

# CO<sub>2</sub> Permeation through Nanoporous Graphene: A Theoretical Study

Zacharias G. Fthenakis<sup>1,\*</sup> , Antonios Fountoulakis<sup>1,2</sup>, Ioannis D. Petsalakis<sup>1</sup>, Nektarios N. Lathiotakis<sup>1</sup>

This work is part of a systematic study on the energy barriers for the permeation of several molecules, like He, H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub> etc, through nanoporous single layer graphene, having pores with different shape, size, and type. In the present work, we focus on the permeation of CO<sub>2</sub> through graphene pores which are constructed when neighboring carbon atoms of the graphene layer are removed from the structure, and nitrogen atoms have replaced the carbon atoms in the boundary of the pore. The energy barriers for each different pore are calculated using 2 different ReaxFF potentials along a path which the molecule would ideally follow in order to pass from the one side of the membrane to the other through the pore. Using the calculated values of the energy barriers, we estimate permeances by employing the kinetic theory of gasses. We give estimates for the preferable sizes and structures of the pores for permeability and demonstrate the ability of nanoporous graphene for CO<sub>2</sub> separation.

## Introduction

One of the most promising fields for application of Nanoporous graphene is that of membranes for gas separation [1-10]. For instance, Wu *et al.*, [7] reported that the fluorine-modified porous graphene membrane can be used for the separation of CO<sub>2</sub> from N<sub>2</sub> molecules, since CO<sub>2</sub> moves easier through such a membrane, contrary to N<sub>2</sub>. Sun *et al.*, [8] identified a nanopore graphene membrane that is permeable to H<sub>2</sub> and He, significantly permeable to N<sub>2</sub> and impermeable to CH<sub>4</sub>. They also showed that pore functionalization may significantly affect the molecular permeation [8]. Similar results have been found by Jiang *et al.*, [9], who reported high selectivity for the separation between H<sub>2</sub> and CH<sub>4</sub> for graphene membranes with nitrogen functionalized pores. The effect of nitrogen functionalization was also reported by Wei *et al.*, [10] and Zhu *et al.*, [11], who showed that porous graphene membranes with pyridinic pores are very efficient in separating He and H<sub>2</sub> over Ne, Ar, N<sub>2</sub>, CO and CH<sub>4</sub>.

In the present work, we investigate theoretically the permeation of CO<sub>2</sub> through pyridinic pores in graphene, as part of a systematic study of gas permeation through graphene membranes. Our study focuses on seven

membrane systems which are shown schematically in Fig. 1. Apart from pristine graphene (Fig. 1(a)), these membranes, are constructed by removing some neighbouring carbon atoms of the graphene layer, while the pore boundary atoms are replaced by nitrogen (pyridinic pores). Using the method described below, we try to reach the transition state for the minimum energy path that transfers the CO<sub>2</sub> molecule from the one side of the membrane to the other through the pore and estimate the energy barrier which corresponds to that transition state. Using the energy barriers, we then estimate the CO<sub>2</sub> permeabilities of the membranes utilizing the kinetic theory of gasses.

## Method

For our study, we devised a classic potential approach based on a combination of two recently proposed ReaxFF potentials. The first one is the so called RDX potential [12], which has been developed for simulations on nitramines and describes interactions between C, N, H and O atoms. The other one is the so-called C-2013 potential [13], which has been developed for simulations on carbon condensed phases and describes interactions only between C atoms. In several tests we performed, the results obtained from this new potential are comparable with those obtained from ab-initio methods. In the rest of this paper, we will refer to this potential as the GR-RDX-2020. More details on the efficacy of this force field to provide reasonable results for interactions between graphene and simple molecules like CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O etc are provided elsewhere [14]. Apart from the hybrid GR-RDX-2020 potential described above, we also employed another ReaxFF potential which was

<sup>1</sup>Institute of Theoretical and Physical Chemistry, National Hellenic Research Foundation, Athens, 11635, Greece

<sup>2</sup>Hellenic Mediterranean University, Heraklion, 71004, Greece

\*Corresponding authors:

E-mail: fthenak@eie.gr; Tel: +30 2107273812

DOI: 10.5185/amlett.2022.031700

recently developed, namely CHON-2019 [15]. All calculations presented here, which utilize either our hybrid GR-RDX-2020 or CHON-2019 ReaxFF potentials, were performed using the LAMMPS code [16,17].

