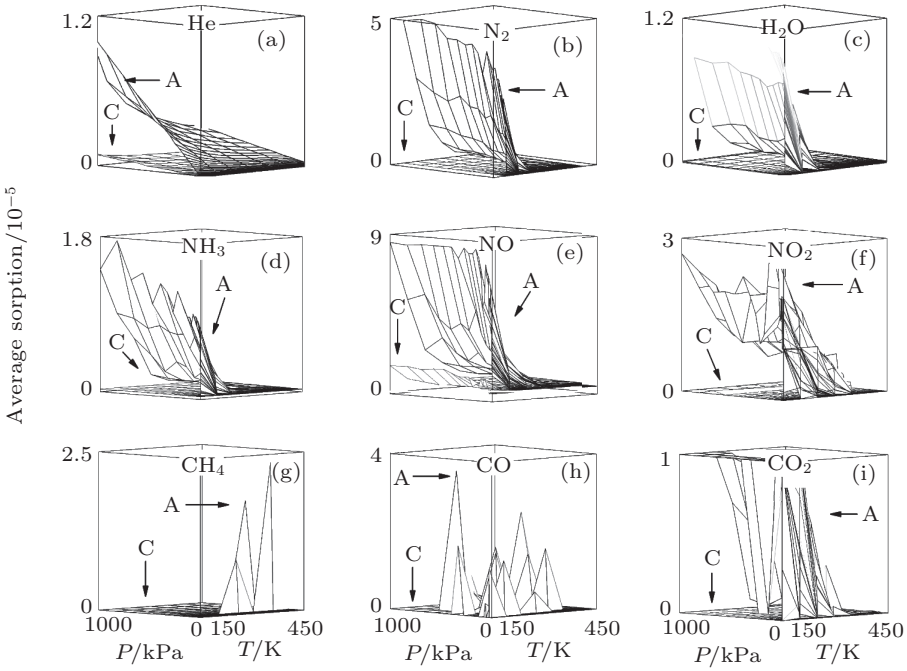


Fig. 6. Average sorption quantities of (a) He, (b) N_2, (c) H_2O, (d) NH_3, (e) NO, (f) NO_2, (g) CH_4, (h) CO, and (i) CO_2 in amorphous (A) and crystalline (C) PPX C membranes.

Moreover, the corresponding initial free volumes of gases are also defined in PPX C membranes. These are the basic walking paths of gases, as shown in Table 3. Therein, nitrogenous gas molecules have higher activity than carbonaceous gas molecules. The reason is the H-bonded physical sorption for absorbing nitrogenous gases and the physical sorption for carbonaceous gases.[9,12,25,26] Hence, the average sorption quantities of carbonaceous gases are less than those of nitrogenous gases in PPX C membranes.

Table 3. Average sorption quantities of gases in PPX C membranes, and the corresponding initial free volumes (V_f).

Gases	Amorphous PPX C		Crystalline PPX C	
	Gas quantity	V_f/nm^3	Gas quantity	V_f/nm^3
None	0	0.91	0	0.55
He	1	0.89	1	0.52
N_2	1	0.87	1	0.51
H_2O	5	0.74	1	0.46
NH_3	1	0.60	1	0.50
NO	1	0.67	1	0.48
NO_2	2	0.59	1	0.45
CH_4	1	0.63	1	0.45
CO	1	0.69	1	0.49
CO_2	1	0.87	1	0.47

3.2. Diffusion behaviors of gases in PPX C membranes

For solving the Einstein diffusion coefficients, we must consider the diffusion behaviors of gas molecules.[26] Gases' diffusion behaviors include mainly vibration and jump diffusions. According to[27]

$$n = \lg d_{\mathrm{MSD}} / \lg t, \tag{10}$$

where d_{MSD} is the mean square displacement, t is the diffusion time, He gas, whose atom diameter is small, belongs to the normal diffusion ($n < 1$) in PPX C membranes. The He atoms walk freely through the free volumes of polymers.

Expert for He, gas molecules vibrate at stable

sites in free volumes, and with the channel campaign jump to the adjacent free volumes.[12,26] They must have enough energy to overcome their jump energy barriers (ΔE). The other gas molecules continue to vibrate or diffuse locally. The corresponding diffusion time will be delayed. These processes belong to the non-normal diffusion ($n > 1$) and the physical diffusion at normal temperature and pressure. Typically, there is a powerful H-bonded interaction between large gas and PPX C molecules. Large diameter gas molecules just vibrate near the stable sorption sites in the free volumes. This vibration term reflects the related micro diffusion frequency. By cluster analyzing on the behaviors of gases, we find that it can be considered as a part of the diffusion term of gases.

