Selectivity trend of gas separation through nanoporous graphene

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Abstract

By means of molecular dynamics (MD) simulations, we demonstrate that porous graphene can efficiently separate gases according to their molecular sizes. The flux sequence from the classical MD simulation is $H_2 > CO_2 \gg N_2 > Ar > CH_4$, which generally follows the trend in the kinetic diameters. This trend is also confirmed from the fluxes based on the computed free energy barriers for gas permeation using the umbrella sampling method and kinetic theory of gases. Both brute-force MD simulations and free-energy calculations lead to the flux trend consistent with experiments. Case studies of two compositions of CO_2/N_2 mixtures further demonstrate the separation capability of nanoporous graphene.

Keywords: gas separation, carbon reduction, porous graphene membrane, 2D materials, molecular dynamics, free energy calculation.

1. Introduction

Gas separation, specifically carbon dioxide removal, plays a key role in various industrial processes. For instance, excess CO_2 have to be removed to meet pipeline and heating value specifications in the natural gas sweetening. Industrial hydrogen production from syngas requires CO_2 separated out in order to produce highly purified hydrogen. Also, CO_2 capture from flue gas (mainly N_2/CO_2 mixture) is one of the most challenging environmental issues to tackle the global climate change and to curb the carbon footprint of electricity generated by coal-fired power plants [1]. Among diverse techniques for gas separation, membrane technology poses a great advantage for CO_2 separation and capture due to its intrinsic energy efficiency and simplicity [2, 3]. Yet, a membrane's performance is usually bound by a tradeoff between permeability and selectivity [4]: membranes with high permeability have low selectivity, and vice versa; researchers continue to explore novel membrane materials, aiming to overcome the Robeson upper bound [5, 6].

In 2009, Jiang *et al.* proposed the idea of porous graphene as a one-atom-thick membrane for gas separations [7]. Following this computational proof-of-concept, porous graphene and other two-dimensional (2D) materials such as planar carbon allotrope with sp and sp^2 hybridized carbons and synthesized polyphenylene have been explored for various gas separations [8-18]. It has been shown that helium isotope separation can be achieved through the nanoporous graphene [9, 13, 14]. Graphdiyne can be a competitive membrane for hydrogen purification [19-21]. More excitingly, Koenig *et al.* have experimentally demonstrated the gas-separating power of a porous graphene by purposefully creating sub-nanometer pores on a graphene sheet and observing different leak rates for various gases [22]. They observed an interesting selective trend, following the order of the leak rate: $\text{H}_2 > \text{CO}_2 > \text{Ar} > \text{N}_2 > \text{CH}_4$. In a more recent work, Li

et al. demonstrated hydrogen separation through the selective structural defects within the 1.8-nm-thick graphene oxide (GO) membrane, which is prepared by a facile filtration process [23]. In contrast, Kim and coworkers presented selective gas separation through few-layered GO membrane by the interlayer spacing between the stacking GO structures [24].

To better understand the gas-selectivity trend in the recent experiment of Koenig *et al.* [22] and to provide a proper estimate on selectivity, herein we applied molecular simulation method to investigate the separation capacity of porous graphene for various molecular gases (H_2 , CO_2 , Ar, N_2 , and CH_4). First, we performed the classical MD simulations to determine flux and to compare with experiments. Second, we calculated the free energy profile of gas permeation to estimate the ideal selectivity. Third, we carried out case studies for the CO_2/N_2 mixtures.

2. Model and Method

We set up a sandwich-like system to simulate gas separation through porous graphene as illustrated in Fig. 1a. The dimension of nanoporous graphene is $100 \text{ \AA} \times 100 \text{ \AA}$ and the nanopore density is $0.0004 \text{ \AA}^{-2}$. The nitrogen functionalized nanopore denoted as 4N4H has a dimension of $3.0 \text{ \AA} \times 3.8 \text{ \AA}$ (Fig. 1b). The porous graphene preparation details and force field parameters can be found elsewhere [25]. All-atom models are used for gas molecules. Three-site H_2 model [26] was adopted to reproduce the quadrupole moment of H_2 of $0.651 \text{ D \AA}$ and the H-H bond length is $0.7414 \text{ \AA}$. Three-site model with three partial charges was applied for CO_2 with a quadrupole moment of $3.794 \text{ D \AA}$ [27]. The distance between C and O atoms is $1.149 \text{ \AA}$. A recent Ar model was utilized [28]. Three-charge-site N_2 model was taken with the N-N bond length of $1.098 \text{ \AA}$ with a quadrupole moment of $1.44 \text{ D \AA}$ [29]. CH_4 is a regular tetrahedron conformation with

carbon atom locating on its center of mass [30]. The C-H bond length is 1.09 Å and the H-C-H angle is 109.3°. The force field parameters of gas molecules are tabulated in Table 1. All cross terms are evaluated by the Lorentz-Berthelot mixing rule.

