Adsorption and diffusion of methane and carbon dioxide in amorphous regions of cross-linked polyethylene: a molecular simulation study

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Abstract

We perform Monte Carlo (MC) and molecular dynamics (MD) simulations to study the adsorption and diffusion properties of methane and CO₂ in cross-linked polyethylene in the temperature range 300 to 600 K. A hybrid MC/MD approach was used to incorporate the effects of framework flexibility and polymer swelling on the gas adsorption. The polymers show negligible swelling at the studied conditions. A nonmonotonic behavior of gas adsorption as a function of the cross-linking degree was obtained. Notably, a similar behavior was observed for the void fraction and pore diameters. This shows a direct correlation between gas adsorption and the pore characteristics of the cross-linked polymer network. Mobility of methane and carbon dioxide in the polymer matrix increases with temperature. Also, gas mobility decreases with increasing cross-linking degree, consistent with experiments. These results can be explained by the fact that the waiting time for a gas molecule in a cavity before the jump increases with decreasing temperature and increasing cross-linking degree. Interestingly, the activation energy for gas diffusion generally decreases with increasing cross-linking. This is possibly due to the fact that increasing the cross-linking degree leads to smaller pore sizes especially at high temperatures. Such a molecular-level understanding of adsorption and diffusion of gases in cross-linked polyethylene is important in improving the performance of polymer networks for potential applications in gas separation, barrier technology, and food packaging.

1 Introduction

A reduction in emissions of greenhouse gases may be achieved by the geologic storage of carbon dioxide. The usage of anthropogenic carbon dioxide for the production of gas and oil from shale reservoirs provides a unique way to reduce emissions.¹⁻⁴ Shale is a sedimentary rock rich in organic matter (such as kerogen) and inorganic constituents (such as clay minerals). Kerogen is an extremely complex material representing a wide range of organic matter types and levels of maturity.^{5,6} For instance, lacustrine source rocks contain algal kerogen (type I), marine environments have clastic source rocks containing kerogen (type II), and type III kerogen is mainly terrestrial in origin. With increasing maturity, the H/C and O/C ratios of kerogen decrease under catagenic conditions and eventually converge during metagenesis at the bottom-left corner in the van Krevelen diagram. Existing theory for the swelling of kerogen⁷ is based on the approximation of kerogen as an effective cross-linked polymer network and the Flory-Rehner theory⁸ that describes the equilibrium swelling of a cross-linked polymer network mixed with solvent molecules. Nevertheless, kerogen differs from a polymer network at both the molecular and supramolecular levels.⁹

Polymeric systems with controlled permeability have potential applications in the fields of gas separation,¹⁰⁻¹³ barrier technology,¹⁴⁻¹⁷ and food packaging.^{18,19} For gas separation membranes, high permeabilities and high selectivities are desirable to reduce cost and obtain high-purity products. However, barrier materials used in fuel tanks, food packagings, carbonated beverage bottles etc. are typically designed to have low permeability to gases. Developing a fundamental understanding of gas adsorption and transport in cross-linked polymers is also essential for wire and cable applications.^{20,21} Such properties can be used to make predictions concerning the time needed for degassing of cross-linked polymers such as cross-linked polyethylene. For example, byproducts such as methane formed during the peroxide-induced cross-linking of polymers must be removed for safety issues related to its flammability. The transport (or Fickian) diffusivity is of critical importance in applications like degassing where

mass transfer effects play an important role. Moreover, atomistic simulations can be employed to examine the adsorption isotherms and transport properties of gases in polymers.^{22–33}