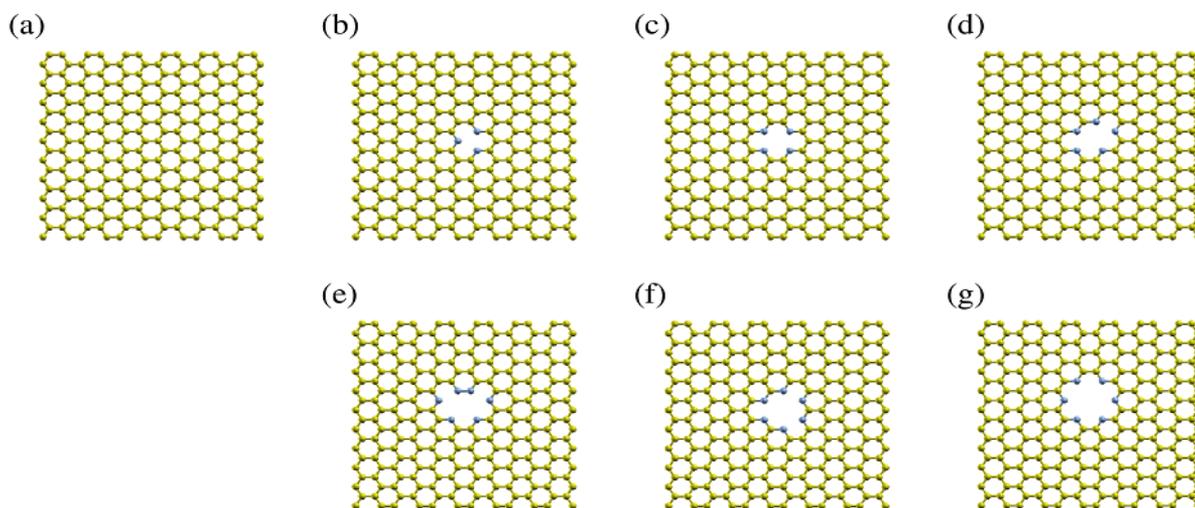
In order to simulate graphene membranes, a 1008 atom rectangular graphene supercell with periodic boundary conditions is considered. As a first step of our calculations, graphene membranes, which are initially located in the xy plane, are optimized. As a second step (and for all the calculations that follow), the optimized positions of the boundary atoms of graphene supercell are frozen in their optimized positions, while the rest of the atoms are allowed to move freely. In the third step, some neighbouring carbon atoms of the graphene layer are removed from the structure, (thus creating a pore in graphene) and a CO<sub>2</sub> molecule, with its axis directed normal to xy plane (i.e., normal to the membrane) is placed on top of the centre of the pore, at a distance  $z = 10 \text{ \AA}$  between the C atom of CO<sub>2</sub> and the xy plane, where the optimized membrane is located. In the fourth step, the whole system is optimized under the constrain that the z coordinate of the carbon atom of CO<sub>2</sub> is kept fixed to its initial value of  $10 \text{ \AA}$  and the energy, as well as the geometry of the optimized system is recorded. In the fifth step, the z coordinate of the CO<sub>2</sub> atoms of the previous step are lowered by  $\delta z = 0.1 \text{ \AA}$ , while the coordinates of the membrane atoms are kept the same with those obtained from the optimization of the previous step. The z coordinate of the C atom of CO<sub>2</sub> is kept fixed in its new position (as in the previous step) and a new optimization calculation is performed for the whole system. When the optimization calculation is finished, the energy of the optimized system is also recorded. The fifth step is repeated recursively, lowering at each next step the z coordinates of the CO<sub>2</sub> atoms by  $0.1 \text{ \AA}$  and the energy of the optimized structure is recorded, till the z coordinate of the C atom of CO<sub>2</sub> becomes  $-10 \text{ \AA}$ .

