

## Short Communication

## Fast mass transport across two-dimensional graphene nanopores: Nonlinear pressure-dependent gas permeation flux

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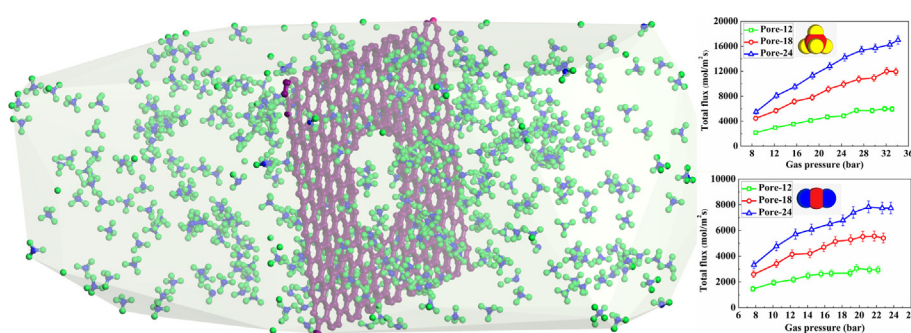
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## HIGHLIGHTS

- A nonlinear pressure dependence of gas permeation flux through graphene nanopores is identified.
- It is attributed to the Langmuir isothermal adsorption of gas molecules on graphene surface.
- A theoretical model is established based on the mass transport resistance network.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Mass transport across two-dimensional nanopores is very essential to the porous graphene and other atomically thin membranes for gas separation. Due to the contribution of gas adsorption and diffusion over the two-dimensional surfaces, mass transport across graphene nanopores cannot be described only by the kinetic theory of gases. We show that the combination of the linear pressure-dependent direct flux, governed by the kinetic motion of gas molecules, and the nonlinear pressure-dependent surface flux, caused by the Langmuir isothermal adsorption characteristics of gas molecules on the two-dimensional surfaces, results in an overall nonlinear pressure dependence of the gas permeation flux through graphene nanopores. Based on the mass transport resistance network connecting the multiple molecular transport processes in direct flux and surface flux, a theoretical model that captures the pressure dependence of permeation flux is established, offering a possible avenue to predict the mass transport rates through the two-dimensional nanopores.

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## 1. Introduction

Nanoporous graphene (NPG), which exhibits nanopores with diameters comparable to molecular sizes, and other two-dimensional materials (Celebi et al., 2014; Dasgupta et al., 2015; Heiranian et al., 2015; Kim et al., 2013; Koenig et al., 2012; Schrier and McClain, 2012) have been demonstrated as very

promising separation membranes, because the mass transport rates in such ultra-thin membranes are expected to be extremely fast. Coupled with excellent mechanical integrity (Carpenter et al., 2014; Cohen-Tanugi and Grossman, 2014; Hu et al., 2015), good chemical durability (Girit et al., 2009) and other distinctive features (Lherbier et al., 2008; Viola Kusminskiy et al., 2011; Yuan et al., 2015), these state-of-the-art membranes have shown promise in gas separation, water desalination, hydrogen storage, DNA sequencing and so on (Cohen-Tanugi and Grossman, 2012; Jiang et al., 2009; Postma, 2010; Schneider et al., 2010; Sun et al., 2015a, 2015b; Surwade et al., 2015).

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Mass transport across the two-dimensional nanopores directly determines the permeance and selectivity of such atomically thin membranes for gas separation. For the graphene nanopores, the two-dimensional surfaces certainly exert a significant effect on the gas molecular transport, resulting in the incompetence of kinetic theory of gases for totally describing the mass transport phenomenon. As other nanoscale mass transport phenomena (Chmelik et al., 2010; Li et al., 2015; Sun and Bai, 2017a,b; Zhao et al., 2015; Ziemys et al., 2012), much attentions must be carefully paid to the contribution of surfaces. The mass transport rates through graphene nanopores are greatly affected by the graphene surface-associated parameters, such as pore porosity, molecular adsorption on graphene surface, chemical modifications of graphene sheet (Dasgupta et al., 2015; Du et al., 2011; Lei et al., 2014; Shan et al., 2012; Sun and Bai, 2017c; Wen et al., 2015; Wu et al., 2014). Among them, the molecular adsorption on graphene surface, caused by the strong interactions between gas molecules and graphene atoms, is of particular importance. Based on the molecular adsorption on two-dimensional surfaces, we proposed a direct mechanism and surface mechanism of gas molecules permeating through graphene nanopores in our early work (Sun et al., 2014). The total permeation flux therefore consisted of direct flux (DF) and surface flux (SF), which were distinguished by whether the molecules crossed the nanopores after being adsorbed on the two-dimensional surfaces or not.

