Atomically Thin Nanoporous Graphene Membranes for Fluid Separation

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Abstract

Membrane separation applications such as water desalination and carbon capture require high permeance and selectivity. For such processes, nanoporous graphene membranes promise 100-fold higher permeance at comparable selectivity to conventional polymer membranes, but remain under development. This thesis reports fluid permeance through both simulated and experimental graphene nanopores. Molecular dynamics simulations were performed to investigate liquid advection-diffusion through graphene nanopores and how the transport rates differ from continuum predictions. Furthermore, a technique for measuring the gas permeance of nanoscopic areas of graphene was developed. Here, a single layer of graphene seals a ~10 nm diameter hole in a multi-layer graphene nanoballoon over a pressurized cavity and atomic force microscopy is used to track its deflection over time. The results demonstrate helium/air selectivity through defects in five-layer graphene. We anticipate that this measurement technique can be adapted to determine the permeance of other atomically thin materials as well.

Keywords

Atomically thin membranes, graphene, nanopore, membrane, flow rate, pore geometry, Sherwood number, Péclet number, molecular dynamics simulation, argon, separation
Summary for Lay Audience

Fluid separation strategies are necessary in industrial processes to meet demands including product output, standards of quality, emissions regulations, among other things. Techniques such as water desalination and carbon capture separate fluid components by forcing them across a porous membrane. A pressure gradient is used to control the direction of fluid flow and undesired materials are removed based on molecular size, spatial arrangement, or other interactions with the membrane. Membrane performance is measured by permeability and selectivity, which relate to how well a fluid can flow through the membrane and how well the membrane can remove unwanted components of the fluid, respectively. Typical membranes are unable to achieve both high permeability and high selectivity and may face problems with chemical reactivity and mechanical strength. Alternatively, single layer graphene provides low resistance to flow, supports selective nanopores, and is mechanically and chemically robust given its size. We analyzed the effects of pore size and applied pressure on various fluids across simulated and experimental single layer graphene nanopores. This thesis reports fluid permeation rates across 1-10 nm diameter pores at applied pressures up to 200 atm (simulated) and 1 atm (experimental). Simulations were performed to understand liquid flow through graphene nanopores, and how these flow rates differ from predictions for larger-scale pores. Furthermore, we discuss the development of a method for measuring gas flow rates through nanoscale areas of atomically thin materials. The results demonstrate helium/air selectivity through defects in five-layer graphene. We anticipate that this measurement technique can be adapted to determine the permeance of other atomically thin materials as well. However, significant development work is still required if graphene is to compete with current membrane technology.
Co-Authorship Statement

This thesis was written by Anika Wong with contributions from supervisor Michael Boutilier. All molecular dynamics simulations, laboratory experimentation, graphene transfer, pressure chamber design, and silicon wafer fabrication were performed by Anika Wong. Molecular dynamics simulation processing was performed by both Anika Wong and Dr. Michael Boutilier.

Scanning electron microscopy, nanofabrication, and FIB drilling was performed at the Nanofabrication Facility at Western University with the help of Tim Goldhawk and Todd Simpson. Pressure chamber fabrication was done by University Machine Services at Western University. This work also made use of the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) program from Sandia National Laboratories and computing resources available at the Shared Hierarchical Academic Research Computing Network (SHARCNET Graham cluster, www.sharcnet.ca) and Compute Canada (CC Cedar cluster, www.computecanada.ca).
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## Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$A$ or $A_p$</td>
<td>nominal membrane pore area</td>
</tr>
<tr>
<td>$a$ or $r_p$</td>
<td>nominal membrane pore, suspended graphene, or support cavity radius</td>
</tr>
<tr>
<td>$A_{avg}$</td>
<td>average membrane pore area</td>
</tr>
<tr>
<td>$A_e$</td>
<td>effective membrane pore area</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
</tr>
<tr>
<td>APS or $(\text{NH}_4)_2\text{S}_2\text{O}_8$</td>
<td>ammonium persulfate</td>
</tr>
<tr>
<td>Ar</td>
<td>argon</td>
</tr>
<tr>
<td>$\Delta C$</td>
<td>concentration difference</td>
</tr>
<tr>
<td>$c$ or $K$</td>
<td>geometric constants</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>methane</td>
</tr>
<tr>
<td>Cu</td>
<td>copper</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
</tr>
<tr>
<td>$\mathcal{D}$</td>
<td>fluid self-diffusivity</td>
</tr>
<tr>
<td>$\delta$</td>
<td>suspended graphene deflection</td>
</tr>
<tr>
<td>$D_c$</td>
<td>distance between the centres of opposing pore edge atoms</td>
</tr>
<tr>
<td>$D_e$</td>
<td>effective membrane pore diameter</td>
</tr>
<tr>
<td>DI</td>
<td>deionized</td>
</tr>
<tr>
<td>$D_m$</td>
<td>diameter of the gas molecule</td>
</tr>
<tr>
<td>$\frac{dn}{dt}$</td>
<td>gas molar flow rate in or out of a microcavity</td>
</tr>
<tr>
<td>$D_p$</td>
<td>nominal pore diameter</td>
</tr>
<tr>
<td>DRIE</td>
<td>Deep Reactive Ion Etch</td>
</tr>
</tbody>
</table>
\[
\frac{dV_b}{dt}
\]
bulge volume leak rate in or out of a microcavity

\[D_{vdw}\]
van der Waals diameter of the pore edge molecule

\[\varepsilon\]
potential well depth for the intermolecular interaction between two atoms

