Molecular dynamics study of hydrogen dissolution and diffusion in different nonmetallic pipe materials

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Abstract. The nonmetallic pipes can effectively avoid the hydrogen embrittlement of metal pipes when transporting hydrogen. However, due to the characters of the nonmetal materials, there will be a large degree of gas permeation when conveying hydrogen by nonmetallic pipes. To select suitable nonmetal pipe materials, the solubility, diffusion, and permeability of hydrogen in PE, PVC and PVDF amorphous polymers are investigated and compared by molecular dynamics simulations at 270~310 K and 0.1~0.7 MPa, providing guidance for the construction of nonmetallic hydrogen transportation pipes. Simulation results indicate that the solubility coefficients of hydrogen in PE and PVDF rise with the increasing temperature, but show an opposite trend in PVC. Both the diffusion and permeability coefficients increase with the rise of temperature. In a small range of pressure variation, the influence of pressure on diffusion and permeation characteristics is ignorable. Among the three studied amorphous polymers, the permeability coefficient of hydrogen in PE is the largest and that in PVDF is the smallest. In addition, the diffusion of hydrogen molecules in the polymer conforms to the hopping mechanism.

Keywords: Hydrogen, Nonmetallic materials, Dissolution, Diffusion, Permeation, Molecular dynamics.

1 Introduction

It is an important measure to reduce carbon emissions to substitute hydrogen for partial natural gas for combustion and utilization. However, the safety problems such as hydrogen embrittlement of metal pipes may occur when transporting hydrogen [1]. To ensure the safety of hydrogen pipeline transportation, nonmetallic pipes such as PE are usually used in engineering practice. However, due to the difference of material properties, nonmetallic pipes demonstrate a greater degree of gas permeation than metal pipes, resulting in energy waste and safety issues. Therefore, it is of great significance to select suitable nonmetallic pipe materials to reduce the permeation of

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hydrogen. In this study, the solubility, diffusion, and permeability of hydrogen in nonmetallic pipe materials (PE, PVC and PVDF) are analyzed and compared under the working temperature (270-310 K) and pressure (0.1-0.7 MPa) of urban nonmetallic pipes by Giant Canonical Monte Carlo (GCMC) and Molecular dynamics (MD) methods, to provide reference for the construction of hydrogen transportation pipelines and material selection of urban nonmetallic pipes.

2 Molecular dynamics model

First, the PE, PVC and PVDF single chains with a polymerization degree of 100 as well as the H_2 molecule are constructed by the all-atomic model. Then, 1000 steps of geometric optimization are performed. Finally, 10 three-dimensional periodic amorphous cells of PE, PVC and PVDF consisting of five polymer chains are constructed, respectively. 30 amorphous cells are optimized with 10000 steps, and the three amorphous PE, PVC and PVDF cells with the lowest energy are selected for further study. After the geometric optimization, further geometric optimization and energy reduction of these nine selected amorphous cells need to be carried out through the following dynamic operations. (1) The NVT ensemble is used for 500 ps relaxation at 300 K. (2) Annealing: the amorphous cell is heated from 300 K to 600 K with a step of 60 K, and then cooled from 600 K to 300 K with the same temperature step. (3) The NPT ensemble is used to relax the amorphous cells for 500 ps at 300 K and 1 GPa. (4) The NPT ensemble is used to balance for 1000 ps at 298 K and 0.1 MPa. The Polymer Consistent Force Field (PCFF) is adopted in MD simulations and the cutoff distance is set as 12.5 Å.

3 Molecular dynamics simulation

3.1 Dissolution simulation

Based on the GCMC principle, the Metropolis method is used to insert, delete, and translate H_2 molecules in amorphous cells, and the probability of occurrence is assumed to be 40%, 40% and 20%, respectively. The adsorption isotherms of H_2 in PE, PVC and PVDF at 270~310 K can be obtained and fitted by the Henry model, as shown in Eq. (1). The solubility coefficient can be calculated by taking the limit slope when the fugacity f tends to 0 for the adsorption isotherms, as shown in Eq. (2). At least five independent dissolution simulations are conducted for three amorphous cells of each material to reduce the errors. Finally, the solubility coefficients of H_2 in amorphous PE, PVC and PVDF are taken as the average values of 15 dissolution simulations results.

$$C = K_{\mathrm{H}} \cdot f \tag{1}$$

$$S = \lim_{f \to 0} \frac{C}{f} = K_{\mathrm{H}} \tag{2}$$

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Here, C is the dissolved concentration of H_2 molecules in polymer, $cm^3(STP)/cm^3$; K_H is the Henry constant; f is the fugacity, MPa; S is the solubility coefficient, which represents thermodynamic characteristics between H_2 molecules and polymers, $cm^3(STP)/(cm^3 \cdot MPa)$.