Figure 7 exhibits the diffusion behaviors of gas molecules in PPX C membranes. As time goes by, the free volumes move, and some gases are transferred.[28] The other gases will go on vibrating at the sorption sites. The transferring ratio of gases depends on the free volumes' fluctuation. The long fluctuation range shows a high gas transferring ratio. In crystalline PPX C membranes, the fluctuation range of free volumes is less than that of amorphous PPX C membranes. It means that the chain-end area of crystalline PPX C membranes does not fit for transferring gases, especially for large gases, such as the carbonaceous and the nitrogenous gases. And it is worthy noting that gas molecules do not walk through the inner part of crystalline PPX C membranes, where there are little free volumes. And the chain-end area considered here just shows the boundary condition near the crystalline areas. It does not really exist in the experimental crystalline PPX C membranes.

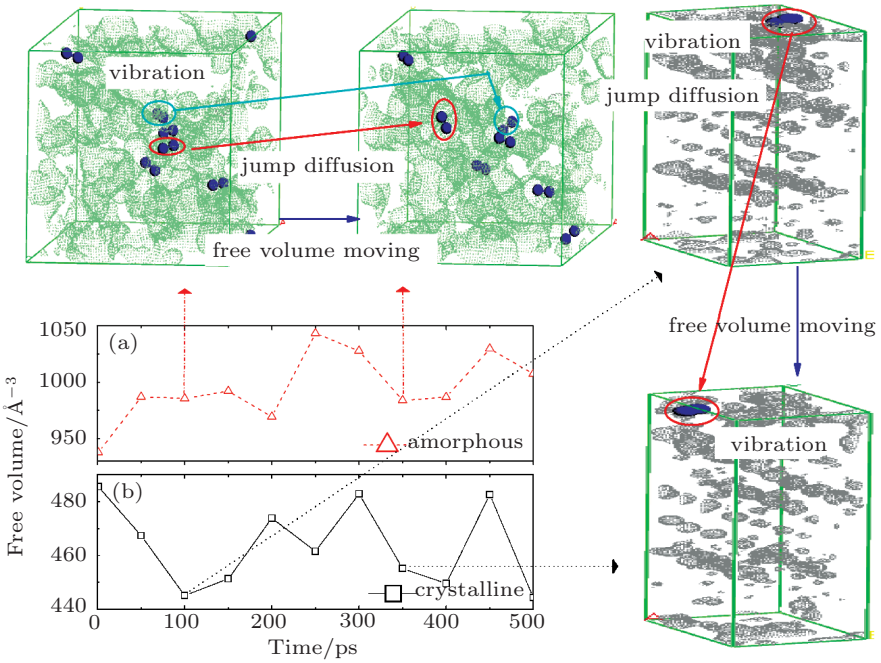


Fig. 7. (colour online) Free volumes of (a) amorphous and (b) crystalline PPX C membranes fluctuate with gases walking. The grid in the cell shows free volumes whose total data fluctuate near the initial points.

In the local free volumes of PPX C polymers, gases exist and move near the polymers molecules. The related atomic distances depend on the surface electronic distributions of polymers. In the chain-end area of crystalline PPX C membranes, the connected free volumes provide the unidirectional electronic potential for absorbing gases, as shown in Fig. 8. This leads gases to move forward on the inner surface of polymers. But the free volumes distribute randomly in amorphous PPX C polymers, and gases will exist at the center sites of surface electronic layers of amorphous PPX C polymers. Consequently, the interatomic distances between gases and polymers molecules are shorter in crystalline PPX C membranes than those in amorphous PPX C membranes. And small free volumes cause large gases to have high ratios for moving forward in the surface chain units of PPX C membranes.

