Short Communication

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

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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

A theoretical model is established based on the mass transport resistance network connecting the multiple molecular transport processes in direct flux and surface flux, offering a possible avenue to predict the mass transport rates through the two-dimensional nanopores.

ARTICLE INFO

Article history:
Received 3 July 2016
Received in revised form 22 February 2017
Accepted 24 February 2017
Available online 1 March 2017

Keywords:
Membrane separation
Graphene nanopore
Mass transport
Permeation flux
Molecular dynamics

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.

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).
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 CH₄ and CO₂ 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 CH₄ and CO₂ 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 CH₄ or CO₂ gas molecules are initially uniformly arranged on the two sides of the graphene of area 3 × 3 nm². The size of the cubic simulation box is 3 × 3 × 3 nm³, 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 \( R_p \), which is obtained from the effective pore area \( A_p (R_p = \sqrt{A_p/\pi}) \); \( A_p \) 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 × 10⁹ MD steps, of which the time step is 0.134 fs. The atomic interactions in graphene and CH₄ molecules are described by the AMBER potential; for CO₂, 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 CH₄ and CO₂ 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 CH₄ molecules (0.38 nm) is larger than that of CO₂ molecules (0.33 nm), the CH₄ 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.
As a part of permeation flux, DF is governed by the gas kinetic motions and therefore can be reasonably described by the kinetic theory of ideal gases (refer to our early work (Sun et al., 2014)), as follows:

$$J_d = \frac{A_p}{A_s} \frac{P}{\sqrt{2\pi RT}} \delta \left( \frac{R_p}{R_m} \right)$$  \hspace{1cm} (1)

where $P$ is the gas pressure, $T$ is the temperature, $M$ is the molar mass, $R$ is the universal gas constant. In this study, the flux is obtained based on the graphene area $A_s$ and thus a conversion constant $A_p/A_s$ is involved. The kinetic theory originally predicts the flux of point particles through a certain area; for the gas molecules of radius $R_m$, a reduction coefficient $\delta \left( \frac{R_p}{R_m} \right)$ must be considered due to the steric effects. The detailed calculation method of $\delta \left( \frac{R_p}{R_m} \right)$ and their values can be found in Section 4 of Supplemental Material. After subtracting the DF predicted via Eq. (1) from the total permeation flux, the SF can be obtained.

The ratio of SF to total flux decreases with increasing the pressure for a given pore and gas molecule, as shown in Fig. 2. It means that the proportion of SF in total flux decreases with the increase of pressure. Recalling the linear pressure dependence of DF (as seen from Eq. (1)), we can conclude that the nonlinear pressure-dependent total permeation flux through the graphene nanopores is a direct result of the non-linearly increasing SF as the pressure increases (see Section 3.3 of Supplemental Material). We also observe that the ratios of SF to total flux for bigger pores are lower than those for smaller pores. For the fixed pore number density in the simulations, bigger pore means smaller surface area available for molecular adsorption and thus the contribution of SF to total flux gets less important. Furthermore, for bigger pores the ratios can get lower because the SF scales as the pore radius (pore perimeter) while the DF scales as the square of pore radius (pore area). We note that the ratios of SF to total flux for CH$_4$ and CO$_2$ are very high (72.6–95.8%), indicating the major contribution of SF for the strongly adsorbed gases.

### 3.2. Molecular adsorption

From the molecular number density distribution along the direction perpendicular to the graphene surface ($z$-direction), it can be seen that the gas molecules strongly adsorb onto the surface to bring a high density zone $0.17 \text{ nm} < |z| < 0.6 \text{ nm}$ (denoted as adsorption layer, the region $|z| < 0.17 \text{ nm}$ is occupied by graphene atoms), as shown in Fig. S3 in Supplemental Material. The model
of the adsorption layer is depicted in Fig. 3(a). Owing to the stronger molecule-graphene interactions, the density of CO\textsubscript{2} molecules in the adsorption layer is higher than that of CH\textsubscript{4} molecules (see Fig. 3(b)). In the adsorption layer, the molecular density near the pore is obviously lower than that far away from the pore, because the molecules in the pore region can permeate to the other side of graphene; meanwhile, it should be noted that the absence of carbon atoms in the pore region for attracting gas molecules can also contribute to this result. Although the molecules in the adsorption layer present an overall heterogeneous distribution, the density of adsorbed molecules on the surface away from the pore region is uniform in principle. The uniform molecular number density just associates with the SF. The height of the adsorption layer is comparable to the molecular diameter, indicating that only one layer of molecules can adsorb on the graphene surface. These behaviors mean that the molecular adsorption on the graphene surface away from the pore region can be reasonably described by the Langmuir adsorption isotherm,