Fig. 1. Schematic illustration of the system setup: (a) the sandwich-like, bi-chamber system to simulate gas permeation; (b) the 4N4H pore structure (carbon, cyan; hydrogen, grey; nitrogen, blue) has dimensions of roughly $3.0 \text{ Å} \times 3.8 \text{ Å}$ [7].

The molecular dynamics (MD) simulations were performed using the LAMMPS package [31] in the canonical (NVT) ensemble with two-dimensional periodic boundary conditions in x - y directions. The framework was frozen during the simulation. Numbers of gas molecules were initially placed on the upper chamber with a height of 100 Å to achieve various feed pressures. The gas pressure was computed using the ideal gas law. During the simulation, the number of permeate molecules was monitored. The Nose-Hoover thermostat was applied to keep the fluid

temperature fixed at 300 K. Free energy profiles for gas permeation through the nanopores were calculated through the umbrella sampling as implemented in the PLUMED tool [32]. Once free energy barrier is known, one can use the kinetic theory of gases to estimate the permeate flux and selectivity [33].

Table 1. Partial charges and Lennard-Jones parameters of gas molecules.

atom	q (e)	σ (Å)	ϵ/k_B (K)
H/H ₂	0.4932	0	0
COM/H ₂	-0.9864	3.038	34.32
C/CO ₂	0.6512	2.757	28.129
O/CO ₂	-0.3256	3.033	80.507
Ar	0	3.345	125.7
N/N ₂	-0.4048	3.318	36.4
COM/N ₂	0.8096	0	0
C/CH ₄	-0.24	3.5	33.23
H/CH ₄	0.06	2.5	15.1

3. Results and Discussion

The classical MD simulations can monitor the number evolution of permeated gas molecules, thereby directly obtaining the gas flux and permeance. The number profile of permeate CO₂ through nanoporous graphene at 82 atm is presented in the inset of Fig. 2; the linear regression gives an estimate of the flux. The purpose of this 82-atm brute-force MD

simulation was to accelerate the passing events (higher pressure means higher driving force) so we could obtain a quick idea of the gas selectivity trend in terms of which gases can pass and which cannot within the simulation timeframe (~ 10 ns). As shown in Fig. 2, H_2 and CO_2 can readily permeate through the nanopores, while Ar, N_2 and CH_4 hardly pass through. H_2 and CO_2 have a much larger flux compared with other gases. The flux with the unit of molecules ns^{-1} is 46 for H_2 , 28 for CO_2 , 0.2 for Ar, 0.4 for N_2 and 0 for CH_4 . The sequence of flux is that $H_2 > CO_2 \gg N_2 > Ar > CH_4$, generally in accord with the trend in kinetic diameters and the experimental findings of Koenig *et al.* [22]. The similar molecular sieving behavior of experimental and simulated porous graphene over various gases indicates the similarity in pore size. Indeed, the experimental pore size is around 3.4 Å and our 4N4H nanopore is about that size.

Fig. 2. Gas flux through the nanoporous graphene at 82 atm with the 4N4H pore which has a dimension of 3.0 Å by 3.8 Å. Inset shows the number profile of permeate CO_2 .

Since the comparison between simulated and experimental fluxes has been discussed before [33], here we focus our discussion on the selectivity of different gas pairs. There are two ways to obtain the selectivity: (a) from the MD trajectory such as shown in Fig. 2; (b) from the free-energy barrier. The first method only applies to the gases for which we can observe enough passing-through events within the simulation conditions and time frame (typically, tens of nanoseconds). Otherwise, we have to rely on the second method. Free energy is more relevant to properly describe the gas permeation through nanopores, especially at ambient conditions, where the activated process with a high barrier under limited driving forces can hardly harvest enough statistics over an accessible time period. As shown in Fig. 2, we could not obtain sufficiently high permeation rates for N_2 , Ar, and CH_4 even at 82 atm, indicating that their permeation is a rare event.

We calculated the free energy profile of permeation through porous graphene at 2 atm using the umbrella sampling method. We chose 2 atm here because that is the feed pressure which Koenig et al. used in their gas-permeation experiment [22]. Free energy profiles for a series of gases are presented in Fig. 3. The sequence of energy barrier is $CH_4 > Ar > N_2 > H_2 > CO_2$, which is generally consistent with what we have seen in the classical MD trajectories (Fig. 2), i.e., the higher the barrier, the lower the flux. Except carbon dioxide, all other gases experience the energy barrier at nanopores with $z = 0$. The binding of CO_2 with the nanopore's negatively charged rim N atoms is energetically favorable, CO_2 molecules perpendicularly pass through the 4N4H nanopores of porous graphene [33], and similar phenomenon was also observed in the DFT calculations [7] and in windowed carbon nanotubes [25]. The energy barrier for CO_2 locates at $z = 1.3 \text{ \AA}$ is due to the reorientation of the CO_2 molecule from parallel to perpendicular to the pore as the CO_2 enters the pore [33].