\[E\]
Young’s modulus

FCC
Face-Centred Cubic

FEB
Focused Electron Beam

FIB
Focused Ion Beam

Ga or Ga\(^+\)
gallium

Gr
graphene

\[H\]
depth of support cavity

H or H\(_2\)
hydrogen

He
helium

HF
hydrofluoric acid

HP
high-pressure

IPA
isopropyl alcohol

\[k_B\]
Boltzmann’s constant

\[L\]
membrane pore length

LAMMPS
Large-scale Atomic/Molecular Massively Parallel Simulator

\[L_e\]
effective membrane pore length

LJ
Lennard-Jones

LP
low-pressure

\[\dot{m}\]
fluid mass flow rate

MATLAB
MATrix LABoratory

MD
Molecular Dynamics
n the fluid number density
N\textsubscript{2} nitrogen
NVT canonical ensemble for molecular dynamics simulations
O\textsubscript{2} oxygen
OH hydroxyl group
\(\Delta P\) pressure difference, \(\Delta P = \)
P or \(P_{int}\) microcavity internal pressure
\(P_{atm}\) atmospheric pressure
PCTEM Polycarbonate Track Etched Membranes
\(Pe\) Péclet number
\(P_{Ext}\) microcavity external pressure
PMMA polymethyl methacrylate
PR Photoresist
\(\sigma\) distance where the intermolecular potential between two atoms is zero
SATP Standard Ambient Temperature and Pressure
SEM Scanning Electron Microscope
SF\textsubscript{6} sulfur hexafluoride
\(Sh\) Sherwood number
SiN silicon nitride
SiO\textsubscript{2} silicon oxide
SPC/F Simple Point-Charge Flexible water potential model
T temperature
TEM Transmission Electron Microscopy
TIP4P Transferable Intermolecular Potential 4 Point water potential model
Viscosity or \(\mu\) fluid viscosity
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V$</td>
<td>average fluid velocity</td>
</tr>
<tr>
<td>$V_o$</td>
<td>cavity volume</td>
</tr>
<tr>
<td>$V_b$</td>
<td>nanoballoon bulge volume</td>
</tr>
<tr>
<td>VMD</td>
<td>Visual Molecular Dynamics</td>
</tr>
<tr>
<td>$W$</td>
<td>graphene wall side length</td>
</tr>
<tr>
<td>$w$</td>
<td>graphene wall thickness</td>
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</tbody>
</table>
Chapter 1

1 Introduction

Membrane-facilitated fluid/particle or fluid/fluid separation processes such as water desalination and carbon capture use porous barriers to determine the removal of specific components (salt and carbon dioxide in the previous examples, respectively) based on criteria ranging from particle size to chemical interaction. In these processes, gradient forces applied across a porous membrane control the fluid flow direction while the membrane pores control component passage and flow rate. Membrane performance is based on the ability for the desired fluid material to pass through the membrane (permeability), and the ability for the membrane to reject all other species that are not the desired component (selectivity). It is also important for a membrane to be operationally robust, such that it is chemically and mechanically strong and can withstand a variety of operating conditions. An ideal membrane can provide high purity filtration at high flow rates.\(^1\) In reality, current industrial membranes face a trade-off between permeability and selectivity which limits the membrane performance. Membranes can also be susceptible to chemical and mechanical damage such as fouling, chemical reactivity, or fracture under high pressures.\(^2\) In cases such as water desalination it would be beneficial for the membrane to be chlorine resistant and for carbon capture processes the membrane must maintain high oxygen permeability.\(^1\) Furthermore, there are economic benefits to producing a membrane with greater permeation abilities. Cohen-Tanugi et al.\(^3\) demonstrated that as permeability for desalination membranes increases by 3 times, the membrane area and energy consumption can be reduced by up to 40%.

New atomically thin materials such as graphene can theoretically overcome the limits of conventional membranes due to their ability to support highly selective nanoscale pores, maximize permeation, and maintain high chemical and mechanical strength.\(^1,4\) Membrane-facilitated gas transport mechanisms depend on membrane pore size, gas condensation, and surface adsorption while liquid mechanisms depend on membrane pore size, electrostatic interactions between the pore and fluid molecules, and steric effects.\(^1\) Porous monolayer graphene possess minimal flow resistance as a result of its atomic thickness of 0.34 nanometers.\(^5\) Pristine graphene can withstand pressure differences of more than one atmosphere and is naturally impermeable to gases, however, nanopores similar in size to
individual molecules can be created in this material through methods such as oxygen plasma etching, UV-ozone exposure, and electron beam drilling to allow fluid molecules to pass through.\textsuperscript{6-8} Molecules smaller than the nanopores can pass through the membrane while larger molecules cannot, resulting in selective species filtration based on molecular size (molecular sieving).

Prior studies have shown that graphene can have high and moderate selectivity in micrometer and centimeter scale areas respectively, even at high flow rates\textsuperscript{1}. Additionally, it has been shown that graphene membranes can exceed conventional membrane permeation rates due to their atomic thickness.\textsuperscript{2,4,7,8} Molecular dynamics simulations have also shown that graphene membranes can potentially provide fluid separation permeation rates in excess of conventional membranes\textsuperscript{9}. These promising indications serve as the basis for further research.

However, the flow rates through nanoscale pores in atomically thin membrane experiments cannot be measured using conventional fluid flow tools. Bunch et al. (2008)\textsuperscript{6} developed a method to indirectly measure the rate of flow through a graphene nanopore or defect. In this process, graphene is suspended over a small cavity and subsequently charged with gas to create a pressure difference across the membrane (Figure 1.1). This gradient produces a deflection in the graphene (a bulge inwards or outwards like a balloon) which can be measured using an Atomic Force Microscope (AFM) (Figure 1.2c). The AFM measures surface height of a sample and the measured graphene “nanoballoon” deflection over time (the rate of inflation or deflation) can be used to determine the flow rate.