The work described here is motivated by the distinct operating mechanisms of the two components of permeation flux; namely, the DF and SF are governed by the gas kinetic motions and the molecular adsorption and diffusion on graphene surfaces, respectively. In this paper, we show that the linear pressure-dependent DF, described by the kinetic theory of gases, and the nonlinear pressure-dependent SF, caused by the Langmuir isothermal adsorption characteristics of gas molecules on the two-dimensional surfaces, jointly induce a nonlinear pressure dependence of the total permeation flux. We also develop a theoretical model for the permeation flux as a function of pressure based on the mass transport resistance network, which connects the multiple molecular transport processes in DF and SF. In short, the present work makes a great contribution on identifying the non-linear pressure-dependent permeation flux and establishing the theoretical model for describing the relationship between permeation flux and gas pressure based on the two different molecular permeation regimes identified in our previous study (Sun et al., 2014). Our results can provide a deep insight into the mass transport phenomena through the two-dimensional nanopores.

## 2. Simulation model

Here, we perform a systematic molecular dynamics (MD) study on the transport of gas molecules across the graphene nanopores under different pressures. The CH<sub>4</sub> and CO<sub>2</sub> molecules are involved, because they can strongly adsorb on the graphene surface and a significant surface contribution on the molecular permeation can be expected. In order to eliminate the complexity related to the time-variation of the pressure difference, we perform the MD simulations in an equilibrium system instead of a non-equilibrium system. It is noted that the one-sided flux through graphene nanopores can be obtained by halving the two-sided flux from crossings in either direction in the equilibrium system; the calculation method is validated by comparing the one-sided permeation flux in non-equilibrium system and the two-sided permeation flux in equilibrium system of CH<sub>4</sub> and CO<sub>2</sub> molecules permeating the same nanopore (see Section 3.2 of Supplemental Material). Although we perform the MD simulations in the equilibrium system, the one-sided permeation flux calculated from the

equilibrium simulations can totally reflect the pressure-driven molecular transport process in the real gas separation process.

In the simulations, 100 CH<sub>4</sub> or CO<sub>2</sub> gas molecules are initially uniformly arranged on the two sides of the graphene of area 3 × 3 nm<sup>2</sup>. The size of the cubic simulation box is 3 × 3 × x nm<sup>3</sup>, where x varies with the system pressure. The lower the pressure is, the higher the height x of the simulation box is. The details of the simulation system are available in Section 1.1 of Supplemental Material. We consider 10 different pressures, namely the initial pressure of the equilibrium system varies from 10 to 55 bar with an interval of 5 bar (x varies from 45 to 8.5 nm). Three graphene nanopores (Pore-12, Pore-18 and Pore-24) with different sizes are involved in this study, which are generated by removing central carbon atoms in the graphene and named after the number of removed graphene rings (see Fig. 1). The sizes of the pores are quantified by an effective radius R<sub>p</sub>, which is obtained from the effective pore area A<sub>p</sub> (R<sub>p</sub> = √A<sub>p</sub>/π); A<sub>p</sub> is calculated by considering the finite size of pore-rim carbon atoms, as described in Section 2 of Supplemental Material. In this study, the graphene nanopores without any chemical functionalization are employed, because the effects of pressure on the permeation flux through these pores can be quantitatively explored with exactly-determined pore areas. During the simulation, the temperature is kept 300 K in a NVT ensemble. The simulations require 1 × 10<sup>8</sup> MD steps, of which the time step is 0.134 fs. The atomic interactions in graphene and CH<sub>4</sub> molecules are described by the AIREBO potential; for CO<sub>2</sub>, the three-site model (Harris and Yung, 1995) is adopted to consider both the dispersive and electrostatic forces. The bond stretch and angle deformation are considered by the harmonic potential model. These potential models are elaborated in Section 1.2 of Supplemental Material.

## 3. Results and discussion

### 3.1. Permeation flux

In order to obtain the permeation flux, we analyze the molecular trajectories to detect the time-varying number of molecular crossing events through the pores in either direction. The molecular crossing event is considered to be effective if the molecule migrates from the gas phase on one side to the gas phase on the other side of graphene. Namely, a molecule is considered to have crossed the graphene nanopore one time if the molecule migrates from one gas phase to the other gas phase no matter how long it moves/vibrates around the nanopore. The gas phase is distinguished from the gas adsorption layer on graphene surface, which will be discussed below. Due to the gas adsorption, the pressure of gas phase is much smaller than the initial pressure of the system. The calculations of permeation flux and gas pressure are described in detail in Section 3 of Supplemental Material. The variations of the one-sided permeation flux with the pressure of gas phase for CH<sub>4</sub> and CO<sub>2</sub> molecules are plotted in Fig. 1. For a certain pressure and gas molecule, the permeation flux through bigger pores is obviously higher owing to the larger permeable areas. Although the kinetic diameter of CH<sub>4</sub> molecules (0.38 nm) is larger than that of CO<sub>2</sub> molecules (0.33 nm), the CH<sub>4</sub> molecules exhibit stronger permeation ability because they are lighter. These gas permeation fluxes through graphene nanopores far exceed those of polymer gas separation membranes (see Section 3.4 of Supplemental Material), indicating the fast mass transport across the two-dimensional graphene nanopores. An important phenomenon can be observed from this figure is the nonlinear increase of permeation flux with increasing the pressure. At lower pressures, the permeation flux increases sharply with increasing the pressure; while at higher pressures, it increases slowly even plateaus to some extent.

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