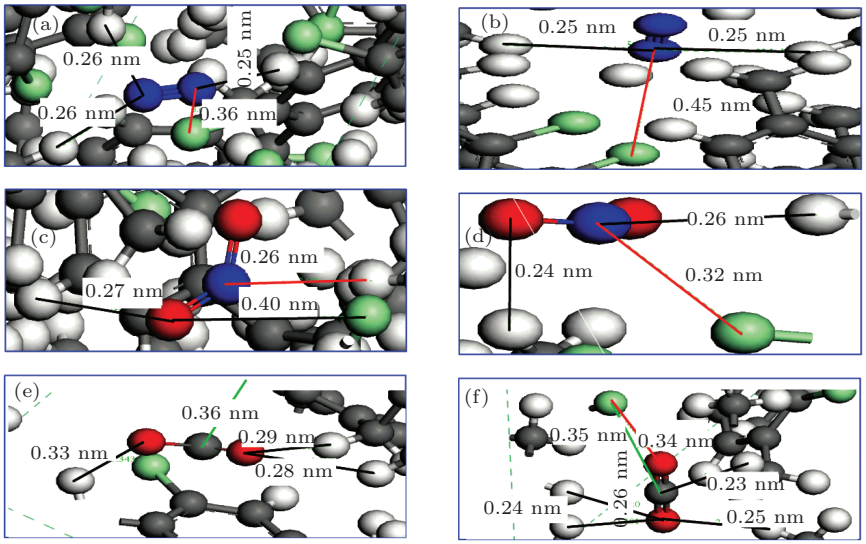


Fig. 8. (colour online) Atomic distances between (a) normal, (c) nitrogen, and (e) carbon gas molecules and amorphous PPX C polymers, and between (b) normal, (d) nitrogen, and (f) carbon gas molecules and crystalline PPX C polymers.

3.3. Diffusion coefficients of gases through PPX C membranes

Mean square displacement data can show the walking trajectories and the step lengths of gases. Its vector direction (positive and negative nature) means that the walking direction of gases and depends on the free volume distributions of polymers. In a previous report,[5] gas molecules would jump back and forth among cut-off free volumes for keeping the minimum system energy. As shown in Fig. 9(b), gases walk along the x axis in crystalline PPX C membranes, however, diffuse randomly among adjacent free volumes in the amorphous area. Thus, gases walk along positive and negative diffusion directions. Therein, the positive diffusion direction of gases shows that the gases walk along the permeable direction. The negative diffusion direction of gases means that the gases walk back to the initial sites for keeping the minimum total energy.

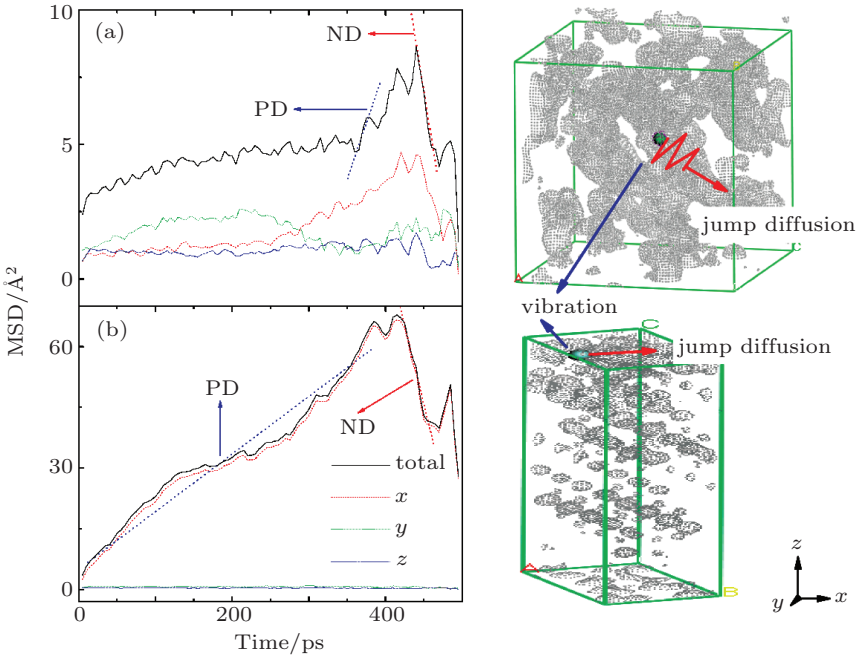


Fig. 9. (colour online) Cluster analyzing on the diffusion coefficients and directions of gas molecules through (a) amorphous and (b) crystalline PPX C membranes. The slope of MSD is calculated based on the least square approximation. The PD shows the positive diffusion direction of gases, ND means the related negative diffusion direction.