\textbf{Figure 1.1:} (a) Side view of the graphene monolayer sealed cavity after transfer. (b) Positive graphene deflection as a result of positive pressure difference. (c) Negative graphene deflection as a result of negative pressure difference.
Figure 1.2: Image obtained from Bunch et al. (2008) (a) Representation of a graphene monolayer sealed cavity with dimensions (inset) 4.75 \( \mu \text{m} \times 4.75 \mu \text{m} \times 380 \text{ nm} \). (b) Positive pressure difference makes the graphene deflect outwards to create a nanoballoon. The SiO\(_2\) layer is 440 nm. (c) Atomic force microscope (AFM) image (tapping mode) of a multilayer nanoballoon under positive pressure difference.

We will use this method to measure permeation rates through porous graphene membranes. We further extend this method to isolate the porous membrane area to \( \sim 10 \text{ nm} \) diameter areas, opening the possibility of measuring precisely machined nanopores in graphene or pores in other atomically thin materials that are difficult to suspend over micron scale areas or that have higher permeance than could otherwise be resolved. Our objective is to develop a general approach for measuring gas permeance through atomically thin materials and to confine the flow to an area sufficiently small to potentially locate in atomic resolution microscopes for later characterization. This work advances efforts to experimentally interrogate the structure-permeance relation of nanopores in atomically thin materials and develop high performance atomically thin membrane technology.

To advance the fundamental understanding of fluid transport through nanopores in atomically thin materials, we further conduct molecular dynamics simulations of liquid flow through graphene nanopores. Prior studies have examined the desalination and small molecule separation performance of subnanometer pores in graphene with various structures (Figure 1.3).\(^5,9,10,11\) However, understanding the permeance of larger graphene nanopores, with low selectivity to solute molecules, is also important in practical membrane design and has received little attention. Defects in the graphene lattice and created during membrane fabrication form nonselective leakage pathways through the membrane that need to be
addressed in membrane design.\textsuperscript{12} Furthermore, nanometer scale pores are intentionally created in nanofiltration or ultrafiltration membranes to provide high permeance. Graphene membrane modelling commonly includes continuum fluid mechanics models for advection and diffusion through these larger nanopores. However, continuum fluid mechanics is not reliable for the <10 nm diameter pores of interest, even for uncharged liquid transport.\textsuperscript{4,8,11,13,14} We use molecular dynamics simulations to quantify the deviation from continuum predictions for solute advection-diffusion through graphene nanopores. The results identify the limit of validity of continuum predictions for these systems and provide simple corrections to estimate sub-continuum flow rates.

\textbf{Figure 1.3}: Figure obtained from Cohen-Tanugi and Grossman (2012).\textsuperscript{9} Side view of the molecular dynamics simulation set up with saltwater on the right (high pressure side) and filtered water on the left (lower pressure side).

This thesis contributes to the understanding of nanoscale fluid dynamics, the advancement of nanoscale membrane technology research and development, and the applications of nanoscale membrane technology in society. Further studies may investigate graphene membrane permeability and selectivity for various compositional fluid mixtures, long-term operational integrity and performance, and economic analysis.
Chapter 2

2 Literature Review

In this chapter, we will review molecular dynamics simulations and current atomically thin membrane technologies as the basis for developing our own molecular dynamics simulations and experimental procedures.

2.1 Molecular Dynamics Simulations

According to Wang et al. (2017), various studies have calculated gas transport properties through graphene using two main approaches: quantum mechanical methods or classical molecular dynamics simulations. Using the former, the pore crossing energy barrier is calculated and used to estimate permeance and selectivity from an Arrhenius equation. Through molecular dynamics simulations, the permeance can be obtained directly. It was found that permeability and selectivity across atomically thin membranes depend appreciably on the diameter disparity between the gas molecule and the pore. Gas transport resembles effusion and depends on spatial arrangement when the pore size is larger than the gas molecule (steric regime), while it depends on the energy barrier created and repulsive interactions when the pore size approaches or is smaller than the gas molecule (activated regime).

In the steric regime, the effective pore area can be approximated by,

\[ A_e \approx \frac{\pi}{4} (D_p - D_m)^2 \]  

(2.1)

Here, \( D_p \) is the pore diameter defined by: \( D_p = D_e - \frac{D_{vdw}}{\sqrt{2}} \), \( D_e \) is the distance between the centers of opposing pore edge atoms, \( D_{vdw} \) is the van der Waals diameter of the molecules along the pore edge (0.34 nm for graphene), and \( D_m \) is the diameter of the gas molecule. This effective pore area is smaller than the nominal pore area given by \( A_p = \pi r_p^2 \) where \( r_p \) is the nominal pore radius. Simulations have shown that this model can predict the effective pore area and that gas transport is separated into the steric or activated regimes.
When there are two gas species involved, a third regime is included. Steric regime gas transport for both molecules occurs when membrane pores are large resulting in high permeance and low selectivity. Here, selectivity between the two gas species would be a ratio of the gas flow rates. Activated regime gas transport for both molecules occur with small pores resulting in low permeability and high selectivity. Steric regime gas transport for the smaller gas molecule and activated regime gas transport for the larger gas molecule occurs when the pore size is between the molecular sizes of the two species. In this last case, high permeability and molecular sieving occurs. These simulations show that a trade-off exists between permeability and selectivity, both of which depend on molecular size. Theoretical and experimental studies are also in agreement with these findings. Special exceptions occur in single layer graphene pores. Limitations of molecular dynamics simulations include quantifying \( >10^3 \) selectivities due to limited \( <100 \) ns simulation time and resulting molecule crossings.

