Increased Tunability of Nanoporous Graphene by Damage Cascade and its Effects on Pore Quality

Jovin Ryan Joseph, Faculty Mentor: Dr. Lin Shao
Texas A&M University Department of Nuclear Engineering

Abstract

Nanoporous graphene holds significant potential for various applications, yet the lack of an industry-scalable manufacturing process for producing controlled pore sizes with high repeatability has been a limitation. Current existing methods are probabilistic and lacks reliability. To address these challenges, we propose a novel method for precise pore production using C60 molecules bombardment. Given that the diameter of a C60 molecule is approximately 7 Å, which exceeds the size of the six-fold rings in graphene, the formation of nanopores is guaranteed. Furthermore, by adjusting the energy of the C60 molecule, we can control the nuclear stopping power and make the pore size larger than the size of the C60 molecules. Additionally, introducing multiple layers of graphene allows for damage cascades, resulting in inter-graphene atomic displacement and further tunability of pore size. In this study, we systematically investigate this phenomenon using molecular dynamics simulations. The findings demonstrate the feasibility of the technique and provide optimized conditions for the subsequent experimental studies.

Objective & Experimental Criteria

Production of nanoporous graphene with tunable nanopores on a large scale, with high reliability and specificity is a great challenge preventing the use of these graphene membranes for various applications like low energy desalination, isotope separation, gas sensing, etc.
There have been Molecular Dynamics (MD) studies of ion bombardment of graphene. However, due to the probabilistic nature and fine constraints on positioning of the ions, we believe C60 fullerene would provide better, reliable pores.

In this study we focus on the tunability of nanopores by C60 cluster ion bombardment and quantify the pore size and quality. We also explore the mechanism of damage cascade as observed in bilayer graphene, and its effects on the tuned nanopore.

5 iterations of simulations were performed for every bombardment energy by introducing random velocity vectors for vibrational motion corresponding to a temperature of 300 K .

Simulation Parameters	Value
dt (Timestep)	1E-5 ps
T (Simulation Duration)	10 ps
ZBL_Cut_in	0.001 Å
ZBL_Cut_out	1 Å
Temperature	300 K
Coordination Cutoff	1.8 Å
Energy Range	10 keV – 1.4 MeV

Methodology

Classical molecular dynamics simulations were created using LAMMPS[1] to simulate the C60 fullerene bombardment of monolayer and bilayer graphene membranes of dimension 100 sq. nm. The bombardment was carried out using Nose-Hoover thermostatting[2] in a microcanonical ensemble.

The interatomic interactions were parametrized using the following potential models:
1) Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO)[3]

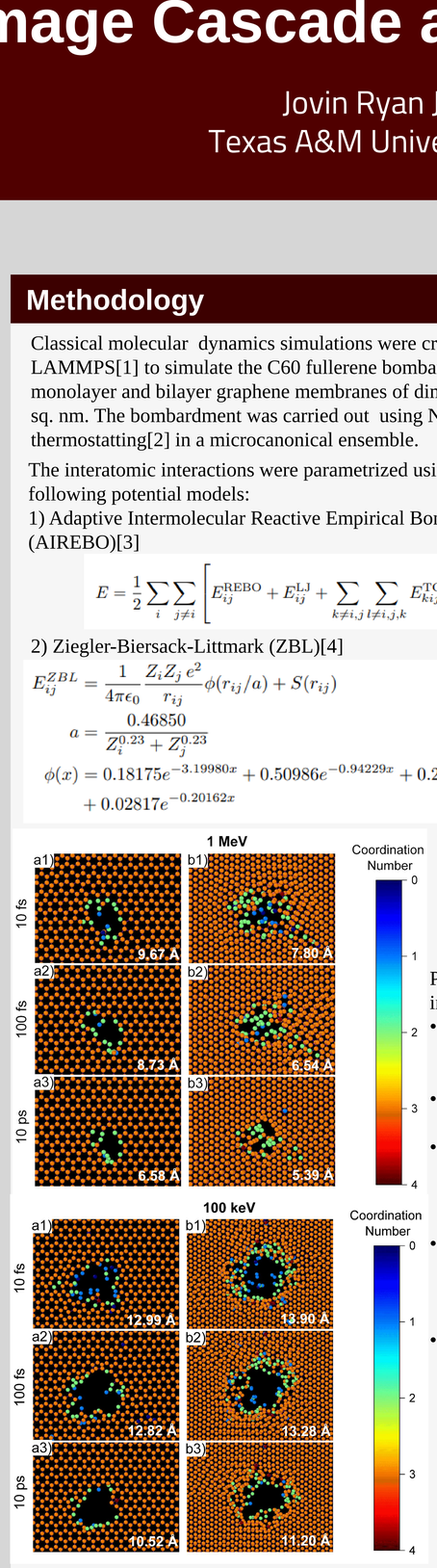
$$E = \frac{1}{2}\sum_i \sum_{j\neq i} \left[E_{ij}^{\mathrm{REBO}} + E_{ij}^{\mathrm{LJ}} + \sum_{k\neq i,j} \sum_{l\neq i,j,k} E_{kijl}^{\mathrm{TORSION}} \right]$$

2) Ziegler-Biersack-Littmark (ZBL)[4]

$$E_{ij}^{ZBL} = \frac{1}{4\pi\epsilon_0}\frac{Z_i Z_j\, e^2}{r_{ij}}\phi(r_{ij}/a) + S(r_{ij})$$

$$a = \frac{0.46850}{Z_i^{0.23} + Z_j^{0.23}}$$

$$\phi(x) = 0.18175e^{-3.19980x} + 0.50986e^{-0.94229x} + 0.28022e^{-0.40290x} + 0.02817e^{-0.20162x}$$



Provides insight into:

- Pore Formation
- Sputtering
- Formation of dangling carbon chains
- Migration and recombination of defects
- Contraction of tuned nanopore

Figure 1. Time evolution of tuned nanopore in monolayer (a1-a3) and bilayer (b1-b3) graphene membranes by C60 fullerene bombardment with energy 1 MeV and 100 keV.

