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 calcualtions 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.

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1. Introduction

Gas separation, specifically carbon dioxide removal, plays a key role in various industrial processes. For instance, excess CO_2 has 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 has 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].

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: $H_2 > CO_2 > Ar > N_2 > CH_4$. 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 $100\,\text{Å} \times 100\,\text{Å}$ and the nanopore density is $0.0004\,\text{Å}^{-2}$. The nitrogen functionalized nanopore denoted as 4N4H has a dimension of $3.0\,\text{Å} \times 3.8\,\text{Å}$ (Fig. 1b). The porous graphene preparation details and force field parameters can be found elsewhere

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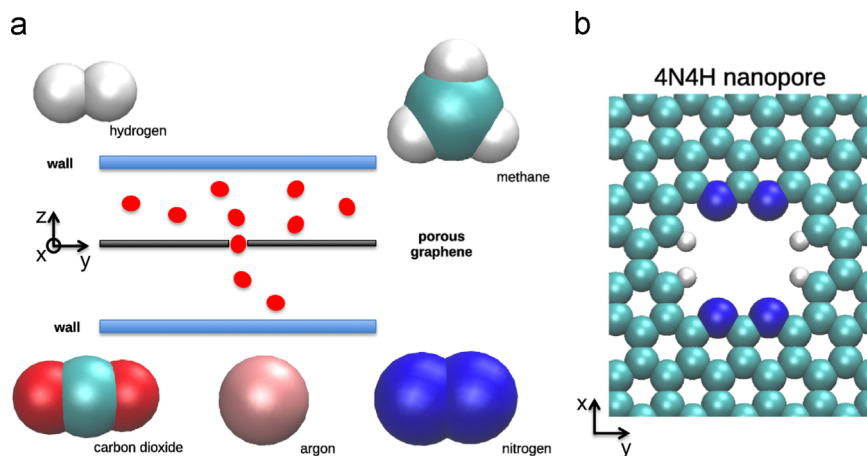
Fig. 1. Schematic illustration of the system setup: (a) the sandwich-like, bi-chamber system to simulate gas permeation; (b) the 4N4H pore structure (carbon, cyan; hydrogen, grey; nitrogen, blue) has dimensions of roughly 3.0 Å × 3.8 Å [7]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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

[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 D Å and the H–H bond length is 0.7414 Å. Three-site model with three partial charges was applied for CO_2 with a quadrupole moment of 3.794 D Å [27]. The distance between C and O atoms is 1.149 Å. A recent Ar model was utilized [28]. Three-charge-site N_2 model was taken with the N–N bond length of 1.098 Å with a quadrupole moment of 1.44 D Å [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.

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].

3. Results and discussion

The classical MD simulations can monitor the number evolution of permeated gas molecules, thereby directly obtaining the
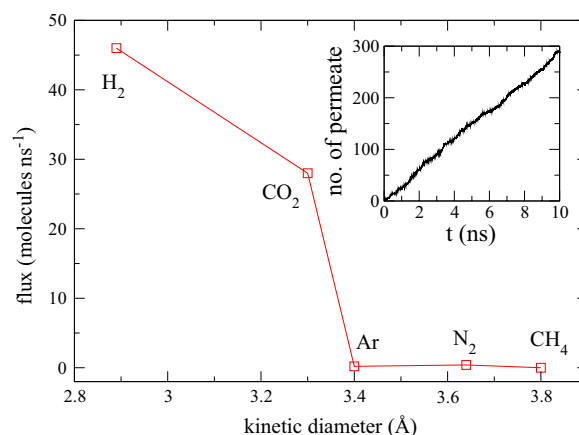
Fig. 2. Brute-force molecular dynamics simulation of gas flux through the nanoporous graphene at 82 atm with the 4N4H pore which has a dimension of 3.0 Å by 3.8 Å. Inset shows the number profile of permeate CO_2.

gas flux and permeance. The number profile of permeate CO_2 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 $H_2 > CO_2 > > N_2 > Ar > CH_4$, 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.

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