\[ N_a = N_{a,m} \frac{kP}{1 + kP} \]

where \( P \) is the gas pressure, \( k \) is the Langmuir adsorption constant, \( N_a \) is the number of adsorbed molecules on the one-side graphene surface away from the pore region, and \( N_{a,m} \) is the maximum number of adsorbed molecules on the corresponding surface.

The SF is related to the molecular adsorption and diffusion on the graphene surface and thus directly proportional to the number of adsorbed molecules away from the pore region \( (N_a) \). Agreeing with the Langmuir adsorption model, \( N_a \) increases sharply with increasing the pressure at lower pressures, while it increases slowly at higher pressures (see Fig. 3(c–e)). Therefore, it is concluded that the Langmuir adsorption characteristics of gas molecules result in the nonlinear pressure dependence of SF and consequently the nonlinear pressure dependence of total permeation flux. Furthermore, we fit the data of \( N_a \) via Eq. (2) of Langmuir adsorption isotherm and obtain the values of \( N_{a,m} \) and \( k \) (see Table S4 in Supplemental Material). The fitted curves are shown in Fig. 3(c–e). It is noted that the range of gas pressure for CO\textsubscript{2} is smaller than that for CH\textsubscript{4} due to the stronger adsorption abilities of CO\textsubscript{2} molecules; at a given initial pressure, stronger adsorption means fewer molecules in the gas phase and thus a lower gas pressure.

### 3.3. Theoretical model

We can see from the above analysis that the nonlinear pressure-dependent permeation flux is mainly caused by the Langmuir isothermal adsorption characteristics of gas molecules on the graphene surfaces. Thus, a model for predicting the permeation flux as a function of pressure is expected to be developed based on the Langmuir adsorption isotherm. Since,

\[ J = J_s + J_d \]

where \( J \) is the total permeation flux, \( J_s \) and \( J_d \) are the SF and DF, respectively. In the SF, the molecular permeation process includes three steps: (1) the adsorption from gas phase, (2) the diffusion along surface to reach the pores, and (3) the penetration through pores to the other side; in the DF, the molecular permeation process can be finished only in two steps: (1) the kinetic motion to pore regions and (2) the penetration through pores. The corresponding mass transport resistances in SF are \( R_{s,1} \), \( R_{s,2} \), and \( R_{s,3} \), while those in DF are \( R_{d,1} \) and \( R_{d,2} \). Accordingly, a resistance network for the molecular permeation through graphene nanopores is depicted in Fig. 4(a). Compared with the others, the molecular adsorption and kinetic motion steps are much faster and thus the

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**Fig. 3.** Molecular adsorption characteristics on the graphene surface. *(a)* The model of the adsorption layer on graphene surface with a height of 0.6 nm. *(b)* Number density distributions of CH\textsubscript{4} and CO\textsubscript{2} molecules in the adsorption layer on the graphene surface with Pore-24 at the initial pressure of 55 bar. The molecular number in this figure is obtained on the unit graphene surface with an area of 1.74 Å\textsuperscript{2}. *(c–e)* Adsorbed molecular number on the graphene surface away from pore region with respect to gas pressure for the Pore-12, Pore-18 and Pore-24, respectively.
resistances $R_{d,1}$ and $R_{d,2}$ can be neglected. The steps (2) and (3) in SF equilibrate with the number density of the adsorbed molecules on the graphene surface away from the pore region ($N_{ad}$), while the step (2) in DF is related to the number density of the pore-region molecules directly from gas phase ($N_{id}$). Therefore, 