Interest in using graphene membranes for desalination has resulted in the majority of molecular dynamics studies of liquid phase separation through graphene membranes focusing on water and ion transports.\(^1\) These studies found that water transport through membrane nanopores mainly depends on pore size. Water molecules permeate easily through nanopores of \( \geq 0.3 \) nm diameter however, hydrogen bonding, spatial arrangement, and functional group interactions affect permeation through nanopores \( <2 \) nm in diameter.\(^1\) It has been shown that hydrophilic groups on the pore edge can double the water permeation rate, while hydrophobic groups on the pore edge can decrease permeation by increasing the energy barrier. Alternatively, charged groups on the pore edge can increase permeation of oppositely charged ions, or decrease permeation of similarly charged ions. Furthermore, the size of hydrated ions can be larger than their dry counterparts which allows for size dependent molecular sieving in comparison to the smaller water molecule. Jain et al. (2015)\(^{15}\) developed simulations to show that graphene nanopores can demonstrate selective ion and water transport as a result of ion hydration and steric effects. Here, pore size and functional group interactions also played a large role in fluid transport. Suk and Aluru (2013)\(^{11}\) produced molecular studies which demonstrated that pressure-driven pure water transport could occur in 0.5 nm diameter
porous graphene membranes and that the resulting water flux is proportional to pore diameter and linear with pressure difference (Figure 2.1).

**Figure 2.1:** Obtained from Suk and Aluru (2013)\textsuperscript{11}. Simulated water flux across porous graphene with varied pore radii and pressure difference. Water flux is proportional with pore radii and linear with applied pressure difference.

Molecular dynamics simulations by Cohen-Tanugi and Grossman (2012)\textsuperscript{9} showed that <5.5 Å graphene pores with hydrogen and hydroxyl terminated bonds could reject salt ions at industrial reverse osmosis operating pressures. They studied how selective transport varied with properties such as pore size, chemistry, and pressure. They also found that forward osmosis salt rejection through graphene membranes was possible at flow rates of 10-100 L cm\textsuperscript{-2} day\textsuperscript{-1} MPa\textsuperscript{-1} or 2-3 times the conventional diffusive reverse osmosis membrane. Cohen-Tanugi and Grossman further concluded that desalination through graphene nanopores showed size and entropic dependent selectivity. They simulated pores with areas of 1.5-62 Å\textsuperscript{2} at applied pressures of 1-1500 MPa with one set of pores terminated with hydrophilic hydroxyl groups and the other set of pores terminated with hydrophobic hydrogen atoms. The pore sizes were selected based on the <1 nm pores used by Suk & Aluru (2013)\textsuperscript{11}, who suggested the possibility of tuning graphene pore functional groups to selectively reject hydrated ions. Cohen-Tanugi and Grossman obtained the flow rate by measuring the amount of water molecules which
crossed the membrane per unit time, and the salt selectivity was obtained by measuring the number of salt ions on the downstream side of the membrane and comparing it to the initial salt concentration on the upstream side. The water permeability demonstrated expected characteristics of flow through a cylindrical pore using the classical fluid dynamics Hagen-Poiseuille equation.\textsuperscript{16}

It was found that the pores with hydroxyl termination groups provided a 69-113\% increase in water permeability and 14-26\% lower salt rejection than the hydrogen terminated pores (Figure 2.2). This was due to the 25\% larger pore area available for water transport when using hydroxyl groups and the way these groups formed hydrogen bonds with both water and salt to facilitate permeation. While the pore water permeability was linearly proportional to pore area, the salt rejection was inversely proportional to pore area and applied difference. This inverse relationship for salt rejection was evident in larger pore sizes while small to medium sized pores for both termination groups demonstrated near 100\% salt rejection. The minimum salt rejection rate was a selectivity of 33\% at 222 MPa and the maximum pore diameter for salt ion selectivity was 5.5 Å.

\textbf{Figure 2.2:} Obtained from Cohen-Tanugi and Grossman (2012).\textsuperscript{9} (a) Representation of the pore area when terminated with H groups (white) and OH groups (red and white). (b) Water permeability linear with pore area and higher for OH-terminated pores. (c) Salt
rejection inversely related to pore area and applied pressure and lower for OH-terminated pores.

The accuracy of intermolecular potential models is a significant factor determining the validity of molecular simulation results. Cohen-Tanugi and Grossman (2012) simulated TIP4P (transferable intermolecular potential 4 point) water which uses a water model that represents water with four interaction sites (a negatively charged pseudo-atom is placed near the oxygen atom between the hydrogen atoms). This model includes water intermolecular polarization but excludes intramolecular polarization. This is because the intermolecular polarization, or steric effect, dominates the system mechanics. This was confirmed through parallel simulations using SPC/F (simple point-charge flexible) water models. This model represents water as a three-site molecule with flexible bonds. The comparison showed that both models provided similar molecular dynamics (MD) simulation results. The SPC/F salt rejection values observed in the largest and second largest pore sizes with hydrogen-terminated pore edges was within 1% of the TIP4P values when both were at an applied pressure of 148 MPa. It was shown that both models could be used but TIP4P was favourable due to the lower computational cost. A 72 g/L salt concentration (double that of seawater concentration) was used to increase interactions between ions and pore edge functional groups for greater result precision given a fixed simulation period. Salt ions and functional groups were modeled with Lennard-Jones and Coulombic parameters. The graphene membrane was fixed in the simulation and salt ions were not polarizable. It was expected that these approximations had negligible effect on transport and calculations were focused on a pressure range of 10-300 MPa for improved statistical convergence. The NVT ensemble at 300 K (Nosé-Hoover) was used which is the Canonical Ensemble in MD simulations where energy exchanges occur using a thermostat.