There have been extensive studies of solubility and diffusivity of small penetrant molecules in polymers.^{34–40} Most molecular simulations^{22–33} and experimental studies^{41–49} have focused on the solubilities and diffusivities of gases in non-cross-linked polyethylene. Typically, polyethylene structures used in the simulations of gas adsorption and transport are purely amorphous, whereas experimental data correspond to semicrystalline polyethylene materials at ambient conditions. This can lead to overestimations of the solubility and diffusion coefficients in simulations. However by combining molecular simulations and semiempirical models may explain the experimental data.^{24,31,50} It has been shown that, in general, gases diffuse by a hopping mechanism where penetrants explore localized voids in the polymer for a significant time and undergo fast jumps between the neighboring voids. However for cross-linked polyethylene, a comprehensive understanding of gas adsorption and diffusion, and swelling is lacking. Here, we perform molecular-level investigations of methane and carbon dioxide in the presence of cross-linked polyethylene with the goal of enhancing the very limited amount of related experimental data^{21,42,51,52} for such systems.

Our earlier studies have shown that Monte Carlo (MC) and molecular dynamics (MD) simulations are powerful tools to provide insight into the bulk and surface properties.^{53–57} In this paper, we use computer simulations to study the adsorption and diffusion properties of methane and CO₂ in cross-linked polyethylene in the temperature range 300 to 600 K. We employ grand canonical Monte Carlo (GCMC) simulation method to calculate the adsorption isotherms, and MD simulations allow us to assess the dynamic properties of the system. In GCMC simulations, a rigid framework is usually employed to reduce the simulation time by avoiding the necessity of computing solid-solid interactions.⁵⁷ However, here we employ a hybrid MC/MD approach³³ to incorporate the effects of framework flexibility and polymer swelling on the gas adsorption. Our results exhibit a nonmonotonic behavior of the gas adsorption as a function

of the cross-linking degree. A key aspect of our study is the insight into this behavior gained from the pore size analysis of the cross-linked polymer. The mobility of gases decreases with increasing cross-linking degree which can be understood by the fact that the waiting time for a gas molecule in a cavity before the jump increases with cross-linking.

2 Simulation details

We performed molecular simulations of adsorption and diffusion of methane and CO₂ in cross-linked polyethylene in the temperature range 300 to 600 K. We carried out GCMC and MD simulations using RASPA⁵⁸ and LAMMPS⁵⁹ packages, respectively. We employed GCMC simulation method to compute the adsorption isotherms of gases and MD simulation method to assess the dynamic properties of the system. The model system was composed of 60 flexible polyethylene chains, each having 80 carbon atoms on the backbone (Fig. 1). A periodic boundary condition was applied in all directions with a box size of 4.2–5.7 nm. The total potential energy is

$$E_{\text{Tot}} = E_{\text{LJ}} + E_{\text{Coul}} + E_{\text{Stretch}} + E_{\text{Bend}} + E_{\text{Dihedral}}. \quad (1)$$

Here, the nonbonded van der Waals interactions are described by⁶⁰

$$E_{\text{LJ}} = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (2)$$

where r_{ij} denotes the distance between the centers of i and j sites, and ε_{ij} and σ_{ij} represent the Lennard-Jones (LJ) parameters for energy and distance, respectively. Each LJ parameter for interactions between unlike atoms was obtained by use of the Lorentz-Berthelot combining rules: $\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$ and $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$. The nonbonded interactions between charged atoms are described by

$$E_{\text{Coul}} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}, \quad (3)$$

where q_i and q_j represent the partial charges of sites i and j , respectively, and ε_0 denotes the dielectric permittivity of vacuum. The long-range electrostatic interactions were

treated using the Ewald summation method (GCMC) or the particle-particle particle-mesh technique (MD) with a precision of 10^{-5} . The nonbond cutoff for interactions was 15.0 Å.

We used harmonic potentials for the bond stretch and angle bend terms:

$$E_{\text{Stretch}} = k_r(r_{ij} - r_0)^2, \quad (4)$$

and

$$E_{\text{Bend}} = k_\theta(\theta - \theta_0)^2, \quad (5)$$

where r_0 is the equilibrium bond length, θ is the bending angle, θ_0 is the equilibrium bending angle, and k_r and k_θ are the corresponding force constants. The motion of the dihedral angle ϕ is governed by a potential of the form

$$E_{\text{Dihedral}} = \sum_{n=1,4} A_n \cos^{n-1}(\phi), \quad (6)$$

where the appropriate constants A_n for the polymer are presented in Table 1.