$$J = \delta N_{ad} + \chi N_{id}$$

where $\delta$ is an effective passage rate in SF, accounting for both the diffusion rate along surface to reach the pores and the penetration rate through pores to the other side; $\chi$ is the rate of the molecular penetration through pores in DF. Namely, $\delta$ scales as $1/(R_{d,2} + R_{c,3})$, and $\chi$ scales as $1/R_{d,2}$. The number density of adsorbed molecules ($N_{id}$) can be described by the Langmuir adsorption isotherm, and the number density of pore-region molecules directly from gas phase ($N_{ad}$) is in direct proportion to the pressure based on the kinetic gas theory ($N_{ad} = \frac{1}{k_B T}$). Adopting the assumption that the molecular diffusivity on graphene surface and the penetration rate through the pores have no dependence with the pressure, we can write Eq. (4) as:

$$J = \delta N_{ad,max} \frac{kP}{1 + kP} + \chi \frac{1}{k_B T} P$$

where $N_{ad,max}$ is the maximum number density of adsorbed molecules on the graphene surface away from the pores ($N_{ad,max}$ is the maximum value of $N_{ad}$); $T$ is the gas temperature, and $k_B$ is the Boltzmann constant. With the definitions of $\alpha = k$, $\beta = \delta N_{ad,max} k + \chi/k_B T$ and $\gamma = \chi/k_B T$, Eq. (5) is simplified as:

$$J = \frac{\beta P + \gamma P^2}{1 + 2P}$$

In this equation, $\alpha$, $\beta$, and $\gamma$ are the pressure-independent parameters. Specifically, $\alpha$ is the Langmuir adsorption constant known from $k$ in Eq. (2), which is determined by gas species, surface properties and temperature; $\beta$ and $\gamma$ are related to molecular adsorption properties, molecular diffusion rate on surface, molecular penetration rate through pores, etc. Here, we obtain the values of $\beta$ and $\gamma$ by fitting the MD data of permeation flux, as listed in Table S5 in Supplemental Material. The fitted curves of permeation flux as a function of pressure are shown in Fig. 4(b and c). We find that the value of $\gamma$ is extremely small, meaning that the DF has a weak contribution to the total permeation flux ($J_d = \frac{\alpha}{P}$). This conclusion agrees with the previous result that the SF accounts for most of the permeation flux (see Fig. 2). We must note that this viewpoint is especially suitable for the strongly adsorbed gases, such as CH$_4$ and CO$_2$ molecules. Meanwhile, we find that the value of $\alpha$ for CO$_2$ is slightly higher than that for CH$_4$, indicating a more remarkable nonlinear pressure dependence of the permeation flux for CO$_2$ with stronger adsorption intensity. It is further noted that in this theoretical model both DF and SF are considered and only SF is correlated with the Langmuir adsorption isotherm.

4. Conclusion

We demonstrate that the combination of the linear pressure-dependent DF, governed by the molecular kinetic motions, and the nonlinear pressure-dependent SF, caused by the Langmuir isothermal adsorption characteristics of gas molecules on the graphene surfaces, results in the nonlinear pressure-dependent gas permeation flux through two-dimensional graphene nanopores. Based on the mass transport resistance network considering direct and surface transport of gas molecules through graphene nanopores, a theoretical model is established to well predict the gas permeation flux as a function of pressure. We note that the phenomenon of nonlinear pressure dependence of permeation flux is especially applicable for the strongly adsorbed gases on graphene surfaces. It is expected that the nonlinearity would be more obvious for the graphene with a lower pore number density owing to the larger specific surface area. More importantly, we believe that
the phenomenon and mechanisms we have identified are valuable for the description of mass transport in the two-dimensional porous materials.

Acknowledgements

We deeply appreciate the kind comments and valuable guidance from Prof. Nicolas Hadjiconstantinou and Prof. Rohit Karnik at Massachusetts Institute of Technology. We acknowledge the financial supports from National Natural Science Foundation of China for Distinguished Young Scientists (51425603), projects No. 51506166.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ces.2017.02.042.

References