3.2 Diffusion simulation

Firstly, the H_2 molecules are adsorbed by amorphous cells at different temperatures and fugacity based on GCMC, in which the fugacity is calculated by the Peng-Robinson equation of state (EoS). Then, the amorphous cells containing H_2 molecules are balanced by 2000 ps NPT. Finally, the 10 ns NVT dynamic operation is carried out on the amorphous PE, PVC and PVDF cells that adsorbed H_2 molecules to calculate the diffusion coefficients of H_2. Through above operations, the Mean Square Displacement (MSD)-time (t) figures of H_2 molecules in amorphous PE, PVC and PVDF cells at different temperatures (270 ~ 310 K) and pressures (0.1 ~ 0.7 MPa) can be obtained. The diffusion coefficients then can be calculated by analyzing the MSD-t figures. At first, the part with the slope of 1 in the log(MSD)-log(t) figure is found, which represents the normal diffusion of H_2 molecules. Then, in the MSD-t figure, the slope a is calculated by linear fitting of the first function for this part, and finally the diffusion coefficient can be calculated by Eq. (3) [2]. In each working condition, at least 10 independent NVT simulations are conducted for three amorphous cells of each material to eliminate the influence of error. Finally, the diffusion coefficients of H_2 in amorphous PE, PVC and PVDF cells are taken as the average values of 30 NVT simulation results.

$$D = \frac{a}{6} \tag{3}$$

Here, D is the diffusion coefficient, cm^2/s; a is the slope of normal diffusion part in the MSD-t figure.

3.3 Permeation simulation

The “dissolution-diffusion” theory can be used to describe the permeation process of H_2 molecules in polymers, as illustrated in Fig. 1. Firstly, the H_2 molecules are dissolved in the polymer. Subsequently, H_2 molecules diffuse through the polymer, and finally H_2 molecules are desorbed to escape from the polymer. Therefore, the permeation of H_2 in PE, PVC and PVDF can be divided into the stage of dissolution and diffusion, and their relationship can be described by Eq. (4) [3].

$$P = SD \tag{4}$$

Here, P is the permeability coefficient, $cm^3(STP) \cdot cm/(cm^2 \cdot s \cdot MPa)$; S is the solubility coefficient, $cm^3(STP)/(cm^3 \cdot MPa)$; D is the diffusion coefficient, cm^2/s.

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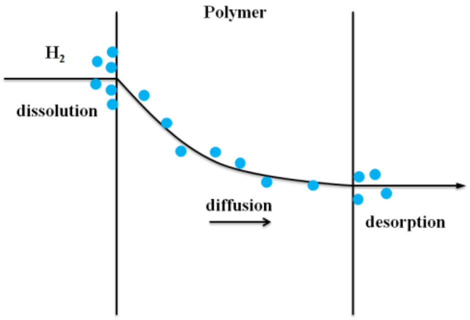
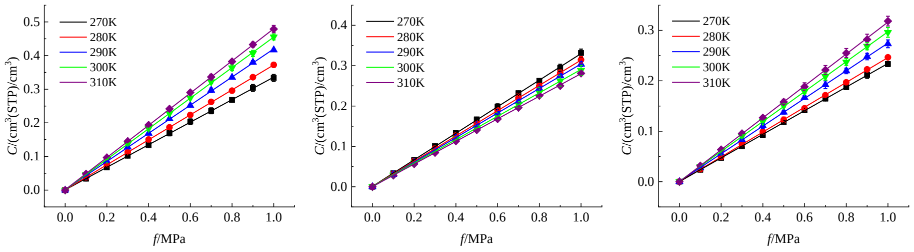


Fig. 1. Permeation process of H_2 in polymers.

4 Results analysis and discussion

4.1 Influences of temperature on the solubility coefficient

The adsorption isotherms of H_2 in amorphous PE, PVC and PVDF cells at 270~310 K are displayed in Fig. 2. The solubility coefficients of H_2 can be obtained by fitting and calculating the data in Fig. 2 using Eqs. (1) and (2), and the results are shown in Fig. 3. It indicates that the solubility coefficients of H_2 in PE and PVDF increase with the rise of temperature, while the solubility coefficient in PVC shows an opposite trend. The reason can be attributed to that the material properties are different. At 270~310 K, the PE and PVDF are in the rubbery state, while PVC is at the glassy state. For PE and PVDF, the pores in the cell become larger with the increasing temperature, and the H_2 molecules can be adsorbed easier. For PVC, the free volume for H_2 dissolution is in the "frozen" state, so the size of pores basically does not change with the increase of temperature. Meanwhile, the density of H_2 decreases with the rise of temperature, which weakens the adsorption and results in the phenomenon that the solubility coefficient decreases with the rising temperature. Fig. 3 also shows that the solubility coefficient of H_2 in PE is the largest. Additionally, the solubility coefficient of H_2 in PVC is larger than that in PVDF when the temperature is lower than 300K.