The polymer was modeled by the transferable potentials for phase equilibria united-atom (TraPPE-UA) force field.⁶¹ In the TraPPE-UA formalism, all H atoms bonded to C atoms are modeled as a single interaction site, for instance, a methyl group is modeled by a single pseudo-atom, CH₃. In addition, the C-C bonds were assumed to be flexible here.⁶² The potential forms with the corresponding parameters are listed in Table 1. Methane (Table 2) is also represented by the TraPPE-UA force field.⁶¹ While, CO₂ molecules are taken with fixed C-O bond length (1.149 Å) and bending angle ($\theta_0 = 180^\circ$) using a rigid version of the EPM2 model suggested by Harris and Yung.⁶³

To obtain the gas adsorption isotherms, the hybrid MC/MD simulation was implemented as follows. First, GCMC simulations were performed assuming a rigid polymer matrix in the μVT ensemble, where μ represents the chemical potential of the sorbate. The chemical potentials of sorbate molecules are calculated from the NPT ensemble MC simulations, using the Widom insertion method.^{57,60} Each GCMC simulation consisted of at least 10^7 Monte Carlo steps. The whole system was allowed to swell at a

given pressure and temperature by carrying out MD simulations in the NPT ensemble for 1 ns. The equations of motion were integrated by the velocity Verlet scheme with a time step of 1 fs. A Nosé-Hoover thermostat (relaxation time of 0.1 ps) was used to control the temperature, and a Nosé-Hoover barostat (relaxation time of 1 ps) was used to control the pressure. Finally, this procedure was repeated 7-10 times, and final few cycles (see below) were considered to evaluate the adsorption isotherms. Six independent trajectories each of length, e.g., 10 cycles were considered to achieve good statistics.

To determine the self- and transport-diffusivities, the final configurations from the hybrid MC/MD simulations are used as the initial configurations in the MD simulations. This was followed by a 15 ns production run in the NVT ensemble. The self-diffusion coefficient D_s was evaluated at a specified concentration c by the Einstein relation:

$$D_s(c) = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle, \quad (7)$$

where $\langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle$ is the mean square displacement (MSD) of the particle and $\vec{r}(t)$ is the position of the particle at time t . The transport diffusivity can be estimated as $D_t(c) = D_0(c)(\partial \ln f / \partial \ln c)_T$.⁶⁴ Here, f represents the fugacity of the bulk phase which is in equilibrium with the adsorbed phase at concentration c , and $D_0(c)$ denotes the corrected diffusivity which can be obtained from the MSD of the center of mass of the adsorbed molecules.⁶⁴

The solubility constant, S , of the the gases in the polymer was calculated from the limiting slopes of the adsorption isotherms using the following equation:

$$S = \lim_{P \rightarrow 0} \frac{c}{P}, \quad (8)$$

where P is the pressure.

As in the previous studies,²²⁻³³ amorphous polyethylene samples are used in all our simulations. Initial structures were constructed using Packmol.⁶⁵ To make sure that the computer simulations generate equilibrium results we begin from random and straight initial conformations, and it is necessary that with appropriate relaxation they

both yield identical averages. Typically, the system was brought rapidly (1 ns MD) to the required condition from a molten state. In the cross-linking procedure,^{66,67} atomic pairs in the polymer melt with an interatomic distance within about 4 Å were randomly selected and linked before further annealing. The new bonds were randomly created using the "fix bond/create" command in LAMMPS. Once the new cross-link is formed, the type of the bonded carbon atoms are changed and the interactions related to those atoms are created simultaneously (see Table 1). In our simulations, cross-links formed by combinations of tertiary carbon atoms were excluded, and this may be attributed to the steric effects. To examine if the choice of cutoff distance created artificially stressed models, bond length distributions were calculated to check if overstretched bonds were formed (see below). The cross-linking degree of the polymer network can be estimated from the ratio of the number of cross-linked units to the total number of monomer units.