2.2 Atomically Thin Membrane Technologies

Recently, atomically thin materials have shown promise in selective mass transport at the nanoscale due to their potential to maximize fluid throughput and purity. These materials can support highly selective, natural or man-made nanometer pores due to their mechanical and chemical strength. Membranes produced from these methods sieve fluid
species based on molecular size and can be influenced based on spatial arrangement or interactions with the pore edge. Additionally, the atomic thickness of these membranes can present low flow resistance and possibly overcome the limits of current membranes. Laboratory experiments and molecular dynamics simulations have been performed to confirm the potential of atomically thin technology.

Three aspects are necessary to produce an atomically thin membrane: a continuous atomically thin material which can support nanopores, a mechanism to produce nanopores in the material, and a support platform to suspend the membrane material over (Figure 2.3). The membrane material must be mechanically robust to allow for handling without fracture, resist wear or delamination, and withstand high pressure gradients. The platform must allow for material suspension, manipulation, and the production of a pressure gradient across the membrane.

**Figure 2.3:** The main parts of an atomically thin membrane: (a) a continuous material layer is transferred onto a support platform and prepared for nanopore introduction. (b) A nanopore is introduced into the material.

In larger area graphene membrane experiments, the graphene is commonly suspended over an array of parallel pores in a support material. This avoids weakness produced by having graphene suspended over large areas. The diameter of the support pore is inversely related to the maximum pressure gradient the suspended membrane can endure. Characteristics of the support platform can affect membrane performance. A
support layer which provides transport resistance can limit leakage outside of selective pore areas, without sacrificing permeability. The support must also allow for membrane suspension and thus be porous to allow membrane surface exposure. It is also useful for the support to be mechanically and chemically robust, have a permeability greater than the membrane material, and have high adhesive properties to allow for membrane attachment. Support materials which have been used in atomically thin membrane experiments include low porosity polycarbonate track etched membranes (PCTEM) and microfabricated silicon.\textsuperscript{8,12}

Graphene has a sufficient mechanical stability for membrane production and analysis. It can withstand strains of 25\%, has a fracture strength of 130 GPa, and has significant adhesion energy and abrasion resistance.\textsuperscript{17-19} Molecular dynamics simulations have also shown that suspended graphene membranes over 1 μm diameter support pores can withstand pressures of up to 570 bar.\textsuperscript{20} Furthermore, it is beneficial for the membrane material to be chemically robust to limit chemical degradation in specific applications. Further studies are required to test the operational integrity (fouling, chemical resistance, etc.) of potential atomically thin membrane materials. The main methods of producing atomically thin membranes are by “top-down” or “bottom-up” synthesis.

### 2.3 Top-down vs. Bottom-up Synthesis

Top-down synthesis describes the manual production of nanopores in a continuous, atomically thin layer to produce a membrane (Figure 2.4a-c). Bottom-up synthesis describes the production of an atomically thin layer from a naturally nanoporous material to produce a membrane (Figure 2.4d-f). Chemical vapour deposition (CVD) and mechanical exfoliation are the main ways of acquiring atomically thin continuous layers of material for experimental applications. Nanopores can be introduced into these materials via ion irradiation, chemical etching, or plasma etching prior to or after layer production.\textsuperscript{1} According to Wang (2017)\textsuperscript{1}, the different methods demonstrate different effects. Oxygen thermal oxidation can produce >10 nm diameter pores in graphene at low density while ozone thermal oxidation can produce gas selective pores at a high density. Oxygen plasma may produce and enlarge a high density of nanopores in monolayer graphene and control the pore size and density of natural defects. Ion irradiation coupled
with electron sputtering or chemical etching can also nucleate graphene defects and produce a high density of uniform nanopores. The ion beam angle of incidence, energy, and type dictate the defect type, and the ion beam fluence dictate the density of defect nucleation. Graphene presents a 30 eV energy barrier for ion irradiation which can result in a substantial pore size distribution in monolayer materials. Focused ion beams (FIB) can create down to 8 nm diameter pores with a smaller size distribution and focused electron beams (FEB) can create subnanometer diameter pores. Among alternatives, electrical pulses from an atomic force microscope (AFM) can be used to create nanopores in an atomically thin material. Chemical or plasma etching can be used to induce pores in large areas of atomically thin materials such as those grown via chemical vapour deposition. Focused ion beams can produce pores to cover smaller areas of material and atomic force microscopy or electron beams can be used for pore production in microscale areas.

**Figure 2.4:** (a-c) Top-down vs (d-f) Bottom-up Synthesis. (a) A single atomically thin continuous layer (e.g. graphene) is obtained and (b) transferred onto a support platform (e.g. Si wafer). (c) A nanopore is introduced into the graphene layer using a focused ion beam (FIB). (d) An intrinsically nanoporous material is obtained and (b) a single layer is removed through mechanical exfoliation (tape technique). (f) The extracted nanoporous layer is transferred onto a support platform (e.g. Si wafer).