Under this procedure, the z coordinate of the carbon atom of CO<sub>2</sub> can be considered as a reaction coordinate for the permeation of CO<sub>2</sub> through the membrane. Therefore, the energy values obtained from the optimizations, are expected to be very close to the corresponding minimum energy path. Consequently, the maximum of the energy as a function of z provides an estimate (upper limit) of the energy of the transition state. Therefore, an upper limit of the energy barrier that the CO<sub>2</sub> molecule must overcome, to be able to pass from the one side of the membrane to the other is the energy difference between that energy maximum and the energy at  $z = 10 \text{ \AA}$ , (which practically is the energy of the system for  $z = \infty$ ).

The value of the energy barrier, the effective area and density of the pores can be used to estimate [18] the permeance through the membrane. The permeance,  $P_e$ , is defined as  $P_e = F/\Delta P$  where  $\Delta P$  is the pressure drop through the membrane and  $F$  is the molar flux. In turn,  $F = Np$ , where  $N$  is the number of incident molecules and  $p$  the probability of a molecule to diffuse through the pore. According to the kinetic theory of gases, (i)  $p = \int_{v_b}^{\infty} f(v) dv$ , where  $f(v)$  is the

Maxwell velocity distribution and  $v_p$  the velocity corresponding to the energy barrier, and (ii)  $N = \frac{\sigma P}{\sqrt{2\pi mk_b T}}$ ,

and  $\sigma$  is a geometrical factor defined as  $\sigma = \rho_{def} S_{def}$  where  $\rho_{def}$  is the number of pores per surface area and  $S_{def}$  the effective area of the pore. A typical experimental value of  $\rho_{def}$  is  $\rho_{def} = 5 \times 10^{-4} \text{ \AA}^{-2}$  which is the value we use in the present study. It is worth noting that an industrially acceptable value for permeance is  $6.7 \times 10^{-9} \text{ mol s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$  [19]. In our study, we examine if the permeance at room temperature or at  $T=1000 \text{ K}$  is above that threshold, and we also give an estimate for the critical temperature for permeances that exceed it.



**Fig. 1.** Pore graphene membranes with Nitrogen atoms at the boundary of the pore. (a) Pure graphene, (b) 1-, (c) 2-, (d) 3-, (e) 4a-, (f) 4b- and (g) 6-membrane (see the definition in the text). Yellow and blue spheres represent C and N atoms, respectively.

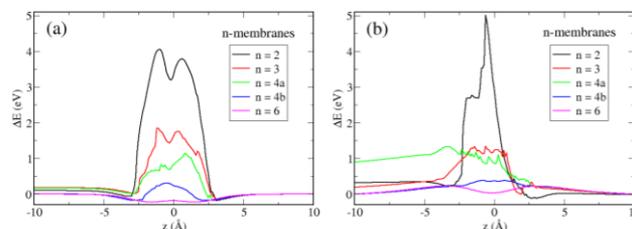
## Results and discussion

For convenience, we will use here the term “*n*-membrane” for a graphene membrane with *n* neighbouring atoms been removed from it. Obviously, in the case of undefective graphene, where no atom is removed from graphene structure, every graphene hexagonal ring should be considered as a pore. In that case, we do not consider any N termination in the pore boundary.