3 Results and discussion

3.1 Influence of cross-linking on polyethylene

Both the gas adsorption and diffusion are sensitive to the structure of the polymer matrix. Figure S1 shows the specific volume of polyethylene as a function of temperature for the range 300 to 600 K at 1 atm. Our simulation data are in good agreement with previous simulation results.^{29,31} We can see that the specific volume of the polymer increases linearly with increasing temperature, but with a slope change at about 450 K (the melting point of polyethylene). The simulation results are also in good agreement with experimental data⁶⁸ above the melting temperature. The difference at ambient conditions is due to the fact that polyethylene structures in simulations are purely amorphous, whereas experimental results⁴¹ correspond to semicrystalline polyethylene materials. Figure S2 shows the time evolution of the specific volume of polyethylene as obtained from the *NPT* MD simulations after annealing. The results

show some characteristic of polymer crystallization and this is evident from, e.g., the poor convergence of the specific volume especially at low temperature. However, the homogeneous nucleation of the crystal phase can be observed only after a very long simulation time.⁶⁹ Furthermore, Figure S3 shows the pore volume, the pore limiting diameter, and the maximum pore diameter in the polyethylene system as a function of temperature at 1 atm. The pore volumes (helium as the probe molecule) and pore sizes considered in this study were obtained using the Poreblazer 3.0.2 package.⁷⁰ The pore limiting diameter is defined such that molecules in the porous material that are smaller than the pore limiting diameter will be able to diffuse in a continuous pathway. Thus, the pore network is accessible to a spherical probe if for this probe a continuous pathway can be formed from one face of the simulation box to the opposite face without overlapping with the framework atoms. While, the maximum pore diameter identifies the largest cavity present in the polymer network. The void fraction increases linearly with increasing temperature, but with a slope change at about 450 K. The void fraction of polyethylene at 600 K is about 6 times higher than that at 300 K. Overall, the pore limiting diameter is in the range 1 – 3 Å. Comparing these values to the dimensions of the adsorbates (see Table 2), 3.73 Å for methane and 3.03 Å (5.33 Å in long axis) for CO₂, indicates that the pore network is not fully accessible to these gases.

The cross-linking process affects the structure and properties of polyethylene. For instance, Figure S4 shows the bond length, bond angle, and dihedral angle distributions for cross-linked polyethylene (cross-linking degree of 20%) at 300 K and 1 atm. The probability distributions of bond lengths, bond angles, and dihedral angles were similar to the corresponding ideal ones ($\sim \exp(-E/kT)$). In the absence of a cross-link, the simulated probability of the polymer to be in the trans state is about four times higher than that in the gauche state. However, for instance, the preference decreases for the trans state in the presence of cross-linked units.

For a completely random cross-linking, bond formations can be regarded as statistically independent events. Therefore, the probability distribution of the number of cross-linked units per chain should be a Gaussian centered around the average num-

ber of cross-linked units per chain. It has been shown that although the monomer units are strongly correlated due to the chain connectivity, the system approaches this distribution independent of the model details.⁶⁶ Figure S5 displays the distribution of the cross-linked units for polyethylene at 300 K and 1 atm for different values of cross-linking degree. As the number of cross-linked bonds introduced into the system increases, the results peak around the average number of cross-linked units per chain.

Monomer units are linked together irrespective of whether they belong to the same chain or not for a random cross-linking, as in irradiation processes. Note that the intra-molecular cross-links are usually regarded as inactive for elasticity. However, these cross-links may form loops which contribute to the elasticity by trapping entanglements (may not be relevant for relatively short chains used here). Figure S6 shows the number of intra- and inter-molecular cross-links as a function of cross-linking degree in the temperature range 300 to 600 K at 1 atm. The number of such cross-links are mostly independent of temperature. Since every site along the chain is a potential cross-linking site,⁶⁶ the number of intra- and inter-molecular cross-links are about equal in all cases.