The benefits of bottom-up synthesis include the creation of specialized pores at high density with features intended for their applications. Graphidyne formed through cross-linking hexaethynylbenzene on copper in nitrogen can potentially allow for selective
hydrogen, water, and proton transport. Top-down synthesis methods such as chemical vapour deposition (CVD), can also be modified into hybrid fabrication techniques. Introducing etchants during CVD, varying the grown precursor and etchant, and using catalytic substrate templating or substitutional doping can produce pores in the material during growth. Typically, top-down synthesis methods have been used for membrane applications as bottom-up synthesis has difficulty producing large areas of continuous membrane material. However, top-down synthesis still has limits on commercial availability and material quality where intrinsic defects, grain boundaries, and wrinkles can produce experimental leaks. The resulting range of pore sizes and defects in the material dictate membrane permeability and selectivity. The largest pore size will determine the selectivity of the fluid species and the existence of leaks can affect the permeability. Even with a high sensitivity to defects, atomically thin membranes are predicted to exceed conventional membranes with levels of permeance which range from $10^4$ to $10^8$ GPU for gas separation and $>1,000$ l m$^{-2}$ h$^{-1}$ bar$^{-1}$ for water desalination.¹

2.4 Current Technologies

Bunch et al. (2008)⁶ showed that pristine graphene is impermeable to gases down to the size of helium which paved the way for creating highly selective graphene membranes with limited leakage. To test this, Bunch used mechanical exfoliation to suspend a single layer of pristine graphene over predefined silicon oxide microcavities. Bunch then placed the membrane sample in a pressure chamber with N$_2$ gas at 690 kPa for 3 hours and measured an outward deflection in the graphene membrane. Placing the sample in a pressure chamber under vacuum (0.1 Pa) for 4 days resulted in an inward deflection. The pressure difference in the balloon could be indirectly measured through the mechanical resonance frequency. Since the surface tension changes when a pressure difference across the membrane exists, the resonance frequency changes. This allows for the measurement of elastic constants of the membrane material. It was shown that atomically thin graphene layers demonstrate bulk graphite stiffness. Consistent helium, argon, and air leak rates were observed in stacks of 1-75 layers of graphene. Since the leak rate was not affected by the number of graphene layers used, this suggested that the measured diffusion was through the SiO$_2$ support material as opposed to through the graphene. Bunch concluded
that graphene layers are impermeable to standard gases and successfully developed a method to measure the leak rate across atomically thin layers with applied pressure gradients. This study showed that the nanoballoons retained the gas volume and that gas transport does not occur even through natural graphene defects. However, other studies have found that the small defects in typically impermeable pristine graphene monolayers could be selectively permeable to protons.¹

![Graphene Leak Rates](image)

**Figure 2.5:** Obtained from Bunch et al. (2008).⁶ Gas leak rates as a function of graphene thickness (number of layers). Leak rates remained constant regardless of thickness, suggesting that pristine graphene is impermeable to standard gases.

Boutilier et al. (2014)²³ explained that the random alignment of defects in multilayer stacked graphene membranes follows an exponential decrease in permeability and a Knudsen limit is approached for selectivity (Figure 2.6). This was further supported by Kim et al. (2013)²⁴ whom used 5-layer stacked graphene to enhance a polymeric membrane barrier for O₂/N₂ separation. This experiment showed a selectivity that exceeded the Knudsen limit likely explained by graphene defects and gas transport between the graphene layers.
Figure 2.6: Obtained from Boutilier et al. (2014)\textsuperscript{23} (a) Pores in the polycarbonate track etched membrane (PCTEM) support platform. (b) Covered PCTEM pores and defect overlaps after a layer of graphene is transferred onto the PCTEM. (c) After a second layer of graphene is stacked onto (b) there are less exposed cavities as a result of defect overlap.

Koenig et al. (2012)\textsuperscript{7} also performed mechanical exfoliation of pristine graphene and suspended two layers over 5 µm diameter pores in a fabricated SiO\textsubscript{2} platform. Photolithography was used to define arrays of circles in the silicon support and reactive ion etching developed these circles into cavities resembling “wells”. The microcavities were charged with various gases at 300 kPa for 4-12 days and an AFM was used to calculate leak rate as a function of membrane deflection. The determined rate was consistent with that through SiO, which was the expected pathway of gas transport. Koenig then produced single gas transport dominant nanopores in the bilayer pristine graphene nanoballoons using ultraviolet induced oxidative etching and monitored gas permeance through the membranes. The nanoballoons with a nanopore deflated in minutes while those without a nanopore deflated in hours. By using a mixture of gases, it was shown that a nanoballoon with a ~0.34 nm diameter pore selectively allowed gas transport of molecules <0.34 nm in size (H\textsubscript{2}, CO\textsubscript{2}) but rejected larger molecules (Ar, N\textsubscript{2}, and CH\textsubscript{4}) (Figure 2.7). Another membrane in this experiment with a ~0.49 nm diameter pore selectively allowed gas molecules smaller in size than SF\textsubscript{6} molecules.
Figure 2.7: Obtained from Koenig et al. (2012). Gas leak rates out of the graphene nanoballoons before (black) and after (red) nanopore introduction as a function of gas molecular size. Nanoballoon Bi-3.4 Å demonstrated H$_2$ and CO$_2$ selectivity (molecular size <0.34 nm).