Along the diffusion directions of gases, the high MSD shows that the gases jump over a wide range among free volumes.[29] The relevant diffusion ratios will be higher than those of low MSD. Figure 9(a) shows that the MSD of gases in amorphous PPX C membranes is less than that in the crystalline chain-end area. This means that the gases have high ratios to walk through the connected chain-end area of crystalline PPX C polymers. The corresponding diffusion coefficients will be enhanced.

According to Akihiko's opinion,[1] the diffusion coefficients of gases are little affected by temperature and pressure. They mostly depend on the total free volumes of polymers and the molecular diameters of gases. High total free volumes are related to the large walking paths of gases. And the diffusion coefficients (D_0) of gas decrease sharply with the gas molecule diameter increasing. As shown in Fig. 10, positive diffusion coefficients of gases are approximate to the related negative diffusion coefficients in the same polymers area. It indicates that the gases have similar ratios among the cut-off free volumes. In contrast to amorphous PPX C membranes, crystalline PPX C membranes have the connected chain-end parts that provide the suitable paths for transferring gases. The permeable time of gases is t = 0.14–31.9 ns for gas molecules through amorphous PPX C membranes, and t = 0.01–2.11 ns in crystalline PPX C membranes, as shown in Table 4. The walking time of gases will be delayed in amorphous PPX C polymers. It can be explained by that the free volumes have been cut off in amorphous PPX C membranes and the jump energy barriers of gases have been increased.

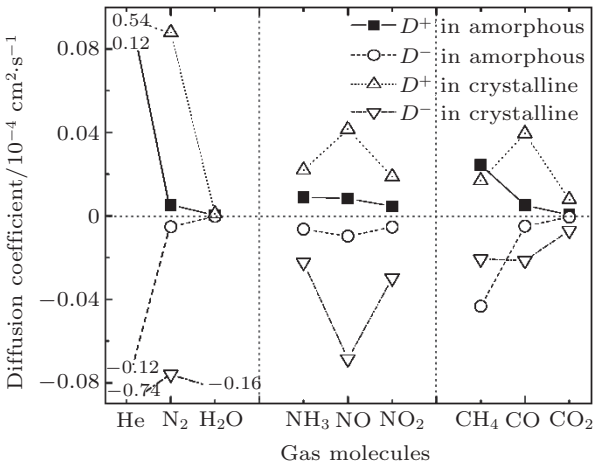


Fig. 10. Diffusion coefficients (D_0) of gas molecules through PPX C membranes, where D^+ shows the positive diffusion coefficient of gases, and the corresponding negative diffusion coefficient is D^-. Simulation time for every point is 500 ps.

Table 4. Diffusion behaviors and time of gases through PPX C membranes.

Gas	Diffusion behavior	Amorphous PPX C/ns	Crystalline PPX C/ns
He	ab-normal	0.14	0.01
N_2	normal	1.75	0.03
H_2O	normal	11.1	0.10
NH_3	normal	1.85	0.76
NO	normal	1.98	0.40
NO_2	normal	3.62	0.88
CH_4	normal	0.68	0.99
CO	normal	3.21	0.42
CO_2	normal	31.9	2.11

3.4. Permeability coefficients of gases through PPX C membranes

The permeability P has been calculated using solubility parameter S[30] and positive diffusion coefficient D[31] according to the following equations:

$$P = DS, \tag{11}$$

$$D = D_0 \exp[-E_a/k_B T], \tag{12}$$

$$E_a = \mathrm{d}(\log D)/\mathrm{d}(1000/T), \tag{13}$$

$$S = E_{\mathrm{CED}}^{1/2}, \tag{14}$$

where the activation energy E_a is defined as a reference data for permeable behaviors. Table 5 shows that E_a in amorphous PPX C membranes is the same as that in crystalline PPX C membranes. The gases have the same activities in amorphous and crystalline areas. As the results of diffusion behaviors of gases, E_a is less than 1 eV. The $\exp[-E_a/k_B T]$ term is close to 1. And E_a has little effective on D of gases in PPX C membranes. Thus gases' permeable processes are all considered as the physical diffusion at 300 K and 100 kPa. The solubility coefficient S is obtained from the limiting slope of the sorption isotherm at zero pressure. The E_a shows the activation energy of

permeation, T is the temperature in K, and $E_{\rm CED}$ is the cohesive energy density.