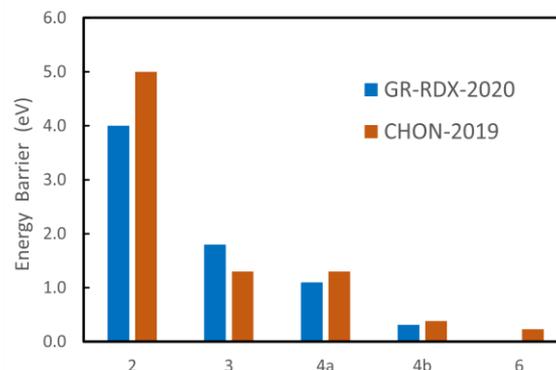
For each one of the membranes of **Fig. 1**, we calculate the energy for the several points of the path that the CO<sub>2</sub> molecule follows in order to pass through the pore, according to the method described above ( $\approx$ minimum energy path). According to our findings, pure graphene and 1-membrane do not allow the permeation of CO<sub>2</sub> molecules. When the CO<sub>2</sub> molecule comes close to those membranes, it dissociates due to the strong interactions that appear, which force the oxygen atoms of CO<sub>2</sub> to form bonds with the C atoms of graphene. Therefore, for those membranes the barrier should be considered as infinity.

For all the other membranes, the energy difference with respect to the energy obtained for the optimized structures (graphene membrane + CO<sub>2</sub> molecule) for  $z = 10 \text{ \AA}$ , which is expected to be very close to the minimum energy path, is shown in **Fig. 2** as a function of the  $z$  coordinate of the C atom of CO<sub>2</sub> for the GR-RDX-2021 potential (**Fig. 2a**) and CHON-2019 (**Fig. 2b**). As one can see, the energy barrier for the permeation of CO<sub>2</sub> through graphene membranes decreases as the size of the pore increases. Although this result is not unexpected, our calculations allow the estimation of the values of these barriers, which are included in **Table 1** for both the GR-RDX-2021 potential (a) and CHON-2019 (b). They are also shown in **Fig. 3**. The large energy barrier for graphene 2-, 3- and 4a-membrane indicate that it is practically impossible for a CO<sub>2</sub> molecule to cross these membranes at room temperature and both potentials agree on this fact. However, for the 3- and 4a-membranes, with barriers ranging between 1.1 and 1.8 eV, the permeation is allowed at elevated temperatures (more than 1000 K). The barriers for the wider pores of 4b- and 6-membranes are much lower or vanish indicating that the permeation of CO<sub>2</sub> through these membranes is much easier. It is worth noting that the size of these pores slightly exceeds 0.5 nm, thus this value is the critical one for the pore size to allow permeation of CO<sub>2</sub> at room temperature.

Although the two potentials we considered agree on the trend of the barriers, there is difference in the values they yield. For the narrow pore 2-membrane, the barrier obtained with the GR-RDX-2020 is larger. On the contrary, for the larger pores of the 4b- and the 6-membrane, CHON-2019 tends to result in higher energy barriers and substantially lower permeances compared to GR-RDX-2020, as shown in **Table 1**. Particularly, GR-RDX-2020 gives zero barrier for the permeation through the 6-membrane.



**Fig. 2.** Energy along the minimum energy path, as a function of the reaction coordinate  $z$  for the *n*-membranes as obtained with GR-RDX-2020 (a) and CHON-2019 (b).



**Fig. 3.** Energy barrier of *n*-membranes obtained with GR-RDX-2020 and CHON-2019 ReaxFF potentials.

**Table 1.** The effective radii of the pore (defect),  $d_{\text{def}}$ , where ( $S_{\text{def}} = \pi d_{\text{def}}^2$ ), the calculated energy barriers, the estimated permeance for  $T=300$  and 1000 K, and a rough estimate of the critical (minimal) temperature,  $T_{\text{cr}}$ , required to obtain industrially acceptable permeance, for the 5 different membrane systems studied, as calculated with the two Reax-FF potentials we considered: (a) GR-RDX-2020 and (b) CHON-2019.