Celebi et al. (2014) produced a gas and water impermeable layer using CVD grown graphene placed onto an SiN$_x$ support containing 4 µm pores. Celebi then proceeded to introduce $10^3$-$10^6$ nanopores in the material using Ga ion and He ion beam milling. Nitrogen gas demonstrated pressure independent and diameter dependent membrane permeability. Transport consistent with the Knudsen effusion was observed in nanopores ≤50 nm in diameter and transport consistent with the modified Sampson’s model was shown in larger pores (Figure 2.8a). Selectivity based on effusion transport behavior is important for applications intended to separate gas mixtures with large mass differences. Celebi et al. (2014) tested species selectivity using gas mixtures (Figure 2.8b). The smallest pores demonstrated selectivity consistent with effusion theory and decreased as pore diameter increased. Furthermore, they recorded water flow rates in 50 nm diameter pore membranes that were 5-7 times greater than the conventional ultrafiltration membrane. Gas transport rates were also observed to be 2-3 times greater than through commercial membranes.
Sacrificial polymer layers have been used to support CVD grown graphene layers during transfer onto other substrates. However, it can lead to surface contamination when the polymer leaves a residue behind after removal.¹ Zhang et al. (2016)²⁵ developed a polymer-free liquid-liquid graphene transfer method to eliminate the effects of polymer residues. In this procedure, CVD grown graphene on copper was floated on top of a layer of 0.1 M (NH₄)₂S₂O₈ (ammonium persulfate) copper etchant while nonpolar, inert, low-viscosity organic hexane was layered on top using a syringe, subsequently covering the top (graphene) side of the graphene on copper piece (Figure 2.9). The hexane acts as a boundary layer, protecting the graphene during the etching and rinsing processes by preventing physical drift and surface tension induced tearing during handling. In previous experiments, CVD grown graphene is typically rinsed on an air-water interface which has a high surface tension of 72.8 mN/m. Using a hexane-water interface lowers the surface tension to 45 mN/m, reducing the shear forces on the graphene. After rinsing, the graphene sheet is transferred to the desired substrate. The hexane rapidly evaporates and leaves no residue on the graphene and no doping occurs. The gentle nature of the nonpolar hexane layer allows for transfer onto desired substrates with topographically

Figure 2.8: Obtained from Celebi et al. (2014).⁸ (a) Nitrogen permeance through various pore diameters which is consistent to Knudsen effusion (horizontal dashed line) for small diameters and modified Sampson’s model (curved dashed line) for large diameters. (b) Gas selectivity for different pore diameters as a function of gas molecular weight (from left to right: H₂, He, CH₄, N₂, CO₂, SF₆).
challenging shapes. Zhang et al. (2016) successfully transferred monolayer graphene membranes onto AFM tips and transmission electron microscopy (TEM) grids.

Figure 2.9: Obtained from Zhang et al. (2016). The polymer free, hexane facilitated CVD grown graphene transfer method onto desired substrates.

According to Wang et al. (2017), most experimental findings agreed with simulated results, however, single layer graphene nanoballoon membranes would present gas transport which fluctuated on the scale of minutes. Experiments on various pores showed that gas and fluid transport in small pores would have dynamic fluctuations with no clear origin. These fluctuations could be limited with improved experimental controls or simulation models. Jain et al. (2015) isolated graphene subnanometer intrinsic pore defects common in CVD graphene fabrication (Figure 2.10). A Ga+ focused ion beam was used to induce a 30-nm diameter nanopore in the SiN support material. CVD grown monolayer graphene was then suspended over the SiN pores using a wet transfer technique. Since there is a 70-nm spacing between graphene defects, Jain recognized that a 30-nm diameter SiN pore would isolate a single defect with high probability. Limiting the area of study can provide results of higher resolution and limit external factors.
Figure 2.10: Obtained from Jain et al. (2015).\textsuperscript{15} (a) The spacing between intrinsic defects in CVD grown graphene is 70 nm. (b) Creating a 30 nm diameter pore in the SiN support material can guarantee that only one defect will be present within the area after (c) graphene transfer on to the support.

2.5 Conclusions

Many theoretical studies provide common evidence that atomically thin membranes have the ability to provide high fluid permeability and selectivity though there are some discrepancies across simulations. Few experiments have been performed to demonstrate these properties. Some major challenges remain to realize practical atomically thin membrane technology. The effects of surface contaminants, pore edge functional groups, and spatial arrangements on fluid transport are still not fully understood. Further experimentation must explore these effects so that atomically thin membranes can be tailored to better suit specific applications. It is difficult to produce arrays of uniform nanopores in membranes at high densities whether by top-down or bottom-up synthesis. Molecular dynamics simulations can be used to identify new nanopore creation methods and atomically thin membrane applications. Nucleation of defects during membrane material synthesis, defect leakage, and poor membrane quality can affect fluid transport. Additionally, the size distribution of the pores or defects could dominate fluid transport if they are larger than the intended pore size. These aspects can be managed through controlled experimentation and improved synthesis. Furthermore, aspects of the membrane itself must be understood to achieve the required performance for the application. Membrane material, support material, and nanopore size distribution dictate membrane permeability and selectivity. The wear of membranes in real applications must also be understood to limit fouling or degradation.
While atomically thin membrane technology requires further work through controlled experimentation and theoretical studies, the potential outcomes could be worth the additional research. Atomically thin membranes have shown promise in exceeding conventional membrane performance. The atomic thickness of the material and the atomic size of the membrane nanopores allow for high permeability and selectivity based on molecular size. It is also possible that the mechanical and chemical strength of the atomically thin membrane material can allow it to operate under harsher conditions by exhibiting chemical resistance for specific applications (e.g., chlorine for desalination), high pressure gradients or concentration gradients, and withstand maintenance procedures.
Chapter 3

3 General Method and Equipment

Multiple iterations of the graphene membrane fabrication process occurred throughout the timeline of our project. While various support substrates and techniques were used to suspend the graphene, a few general steps for graphene transfer remained the same. These commonalities will be described here followed by a description of the common equipment used. Unique characteristics of each transfer process will be outlined in full in Appendix B-D.