Results

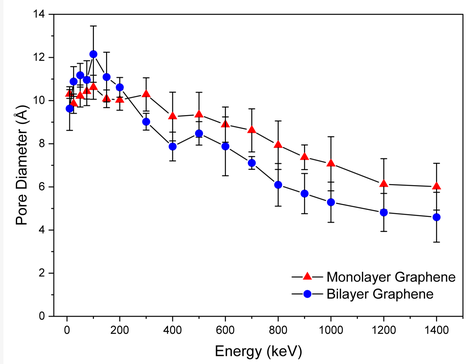


Figure 2. Pore diameters of nanopores tuned by carbon-60 fullerene bombardment with energy 10keV - 1.4MeV.

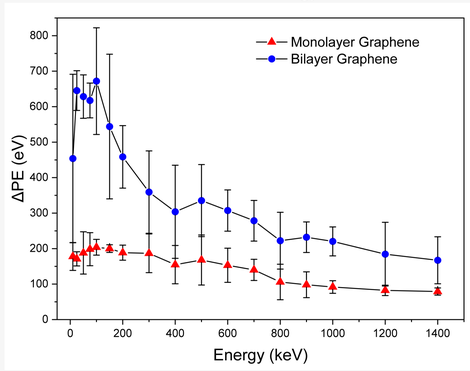


Figure 3. Change in PE of graphene membrane after bombardment as a function of C60 bombardment energy.

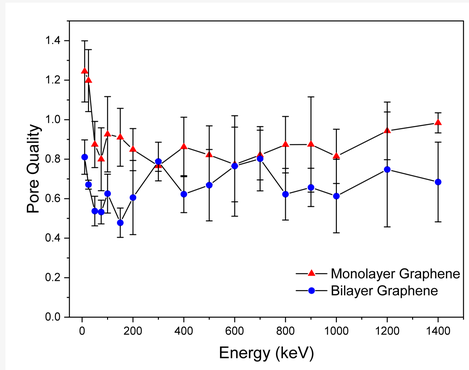


Figure 4. Quality of tuned nanopore on monolayer and bilayer graphene. The figure depicts pore quality as a function of C60 energy.

The Pore quality is a relative measure comparing the pore edge of tuned nanopores to ideal circular pores created using a Python program, based on the diameter. A value of 1 indicates ideal nanopore quality.

Discussion

Based on the findings presented in **figure 2**, it was concluded that bilayer graphene showed a greater tunability (7.559 ± 1.743 Å) compared to monolayer graphene (4.608 ± 1.220 Å), showing a larger maximum pore diameter as well as a lower minimum pore diameter.

This phenomenon was attributed to the damage cascade made possible by the existence of an adjacent plane of graphene. It also allowed for the inter-layer bonding of dangling carbon chains, causing a decrease in effective pore size.

The damage caused by the damage cascade in bilayer graphene is made visible in **figure 3**, around the energy range of 25keV – 100 keV. The same energy range where the pore diameter is maximum, and the pore quality is at a minimum.

Pore quality was found to be higher for lower relative bombardment energies.
It was observed that for low energies, perfectly circular pores were tuned in monolayer graphene. The self healing ability of graphene[5] also allowed for recombination of the produced defects, greatly increasing the pore quality.

Conclusion

Classical molecular dynamics simulations were performed to simulate the production of nanopores on monolayer and bilayer graphene membranes.
C60 fullerene bombardment of graphene was proved to be a valid and precise method for producing nanoporous graphene membranes.

By analyzing and comparing the properties of tuned nanopores on monolayer and bilayer graphene, the mechanism of damage cascade and its effects on the tuned nanopore was delineated

Acknowledgements & References

A special thanks to my PI, Dr. Lin Shao, and my graduate student mentor, Kenneth Cooper, for their invaluable guidance and effort, making this study possible.

I would also like to acknowledge the TAMU HPRC as being a crucial resource in making my research possible.

1) Thompson, A. P., Aktulga, H. M., Berger, R., Bolintineanu, D. S., Brown, W. M., Crozier, P. S., in 't Veld, P. J., Kohlmeyer, A., Moore, S. G., Nguyen, T. D., Shan, R., Stevens, M. J., Tranchida, J., Trott, C., & Plimpton, S. J. (2022). LAMMPS - a flexible simulation tool for particle-based materials modeling at the Atomic, Meso, and continuum scales. *Computer Physics Communications*, *271*, 108171. https://doi.org/10.1016/j.cpc.2021.108171
2) Evans, D. J., & Holian, B. L. (1985). The nose–hoover thermostat. *The Journal of Chemical Physics*, *83*(8), 4069–4074. https://doi.org/10.1063/1.449071
3) Stuart, S. J., Tutein, A. B., & Harrison, J. A. (2000). A reactive potential for hydrocarbons with intermolecular interactions. *The Journal of Chemical Physics*, *112*(14), 6472–6486. https://doi.org/10.1063/1.481208
4) Ziegler, J. F., & Biersack, J. P. (1985). The stopping and range of ions in matter. *Treatise on Heavy-Ion Science*, 93–129. https://doi.org/10.1007/978-1-4615-8103-1_3
5) VijayaSekhar, K., Acharyya, S. G., Debroy, S., Miriyala, V. P., & Acharyya, A. (2016). Self-healing phenomena of graphene: Potential and applications. *Open Physics*, *14*(1), 364–370. https://doi.org/10.1515/phys-2016-0040