Fig. 2a shows the specific volume of polyethylene as a function of cross-linking degree at 300 K and 1 atm. Our simulation data are in good agreement with previous simulation results.⁶⁷ We see that the specific volume of polyethylene decreases with increasing cross-linking degree. However, experiments^{71,72} have shown that the specific volume of polyethylene usually increases with cross-linking degree. This can be understood by the reduced crystallinity in the experimental system and hence the increase in the free volume due to the cross-linking process. Nevertheless, the corrected^{24,41} experimental solubility and diffusion data may be compared with those of a hypothetical completely amorphous polyethylene as obtained from the simulations (see below). Furthermore, Fig. 2b shows the specific volume of the cross-linked polyethylene as a function of temperature for the range 300 to 600 K at 1 atm. The volume curves become less steep with increasing cross-linking degree. It seems that the transition temperature of the cross-linked polyethylene increases with cross-linking degree. This may be described by an equation similar to that used for the dependence of the glass

transition temperature on the cross-linking degree.⁷³ Therefore, the transition temperature $T_m = T_m^0/(1 - KX)$ (dashed line in Fig. 2b), where T_m^0 is the transition temperature of the uncross-linked polymer, K is a constant, and X is the cross-linking degree. K is about 0.09 in our case. Whereas, experiments^{71,72} show the opposite behavior which may be attributed to the reduced crystallinity of the system due to the cross-linking process. Our simulations underestimate experimental specific volumes at higher cross-linking degrees. This may be due to the fact that, in the experiments, it is generally impossible to reach such high cross-linking degrees considered in this study. For example, the molecular weight between cross-links is about 660.76 g/mol (≈ 47 -CH₂- units) with 2.5% peroxide content.⁷² Therefore, the cross-linking degree is $(2/47) \times 100 \approx 4.2\%$ with the assumption of a cross-link at each end of this 47-unit chain segment. Note that the specific volume of the cross-linked polyethylene decreases with increasing chain length (see Fig. 2a).

Fig. 3 shows the void fraction in the cross-linked polyethylene as a function of cross-linking degree in the temperature range 300 to 600 K at 1 atm. Our results show that the void fraction decreases with increasing cross-linking degree at high temperatures. However, the void fraction demonstrates a nonmonotonic variation with the cross-linking degree at low temperatures. Similar behavior is observed for both the pore limiting diameter and the maximum pore diameter in the cross-linked polyethylene system (Figure S7). The range of the pore limiting diameter decreases with increasing cross-linking degree indicating that the cross-linked network is relatively less accessible to gases. Note that the influence of pressure on the structure of cross-linked polyethylene is negligible in all studied cases ($P \leq 15$ atm). Overall, our results show that the structure and pore size of the cross-linked polyethylene below and above the melting temperature are very sensitive to the cross-linking degree.

3.2 Adsorption of methane and CO₂ in cross-linked polyethylene

Hybrid MC/MD simulations were carried out to compute adsorption isotherms for methane and CO₂ in cross-linked polyethylene. The influence of framework flexibility and polymer swelling on the adsorption isotherm may be significant, with equilibrium being reached in about 6 cycles, as shown in Figure S8. Notably, our results show that the extent of swelling is negligible for cross-linked polyethylene at the studied conditions (Figures S9-S10). Also, previous simulations^{30,32} and experimental observations^{46,49} have shown that the swelling of such polymer during the sorption process is important only at high pressures. The computed isotherms in the temperature range 300 to 600 K are shown in Figs. 4 and S11-S12 as symbols. These figures also show best fits (lines) to the simulated isotherms. The adsorption isotherms were fitted using the dual-mode sorption model:^{25,74}