Pores	$d_{\text{def}}$ (nm)	Barrier (eV)	Permeance ( $\text{mol s}^{-1} \text{m}^{-2} \text{Pa}^{-1}$ )		$T_{\text{cr}}$ (K)
			300 K	1000 K	
2	0.40	(a) 4.0	0	0	-
		(b) 5.0	0	0	-
3	0.44	(a) 1.8	0	$2 \times 10^{-12}$	1700
		(b) 1.3	0	$6 \times 10^{-10}$	1150
4a	0.47	(a) 1.1	0	$7 \times 10^{-9}$	1000
		(b) 1.3	0	$7 \times 10^{-10}$	1200
4b	0.52	(a) 0.31	$3 \times 10^{-8}$	$4 \times 10^{-5}$	250
		(b) 0.38	$2 \times 10^{-9}$	$2 \times 10^{-5}$	350
6	0.56	(a) 0.0	$\infty$	$\infty$	0
		(b) 0.23	$7 \times 10^{-7}$	$1 \times 10^{-4}$	200

## Conclusion

The present work, as part of a systematic study of the energy barriers for the permeation of gas molecules through nanoporous single layer graphene, investigates the permeation of CO<sub>2</sub> molecule through seven graphene membranes, which are shown in **Fig. 1**. For all these membranes, the carbon atoms at the boundary of the pores are replaced by nitrogen atoms (pyridinic pores). Utilizing a combination of two ReaxFF potentials (RDX and C-2013), we introduced a potential that we call GR-RDX-

2020 which was applied to the study of several membranes together with the CHON-2019 using the LAMMPS code. According to our findings, graphene, 1- and 2-membranes do not allow the permeation of CO<sub>2</sub>. The energy barrier 3- and 4a-membranes is large enough, and they allow the permeation only in the regime of high temperatures (>1000). The 4b- and the 6-membrane have small energy barriers and therefore the permeation of CO<sub>2</sub> through them is significant. Therefore, the 4b- and 6- membranes, are expected to be a possible candidate for the separation of CO<sub>2</sub> from other molecules, for which the energy barriers for permeation are larger. It is worth noting that the size of these pores is 0.5 nm, which is our predicted critical size for permeation at room temperature. As a final note, we report here significant theoretical predictions regarding the size and type of nano-pores in graphene that can be useful in experimental research for utilizing such membrane systems for CO<sub>2</sub> separation.

#### Acknowledgements

We acknowledge support by the project “nanoporous Graphene membrane made without Transfer for gas Separation – GATES” (MIS 5041612) funded by the Operational Program “Competitiveness, Entrepreneurship and Innovation” (NSRF 2014-2020), co-financed by Greece and the European Union (European Regional Development Fund).

#### Conflicts of interest

There are no conflicts to declare.

#### Keywords

Graphene, membrane, gas separation, ReaxFF, DFT.