(a) PE (b) PVC (c) PVDF

Fig. 2. Adsorption isotherms of H_2 in amorphous PE, PVC and PVDF cells at 270~310 K.

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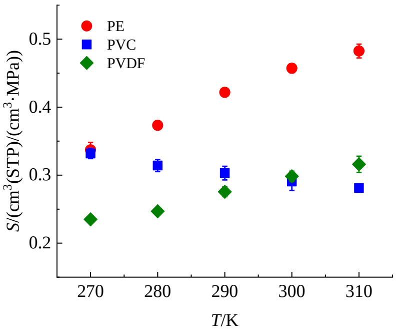

Fig. 3. Solubility coefficients of H_2 in amorphous PE, PVC and PVDF cells at 270~310 K.

4.2 Influences of temperature on the diffusion coefficient

Through the 10 ns NVT simulation and the processing of MSD-*t* figures, the diffusion coefficients of H_2 in amorphous PE, PVC and PVDF cells at 270~310 K can be obtained, as shown in Fig. 4. It exhibits that the diffusion coefficients of H_2 increase with the rise of temperature, this is because the kinetic energy of H_2 molecules and the kinetic ability of polymer chains increase with the rising temperature, which makes the H_2 molecules diffuse easier. Furthermore, the diffusion coefficient of H_2 in amorphous PE cell is the largest and that in amorphous PVDF cell is the smallest at 270~310 K.

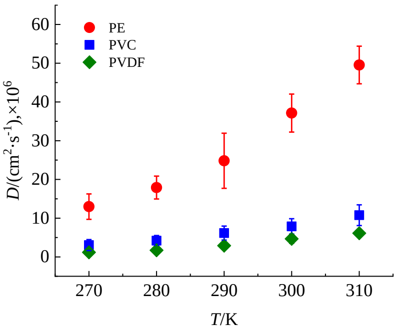

Fig. 4. Diffusion coefficients of H_2 in amorphous PE, PVC and PVDF cells at 270~310 K and 0.1 MPa.

4.3 Influences of pressure on the diffusion coefficient

In addition to studying the effect of temperature on the diffusion coefficient, the effect of pressure (0.1 ~ 0.7 MPa) on the diffusion coefficient is also analyzed, as shown in Fig. 5. It demonstrates that the pressure change has a tiny effect on the diffusion coefficient, because the change of studied pressure is small in this work, resulting in that the change of diffusion coefficient is smaller than the error fluctuation. Therefore, it is difficult to observe obvious changes of diffusion coefficient when the range of pressure change is tiny.

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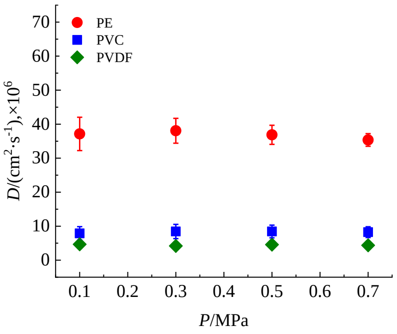

Fig. 5. Diffusion coefficients of H_2 in amorphous PE, PVC and PVDF cells at 0.1~0.7 MPa and 300 K.

4.4 Influences of temperature and pressure on the permeability coefficient

The data in Figs. 3 and 4 are calculated by Eq. (4) to investigate the influence of temperature (270~310 K) on permeability coefficients of H_2 in amorphous PE, PVC and PVDF cells, as presented in Fig. 6. It displays that the permeability coefficients increase with the rise of temperature. For PE and PVDF, this is because their solubility and diffusion coefficients of H_2 increase with the rising temperature. For PVC, the solubility coefficients decrease while the diffusion coefficients increase with the rise of temperature, indicating that the increase extent of the diffusion coefficient is larger than the decrease extent of the solubility coefficient with the increasing temperature, finally resulting in that the permeability coefficient increases with the rise of temperature. Moreover, the order of permeability coefficient of H_2 from large to small is PE, PVC and PVDF, respectively.