Fig. 3. Free energy profile of permeation as a function of the distance between the center-of-mass of a gas and the pore center along the z direction. The corresponding free energy barrier in unit of kcal/mol is given for each gas.

From the free energy barriers, we calculated the fluxes of the gases with aid of the kinetic theory of gases [33], and then obtained the gas-pair selectivity as a ratio of their fluxes. The predicted selectivities of H_2/CO_2 , CO_2/Ar , CO_2/N_2 , and CO_2/CH_4 are compared with the experiment (Table 2). Our computed H_2/CO_2 selectivity agrees with the experiment excellently; here we note that although Fig. 3 shows that H_2 has a higher free-energy barrier of permeation than CO_2 , H_2 flux from the kinetic theory of gases is in fact higher than CO_2 flux, due to H_2 's much lighter mass and hence larger collision rate. The H_2/CO_2 selectivity from the free-energy barriers and the kinetic theory of gases (Table 2) also agrees with that from the brute-force MD simulation ($S_{\text{H}_2/\text{CO}_2}=1.64$, Fig. 2). Table 2 also shows that the agreement between our predicted and the experimentally measured CO_2/Ar and CO_2/N_2 selectivities is within about one order of

magnitude. However, our simulation predicts a much higher selectivity for CO₂/CH₄ than the experiment. Note that the experimental leak rates for Ar, N₂, and CH₄ have a large uncertainty because they are comparable to or smaller than the intrinsic leak rate of the apparatus, thus the CO₂/Ar, CO₂/N₂, and CO₂/CH₄ selectivities experimentally estimated based on these rates are just roughly approximate. In addition, both pore geometry and functionality in the present study could be quite different from those created in the experiment, so one should view the comparison between the present simulation and the previous experiment [22] as a qualitative guide in terms of the selectivity trend.

Table 2. Comparison of ideal gas selectivity between simulation (from free-energy barriers and kinetic theory of gases [33]) and experiment [22] at 2 atm.

	H ₂ /CO ₂	CO ₂ /Ar	CO ₂ /N ₂	CO ₂ /CH ₄
Simulation	1.6	1400	230	6.6×10 ⁷
Experiment ^a	1.7	500	7000	9000

^a The experimental porous graphene “Bi-3.4Å” was chosen for comparison. Experimental leak rates of Ar, N₂, and CH₄ have a large uncertainty.

Fig. 2, Fig. 3, and Table 2 all suggests that the 4N4H pore with its dimensions of 3.0 Å by 3.8 Å (Fig. 1b) can distinguish the five gases (H₂, CO₂, Ar, N₂, and CH₄) into two groups by their sizes: facile permeation, H₂ and CO₂; difficult permeation, Ar, N₂, and CH₄. To further clarify the pore functionality effect (especially the negatively charged N atoms) on H₂ and CO₂ permeation, we artificially set the 4N4H pores to be neutral by adjusting the charges of all rims atoms to be zero so that the pore size is the dominating factor. The free energy profiles for H₂

and CO₂ between the original porous graphene and neutralized one are compared in Fig. 4; the estimated fluxes from the kinetic theory of gases are listed in Table 3. One can see that in the hypothetical case where the role of functionalization is minimal, the free-energy barrier increases by 0.7 kcal/mol to 3.0 kcal/mol and the permeation rate decreases by 65% for CO₂. For H₂, the free-energy barrier increases by only 0.2 kcal/mol to 3.2 kcal/mol and the permeation rate decreases by 28%. In other words, functionalization (namely, negatively charged N atoms around the pore rim) helps increase CO₂ permeation much more than it does H₂.

Fig. 4. Free-energy profiles of H₂ and CO₂ permeation at 2 atm: (i) with normal, charged pore rim atoms (solid lines) and (ii) with atomic charges on the pore rim turned off (dashed lines).

Table 3. Effect of nanopore functionality on gas permeation barrier (ΔG) and estimated flux of H_2 and CO_2 .