#### References

1. Achtyl, J. L.; Unocic, R. R.; Xu, L.; Cai, Y.; Raju, M.; Zhang, W.; Sacci, R. L.; Vlasiouk, I. V.; Fulvio, P. F.; Ganesh, P.; Wesolowski, D. J.; Dai, S.; van Duin, A. C. T.; Neurock, M.; Geiger, F. M.; *Nat. Commun.*, **2015**, *6*, 6539.
2. Eliseev, A. A.; Kumskov, A. S.; Falaleev, N. S.; Zhigalina, V. G.; Eliseev, A. A.; Mitrofanov, A. A.; Petukov, D. I.; Vasiliev, A. L.; Kiselev, N. A.; *J. Phys. Chem. C*, **2017**, *121*, 23669.
3. Sun, C.; Wen, B.; Bai, B.; *Chem. Eng. Sci.*, **2015**, 138, 616.
4. Lee, J.; Du, C.; Sun, K.; Kioupakis, E.; Lu, W. D.; *ACS Nano*, **2016**, *10*, 3571.
5. Blankenburg, S.; Bieri, M.; Fasel, R.; Mullen, K.; Pignedoli, C. A.; Passerone, D.; *Small*, **2010**, *6*, 2266.
6. Koenig, S. P.; Wang, L.; Pellegrino, J.; Bunch, J. S.; *Nat. Nanotech.*, **2012**, *7*, 728.
7. Wu, T.; Xue, Q.; Ling, C.; Shan, M.; Liu, Z.; Tao, Y.; Li, X.; *J. Phys. Chem. C*, **2014**, *118*, 7369.
8. Sun, C.; Boutilier, M. S. H.; Au, H.; Poesio, P.; Bai, B.; Karnik, R.; Hadjiconstantinou, N. G.; *Langmuir*, **2014**, *30*, 675.
9. Jiang, D.; Cooper, V. R.; Dai, S.; *Nano Lett.*, **2009**, *9*, 409.
10. Wei, S.; Zhou, S.; Wu, Z.; Wang, M.; Wang, Z.; Guo, W.; Lu, X.; *Apl. Surf. Sci.*, **2018**, *441*, 631.
11. Zhu, L.; Xue, Q.; Li, X.; Wu, T.; Jin, Y.; Xing, W.; *J. Mat. Chem. A*, **2015**, *3*, 21351.
12. Strachan, A.; van Duin, A.C.T.; Chakraborty, D.; Dasgupta, S.; Goddard, W. A. III; *Phys. Rev. Lett.*, **2003**, *91*, 098301.
13. Srinivasan, S. G.; van Duin, A.C.T.; Ganesh, P.; *J. Phys. Chem. A*, **2015**, *119*, 571.
14. Fthenakis, Z. G.; Petsalakis, I. D.; Tozzini V; Lathiotakis, N. N; to be published.
15. Kowalik, M.; C. Ashraf, C; Damirchi, B; Akbarian, D; Rajabpour, S; van Duin, A.C.T; *J. Phys. Chem. B*, **2019**, *123*, 5357
16. Plimpton, S.; *J. Comp. Phys.*, **1995**, *117*, 1.
17. <https://lammps.sandia.gov/index.html>

18. Zhu, L.; Jin, Y.; Xue, Q.; Li, X.; Zheng, H.; Wu, T.; Ling, C.; J. Matter. Chem A **2016**, *4*, 15015.
19. Zhu, L.; Xue, Q.; Li, X.; Wu, T.; Jin, Y.; Xing, W.; *J. Matter. Chem A*, **2015**, *3*, 21351.

#### Authors biography



**Dr. Zacharias G. Fthenakis** is postdoctoral associate at the Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece. His research interests focus on the investigation of material properties, including structural, electronic, mechanical, magnetic, ferroelectric, transport etc properties, using several theoretical methods ranging from ab-initio DFT methods to molecular dynamics simulations based on classical potentials. He is co-author of 30 publications in peer-review journals and has received 300 citations (h-index 10).



**Dr. Antonios Fountoulakis** is a highly experienced and devoted schoolteacher and researcher. He has served as director of many schools, he is a part-time lecturer at the Hellenic Mediterranean University and collaborating researcher at the Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation. His research area is in computational physics and quantum information and also in educational technology. He has published many papers in prestigious journals and conferences (Google Scholar h-index: 8).



**Dr. Ioannis D. Petsalakis** research interests lie mainly in the field of theoretical molecular physics. Of particular interest are the determination of excited states of molecules as well as the interaction of molecules with electromagnetic radiation. Both development of theoretical methods and applications have been carried out. They are within the framework of Quantum Mechanics and lately are devoted to theoretical studies on donor-acceptor carbon-based materials (photovoltaics, photonics, OLED etc.). He is co-author of 180 publications in peer review journals.



**Dr. Nektarios N. Lathiotakis** is senior researcher at the Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece. He is an expert in the theory of the electronic structure of materials, and more specifically Density and Density matrix functional methods with contribution in the development, implementation, and application of theoretical methods in finite and periodic systems. He has co-authored 80 publications in peer review journals and has received 2220 citations (h-index 27).

#### Graphical abstract

CO<sub>2</sub> permeation through pyridinic pores in graphene calculated with GR-RDX-2020 and CHON-2019 ReaxFF potentials.