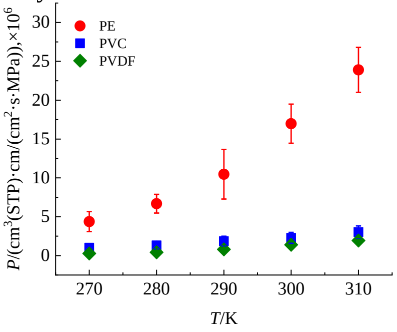

Fig. 6. Permeability coefficients of H_2 in amorphous PE, PVC and PVDF cells at 270~310 K and 0.1 MPa.

4.5 Diffusion mechanism

Figure 7 exhibits the diffusion trajectories of H_2 molecules in amorphous PE, PVC and PVDF cells at 300 K and 0.1 MPa. It can be clearly seen that the diffusion range of H_2 in PE is the largest, and that in PVDF is the smallest, which is consistent with

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the results shown in Fig. 4. That is, the diffusion coefficient of H_2 in amorphous PE is the largest, and that in amorphous PVDF is the smallest.

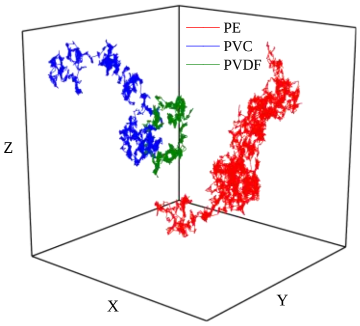

Fig. 7. Diffusion trajectories of H_2 molecules in amorphous PE, PVC and PVDF cells at 300 K and 0.1 MPa.

The diffusion distances of H_2 in amorphous PE, PVC and PVDF cells are obtained by calculating the data in Fig. 7 by using Eq. (5), as shown in Fig. 8. It indicates that the diffusion distance of H_2 molecules is the largest in PE, the second in PVC, and the smallest in PVDF, which is consistent with the diffusion coefficients in Fig. 4 and the diffusion ranges in Fig. 7. The diffusion distances of H_2 in these three materials increase with the rise of temperature because the temperature increases the kinetic energy and motion ability of H_2 molecules, and then H_2 molecules diffuse easier. In addition, it is also found in Fig. 8 that H_2 molecules vibrate in the polymer pores for a long time during the diffusion process, as shown in the black circle, and then quickly hop to other polymer pores in a short time, as marked in the purple circle, indicating the law of “long time vibration + short time hopping” as a whole.

$$D_d = \sqrt{(x_t - x_0)^2 + (y_t - y_0)^2 + (z_t - z_0)^2} \quad (5)$$

Here, D_d is the diffusion distance of H_2 molecule, Å; x_t, y_t, z_t are the x, y, z coordinates of H_2 molecule at any time t; x_0, y_0, z_0 are the x, y, z coordinates of H_2 molecule at the initial time.

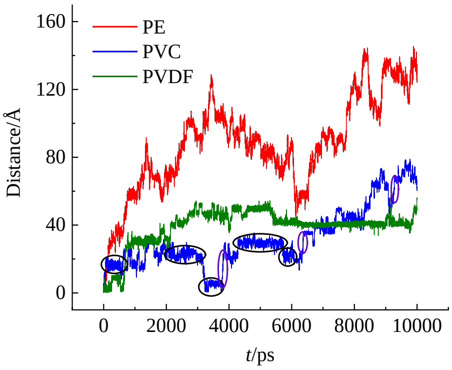

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Fig. 8. Diffusion distances of H_2 molecules in amorphous PE, PVC and PVDF cells at 300 K and 0.1 MPa.

5 Conclusions

The dissolution, diffusion and permeation characteristics of H_2 in amorphous PE, PVC and PVDF materials at 270~310 K and 0.1~0.7 MPa are analyzed and compared by Grand Canonical Monte Carlo and molecular dynamics simulations in this study. The following main conclusions are summarized.

(1) The solubility coefficient of H_2 decreases with the increasing temperature in PVC, but shows an opposite trend in PE and PVDF. The diffusion and permeation coefficients of H_2 increase with the rise of temperature. The pressure has slight influence on the permeability of H_2 in PE, PVC and PVDF when the range of pressure variation is small.

(2) Among the amorphous PE, PVC and PVDF, the permeability coefficients of H_2 in PE are the largest and that in PVDF are the smallest. The diffusion of H_2 molecules in amorphous PE, PVC and PVDF accords with the “hopping” mechanism. The H_2 molecules vibrate in the pores for a long time and then hop to adjacent pores to complete the diffusion for a short time.

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