The solubility is related to the free energies of gas and polymer molecules. Nowadays, the standard way is to use the Henry constant to describe the solubility. The Henry constant shows the sorption ratios of gases and can be measured experimentally by determining the sorption volumes of gases in PPX C membranes. It depends on the equilibrium temperature of system. According to Henry's law (Eq. (14)), S is the square root of the cohesive energy density.[8,11] The high cohesive energy indicates that the van der Waals energy of gases enhances in PPX C polymers. This will provide sufficient energy for absorbing gases. Thus, the amorphous PPX C area has higher solubility of gases compared to the crystalline area, as S shown in Table 5.

Table 5. Activation energy ($E_{\rm a}$), solubility S, and permeable parameters of gases through amorphous and crystalline PPX C membranes.[1,11,1227,32,33]

Gas	$E_{\rm a}$/eV	Amorphous PPX C		Crystalline PPX C		$P_{\rm Exp}/10^{-12}$ cm^3 (STP)·cm·cm^{-2}·s^{-1}
		S/cm^3 (STP)·cm^{-3}(atom)	$P_{\rm Calc}/10^{-12}$ cm^3 (STP)·cm·cm^{-2}·s^{-1}	S/cm^3 (STP)·cm^{-3}(atom)	$P_{\rm Calc}/10^{-12}$ cm^3 (STP)·cm·cm^{-2}·s^{-1}	
He	0.11	3.36×10^{-5}	4.02	3.33×10^{-5}	99.3	152
N_2	0.30	1.43×10^{-4}	0.21	1.23×10^{-4}	75.3	1.09
H_2O	0.62	3.16×10^{-3}	0.13	3.05×10^{-3}	0.25	< 0.1
NH_3	0.27	0.06	57	2.20×10^{-5}	0.48	–
NO	0.11	0.02	168	5.13×10^{-3}	213.41	–
NO_2	0.23	0.04	184	1.61×10^{-3}	30.43	–
CH_4	0.18	0.02	491	2.12×10^{-5}	3.58	–
CO	0.15	0.03	156	1.69×10^{-3}	66.75	–
CO_2	0.42	0.10	52.6	7.39×10^{-4}	5.27×10^{-3}	15.9

The calculated permeability is comparable to the experimental results[1,11,12,27,32,33] in Table 5. They have the same order of magnitude. Although crystalline PPX C membranes can transfer gases easily, they have fewer total paths for dissolving gases.[34] The corresponding permeability decreases. Comparing to amorphous PPX C membranes, the crystalline PPX C membranes are better barriers for blocking gases.

It should be noted that there is no permeable path of gases in the inner part of crystalline PPX C membranes except for the chain-end area. However, in the real protective films, gases walk along the z axis of the inner part of crystalline PPX C membranes. Consequently, the crystalline PPX C membranes should be thick enough, as supported by the experimental results.[1,12,26]

4. Conclusions

In this work, a novel computational technique was developed for constructing PPX C membranes. First-principles calculations were carried out for describing the binding states of PPX C chain units and studying their surface electronic distributions. Amorphous and crystalline PPX C membranes were built via NVT+NPT-MD and GRS methods, respectively. The calculated molecular structures, densities, and glass transition temperatures were close to the experimental data. The corresponding free volumes were defined via the homology cluster method. Compared to crystalline PPX C membranes, amorphous PPX C membranes had larger free volumes providing more sorption sites and walking paths of gases.

The sorption and diffusion properties of gases were determined by using the GCMC technique and based on the free volumes of polymers. The results show that gases can be readily absorbed in amorphous PPX C membranes by H-bonded sorption, however, hardly in the chain-end area of crystalline PPX C polymers through physical sorption. Their sorption quantities tend to have the minimum data at high pressure and low temperature. After defining the sorption sites and ratios of gases in PPX C, this work used the cluster analysis method to describe and calculate the relative diffusion behaviors. Through PPX C membranes, gases vibrate and then walk back and forth along the x axis in the crystalline cell, however, randomly in the amorphous area. The corresponding diffusion coefficients were obtained at the same time. Considering the solubility of gases in PPX C, we found that amorphous PPX C membranes have higher ratios

for transferring gases than that of crystalline PPX C membranes.

This work demonstrated how gases walk through amorphous and crystalline PPX C membranes. However, in experiments, there is a boundary layer between two layers. Therefore, the results of this work are insufficient to establish the boundary layers between amorphous and crystalline polymers. Further theoretical studies should include the boundary layers of PPX C membranes to understand better the permeability of gases through the total polymers. This work, however, provides useful information on the diffusion behaviors and the walking directions of gases through PPX C membranes, and on understanding the relation between free volumes and permeability of PPX C membranes.

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