$$c = \frac{k_1 \times P}{k_2 + P} + k_3 \times P. \quad (9)$$

The first term is described by a Langmuir isotherm, where k_1 is the saturation concentration of the gas, and $1/k_2$ is the affinity constant. The second term corresponds to Henry's law with Henry's constant k_3 . Thus the dual-mode sorption model assumes two distinct mechanisms of sorption, ordinary dissolution described by Henry's law and trapping in holes or microvoids described by Langmuir adsorption. The microvoids are consequences of the slow relaxation processes of the polymer chains. The two sorbed populations may execute diffusive movements with different mobilities. This model predicts that a plot of c versus P consists of low-pressure and high-pressure linear regions connected by a nonlinear region. As expected, the adsorption capacities of methane and CO₂ decrease with increasing temperature. Our results also show that the adsorption capacities of gases decrease with increasing cross-linking degree at high temperatures. However, the adsorption capacities demonstrate a nonmonotonic variation with the cross-linking degree at low temperatures. A similar behavior was obtained for the void fraction and pore diameters, as shown above (see Figs. 3 and S7). Thus,

it can be inferred that such properties plays an important role in adsorption.

In the zero-pressure limit, the concentration of the gas in polymer can be obtained from eq. (9) as

$$c = \left(\frac{k_1}{k_2} + k_3 \right) \times P = S \times P, \quad (10)$$

where S is the solubility constant. The solubility constants were evaluated from the limiting slopes of the adsorption isotherms (see, e.g., eq. (8) and Fig. 4). As seen in Fig. 5, the simulated solubility constants for gas molecules in polyethylene are in qualitative agreement with experiments.^{41–45,47} The differences are possibly due to the effects of molecular weight, polydispersity, and branching. Note that, below the melting point we have corrected the experimental solubility $S_{\text{exp}} = \alpha S_{\text{cor}}$,⁴¹ where S_{cor} is the solubility constant in a hypothetical completely amorphous polyethylene and α denotes the volume fraction of the amorphous part. Furthermore, our results are in good agreement with previous simulation studies.²⁹ The solubility constant for a gas in the amorphous polyethylene decreases with increasing temperature and has a non-Arrhenius behavior. To emphasize the slope change, linear fits of the low- and high-temperature regions are included in Fig. 5. As in the case of adsorption, the solubility constant decreases with increasing cross-linking degree at high temperatures and has a nonmonotonic variation with the cross-linking degree at low temperatures (Fig. 6). The heat of solution ΔH_S based on the van't Hoff expression ($S \sim \exp(-\Delta H_S/RT)$) for methane and CO₂ in polyethylene are about -3.5 and -10.4 kJ/mol, respectively. The heat of solution for methane and CO₂ in the cross-linked polyethylene are about -16.6 and -23.4 kJ/mol, respectively (cross-linking degree of 80%). Experimental studies of cross-linked polyethylene in the presence of methane have shown an increase in the solubility of methane as a function of the irradiation dose at low temperatures.⁴² Other studies have reported a decrease in methane solubility with increasing dose.⁵¹ Care must be taken in analyzing solubility data due to the presence of scission products or impurities in experimental samples, which can be expected to affect the gas solubility. Any change in crystallinity due to the cross-linking process could also affect

the solubility values.

3.3 Diffusion of methane and CO₂ in cross-linked polyethylene

MD simulations in the NVT ensemble were performed to calculate diffusion coefficients of methane and carbon dioxide in cross-linked polyethylene. Figure S13 shows the displacement of gas from its initial position in the cross-linked polyethylene at 300 and 600 K. We see that gases diffuse by a hopping mechanism where penetrants explore voids in the polymer for a significant time and undergo fast jumps between the neighboring voids. The waiting time for a gas molecule in a cavity before the jump increases with decreasing temperature and increasing cross-linking degree. Note that the local motion of the chains has significant influence on gas diffusion.^{75,76} Furthermore, we plot in Fig. 7 the average MSDs of methane and CO₂ molecules as a function of time on a log-log scale. Three regimes (ballistic, subdiffusive, and Fickian diffusive) are observed. The ballistic regime at short times is followed by the subdiffusive regime and finally the Fickian regime. Notably, the motion of gases at relatively short time scales is subdiffusive as it is coupled to the segmental dynamics of polymers.^{75,76} It is evident from Fig. 7 that this regime increases with decreasing temperature and increasing cross-linking degree.