		H_2	CO_2
Charged rim atoms	ΔG (kcal mol ⁻¹)	3.0	2.3
	Flux (ns ⁻¹)	0.18	0.11
Neutral rim atoms	ΔG (kcal mol ⁻¹)	3.2	3.0
	Flux (ns ⁻¹)	0.13	0.038

The high flux and high selectivity towards CO_2 of the 4N4H pore examined here indicate that this porous graphene is highly promising for CO_2 removal. However, both previous studies [33] and Figs. 2 and 3 have focused on the pure gases, not the more realistic gas mixtures. Thus, we further evaluated the performance of porous graphene to separate CO_2 from CO_2/N_2 mixtures at 300 K. Here we chose 300 K because that is the temperature at which the majority of experiments and simulations of CO_2/N_2 separation are done. In the simulations, we used an initial feed pressure of 27 atm to facilitate permeation, and guarantee adequate sampling to characterize the separation process in a reasonable timeframe. But we expect that the same trend would hold at the atmospheric pressures by extrapolation, as demonstrated in previous work for hydrogen and carbon dioxide [33, 34]. Two compositions were investigated: equimolar (50:50 $CO_2:N_2$) and simulated flue gas (16:84 $CO_2:N_2$). Number of permeate molecules as a function of time is presented in Fig. 5. Preferential permeation of CO_2 over N_2 is evident; none of N_2 passing-through events was observed for the simulated mixtures over a time period of 10 ns.

Fig. 5. Separation of the CO₂/N₂ mixtures through porous graphene. No N₂ permeation was observed during the 10-ns period. The CO₂ flux determined by the linear regression is given.

Next we compared CO₂ flux in the mixture with CO₂ flux in the pure gas under the same CO₂ partial pressure. In the CO₂/N₂ mixtures, the CO₂ flux is 2.0 molecules ns⁻¹ at $p_{\text{CO}_2} = 4.3$ atm (CO₂:N₂=16:84) and 7.0 molecules ns⁻¹ at $p_{\text{CO}_2} = 13.5$ atm (CO₂:N₂=50:50). The CO₂ flux in the pure gas (obtained through interpolation) is at 1.9 and 6.9 molecules ns⁻¹ at 4.3 and 13.5 atm, respectively [33]. Therefore, within the uncertainty, the CO₂ flux is the same in the gas mixture and in the pure gas. This is a characteristic of the gas-phase pathway, in which the permeation rate of one species is only dependent on its own partial pressure [35]. The gas-phase pathway usually dominates the permeation through smaller pores under 1 nm, which is the case for our nanopores of 3.0×3.8 Å. In addition, we expect that ideal selectivity from the pure gas calculations should provide a reliable estimate on selectivity of the mixtures. Although the adsorbed phase pathway might play an insignificant role here, especially under lower pressures, we did observe the selective adsorption of CO₂ over N₂ at the surface of the porous graphene.

The preferred adsorption of CO₂ over N₂ can be clearly seen in the probability density of CO₂ and N₂ of the mixture above the porous graphene (Fig. 6). Such a preferential adsorption of CO₂/N₂ on nitrogen functionalized porous graphene was also computationally observed in a recent study [36]. Of note here is that we simulated two compositions of CO₂/N₂ mixtures at 300 K. To simulate the real flue gas, one has to consider other important factors such as higher temperature and the water vapor. We are currently examining these effects for a future publication.

Fig. 6. Probability density functions of the N₂/CO₂ mixture near porous graphene. Porous graphene locates at $z = 0$.

From the first computational proof-of-concept [7] to the recent experimental breakthroughs [22-24], porous graphene for gas separation has now become a reality. In this work, we have combined the classical MD simulations and free energy calculations to understand the selectivity trend. This approach provides not only the correct flux trend for various gases, but also reliable estimates on selectivity. Both permeability and selectivity are

crucial to materialize these novel materials for the practical separation application in the foreseeable future. Armed with modern computational tools, we can further optimize the permeability and selectivity, by varying pore size and functionality, to expedite the development of planar porous materials.

4. Conclusions

In summary, we have demonstrated from molecular dynamics simulations that a graphene membrane with a nitrogen-functionalized nanopore can separate gases with a flux sequence of $H_2 > CO_2 \gg N_2 > Ar > CH_4$, which generally follows the trend in kinetic diameter and agrees well with a recent experiment which created similar-sized pores in the graphene sheet. Umbrella sampling simulations not only yielded free energy barriers of gas permeation that showed a selective trend consistent with the direct MD simulation and the experiment, but also allowed us to obtain more accurate estimates of selectivities of gas pairs. Simulation of the pore with the partial charges of the pore rim atoms set at zero suggested that nitrogen groups increase CO_2 flux by two times. Case study with CO_2/N_2 mixtures further demonstrated the capacity of the nitrogen-functionalized nanoporous graphene to sieve CO_2 from other gases. Hence this work suggests that MD simulations coupled with free-energy calculations are a useful tool to reveal gas-separation mechanisms of porous graphenes of different morphology, chemistry, and thickness for targeted gas pairs or mixtures [23, 24].

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Classical molecular dynamics simulations show the flux trend of $\text{H}_2 > \text{CO}_2 \gg \text{N}_2 > \text{Ar} > \text{CH}_4$ for their permeation through a porous graphene, in excellent agreement with a recent experiment.