The self-diffusion coefficients were estimated from the linear slope of the MSD vs time plots (see eq. (7)). Fig. 8 shows the self-diffusion coefficients of methane and CO₂ molecules in polyethylene in the temperature range 300 to 600 K at 1 atm. As seen in Fig. 8, the simulated self-diffusion coefficients are in qualitative agreement with experiments.^{41,43,44,47,48} Note that, below the melting point we have corrected the experimental diffusion coefficient $D_{\text{exp}} = (2/3)\alpha D_{\text{cor}}$,²⁴ where D_{cor} denotes the gas diffusion coefficient in a hypothetical completely amorphous polyethylene. Furthermore, our results are in good agreement with previous simulation studies.^{24,29} It can be seen that the simulated diffusion coefficient decreases with increasing chain length. Gas mobility in the amorphous polyethylene increases with temperature and has an Arrhenius-like behavior. The activation energies for methane and CO₂ in polyethylene

are about 17.5 and 15.0 kJ/mol, respectively.

Diffusion of methane and CO₂ in the cross-linked polymer increases with increasing temperature, as shown in Fig. 9. The gas mobility decreases with increasing cross-linking degree, qualitatively consistent with experiments.^{42,51,52} These can be explained by the fact that the waiting time for a gas molecule in a cavity before the jump increases with decreasing temperature and increasing cross-linking degree. We see that, in general, the activation energy for diffusion decreases with increasing cross-linking degree. For example, the activation energies for methane and CO₂ in the cross-linked polyethylene are about 5.5 and 2.5 kJ/mol, respectively (cross-linking degree of 80%). This is probably because the pore sizes decrease with increasing cross-linking degree especially at high temperatures (see Figs. 3 and S7). The transport diffusivity was also estimated using the corrected diffusivity and the adsorption isotherms ($D_t(c) = D_0(c)(\partial \ln f / \partial \ln c)_T$).⁶⁴ The self, corrected, and transport diffusivities are similar in all cases (see, e.g., Figure S14). Note that the influence of pressure on the self, corrected, and transport diffusivities was found to be negligible in all studied cases.

4 Conclusions

We have studied the adsorption and diffusion properties of methane and CO₂ in cross-linked polyethylene in the temperature range 300 to 600 K. We employed GCMC simulation method to calculate the adsorption isotherms, and MD simulations allowed us to assess the dynamic properties of the system. Note that a hybrid MC/MD approach was used to incorporate the effect of framework flexibility and polymer swelling on the gas adsorption. Interestingly, a nonmonotonic behavior for the gas adsorption amount as a function of the cross-linking degree was observed in our simulations (see, e.g., Fig. 4). A key aspect of our study is the insight into this behavior gained from the pore size analysis of the cross-linked polymer. A similar behavior was observed in cases of the void fraction and the pore diameters (see, e.g., Fig. 3). This displays a direct correlation between the adsorption amounts and the pore characteristics of the

cross-linked polymer network.

Diffusion of methane and CO₂ in the polymer system increases with increasing temperature and decreases with increasing cross-linking degree, in agreement with experiments. An important finding is that the activation barrier for diffusion of methane and CO₂ generally decreases with increasing cross-linking degree. This is probably because the pore sizes decrease with increasing cross-linking degree and is supported by the analysis of the pore size distribution curves (see, e.g., Fig. 3). The insights from this study are expected to provide knowledge that may eventually be applied to processes such as degassing and understand gas adsorption and diffusion in, e.g., immature kerogen. Further studies are needed to understand the gas adsorption and diffusion properties at high pressures, where the swelling of the polymer is more pronounced.³⁰

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Supporting Information

Additional details of simulation analysis are provided in the Supporting Information.

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Table 1: Potential forms and parameters of the cross-linked polyethylene.^{61,62}

Potential form	Type	Parameters
Non-bonded LJ:		ϵ_{ii} (kcal/mol) σ_{ii} (Å)
$E_{\text{LJ}} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$	CH ₃	0.195 3.75
	CH ₂	0.0914 3.95
	CH	0.0199 4.68
Harmonic bond:		k_b (kcal/mol/Å ²) l_0 (Å)
$E_{\text{Stretch}} = k_b(l - l_0)^2$	CH _x -CH _y ($x, y = 1, 2, 3$)	449.57 1.54
Harmonic bend angle:		k_θ (kcal/mol/rad ²) θ_0 (deg)
$E_{\text{Bend}} = k_\theta(\theta - \theta_0)^2$	CH _x -CH ₂ -CH _y	62.100 114
	CH _x -CH-CH _y	62.100 112
Dihedral angle:		A_1 (kcal/mol) A_2 A_3 A_4
$E_{\text{Dihedral}} = \sum_{n=1,4} A_n \cos^{n-1}(\phi)$ ($\phi = 180^\circ$ at trans)	CH _x -CH ₂ -CH ₂ -CH _y	1.967 -4.052 0.271 6.290
	CH _x -CH ₂ -CH-CH _y	0.785 -1.779 0.445 3.508
	CH _x -CH-CH-CH _y	0.785 -1.779 0.445 3.508

Table 2: Charges q and LJ parameters ϵ and σ of methane and carbon dioxide.^{61,63}

Molecule	Atom	ϵ_{ii} (kcal/mol)	σ_{ii} ($\text{\AA}$)	q (e)
Methane	CH ₄ (single – site)	0.2941	3.73	0.0
Carbon dioxide	CO ₂ -C	0.0559	2.76	0.6512
	CO ₂ -O	0.1600	3.03	-0.3256

Figure 1: Equilibrium snapshots of cross-linked polyethylene in the presence of (a) methane and (b) CO_2 at 300 K and 15 atm. The cross-linking degree is 40%. Color code: CH_4 : Tan; CH_3 : Cyan; CH_2 : Blue; CH : Red; C: Yellow; O: Green.

Figure 2: (a) The specific volume of polyethylene as a function of the cross-linking degree at 300 K and 1 atm. (b) The specific volume of the cross-linked polyethylene as a function of the temperature at 1 atm. Solid lines are a guide to the eye. The dashed line represents the transition temperature $T_m = T_m^0 / (1 - KX)$, where T_m^0 is the transition temperature of the uncross-linked polymer, X is the cross-linking degree, and the value of the constant K is about 0.09.

Figure 3: The void fraction in the cross-linked polyethylene system as a function of cross-linking degree at 1 atm. The lines are a guide to the eye.

Figure 4: Adsorption isotherms as computed from simulations (symbols) of methane (left panels) and CO₂ (right panels) in the cross-linked polyethylene system at 300 K (top panels) and 600 K (bottom panels). The lines are fitting results to the simulation data.

Figure 5: Temperature dependence of the solubility constants for gas molecules in polyethylene. Solid lines are a guide to the eye.

Figure 6: Temperature dependence of the solubility constant of (a) methane and (b) CO₂ in cross-linked polyethylene. The lines are a guide to the eye.

Figure 7: Log-log plot of the MSDs of methane (left panels) and CO₂ (right panels) as a function of time in the uncross-linked (top panels) and 40% cross-linked polyethylene (bottom panels) systems at 1 atm.

Figure 8: Temperature dependence of the self-diffusion coefficient of (a) methane and (b) CO_2 in the polyethylene system at 1 atm. The lines are a guide to the eye.

Figure 9: Temperature dependence of the self-diffusion coefficient of (a) methane and (b) CO_2 in cross-linked polyethylene at 1 atm. The lines are a guide to the eye.

TOC Graphic