3.1 Graphene Transfer

First, approximately 1cm$^2$ pieces of monolayer graphene on copper (from Graphenea or ACS Materials) were cut with razor blades. These pieces were then floated in a dish of ammonium persulfate solution (APS) such that the copper backside was in contact with the etchant surface (Figure 3.1). The graphene on copper (Gr/Cu) piece was etched until visual confirmation that the copper layer has been completely removed, leaving a clear graphene piece. At first visual of complete etching, a timer for 2 minutes was set for “over-etching” to ensure all the copper was removed. Afterwards, a glass slide was used to transfer the graphene into three consecutive deionized (DI) water baths and rinsed for 5 min each. The desired material (support substrate or another Gr/Cu piece) was then used to scoop out the graphene. The sample was air dried followed by an optional anneal step on a hot plate. If the graphene on copper piece suddenly turned significantly darker (indicating graphene contamination), or the floating graphene piece was torn significantly, a new Gr/Cu piece was etched. Larger pieces of Gr/Cu were used to minimize the effects of inevitable tears. Multilayer stacks of graphene were obtained by scooping the graphene layer onto new Gr/Cu pieces followed by transfer to the support substrate, or by scooping multiple times onto the existing support substrate.
Figure 3.1: Schematic of the graphene on copper etching process. (a) Etching, (b) scooping, and (c) rinsing steps are depicted. (d) Transfer onto a second piece of graphene on copper to create 2-layer graphene or (e) transfer onto a support substrate is possible.

3.2 Three Approaches

Two support materials and three graphene transfer techniques were used experimentally in this study. We ordered 10 µm thick polycarbonate track etch membranes (PCTEM) from Sterlitech which had random arrangements of either 0.2, 5, or 10 µm diameter through holes. Stacks of 0-3 layers of graphene were transferred onto each side of the PCTEM using a chlorotrimethylsilane-facilitated transfer method. The graphene adhered with van der Waals forces. Annealing was used optionally to relax the graphene and promote greater surface-surface contact for van der Waals adherence.

We started from adapting the procedure developed by Wang et al. (2015)\textsuperscript{22} and used a wet transfer process to place pristine single layer graphene over wells in PCTEM filters to create sealed volumes of gas. An AFM was used for visual confirmation of the transfer.\textsuperscript{6,7,22} The sample was then placed in a pressure chamber and pressurized with gas.
or subjected to vacuum so that the graphene bulges outward or inward respectively (Figure 3.2). This graphene deflection was measured via AFM as a function of time. Number of graphene layers and support material pore diameter was varied and gas flow rate was measured again.

![Figure 3.2: Representation of (a) suspended graphene over the support cavity and, (b) positive and (c) negative graphene deflection due to positive and negative pressure differences.](image)

Facing low graphene coverage on the PCTEM, difficulty locating the same pore for further analysis, and upon research providing support for longer deflation periods in silicon substrates, we developed our own Si wafer support platform with various cavity well sizes to use as a platform for testing atomically thin material membranes (more details in Chapter 5). Facing difficulties with graphene surface tearing during multilayer stacking, polymethyl methacrylate (PMMA) covered graphene was used to keep the graphene intact and improve stacking ability. After testing samples using this modified stacking technique on a new support material, further research regarding polymer residue effects on membranes and discovering a new polymer free transfer technique facilitated a final graphene membrane fabrication iteration.

A polymer free liquid-liquid wet transfer technique was used to transfer and stack single layers of graphene onto the SiO₂/Si wafer. Nanopores were then introduced in the
graphene multilayer stack via Focused Ion Beam (FIB) and graphene membrane deflection was measured again with the AFM. Finally, a single layer of graphene was used to cover the FIB introduced nanopore and deflection was analyzed. Ion bombardment was performed on the total area of the pore in expectation of creating a sub-nanometer pore in the previous FIB nanopore area (Figure 3.3). Gas flow rate was then analyzed again along with controls for comparison.

![Diagram](image)

**Figure 3.3:** Representation of the cavity and membrane after (a) a FIB nanopore is introduced, (b) after final layer of graphene is transferred to cover the FIB nanopore, and (c) after a nanopore is introduced via ion bombardment.

### 3.3 Optical Microscope

A Zeiss Axioscope optical microscope was used for wafer characterization. The reflected light and transmitted light options were used to identify the cavities. An Epi BF filter, 20x magnification and 0.4 HD EC EPIPLAN lens was used for image capture and wafer characterization.

### 3.4 Atomic Force Microscope

After graphene transfer using one of the three approaches, graphene deflection measurements were performed for successful samples using an Atomic Force Microscope (AFM) in ambient conditions or after charging with gas or vacuum. The resulting
membrane deflection measurement could be used to determine fluid permeance. The AFM measurement system contains five main parts: the sample stage, probe, cantilever, laser, and photodiode (Figure 3.4). The stage can be used to position and stabilize the sample with micrometer resolution. An AFM probe has a flexible cantilever which bends easily and behaves like a spring depending on the amount of force applied on the probe. A laser is focused on the cantilever and the intensity of reflected light is recorded by photodiodes to measure its deflection in response to applied force from the sample surface. The AFM probe can be used in direct contact with the sample (direct contact mode) or is oscillated near the surface of the sample at the cantilever’s resonant frequency (tapping mode). In both modes, the cantilever responds with high resolution to the sample topography.26

![Diagram of AFM features](image)

**Figure 3.4:** Schematic of the main AFM features.

An Oxford Instruments MFP-3D Origin AFM was purchased from Asylum Research for our deflection measurements. AFM Micro Cantilevers were purchased from Asylum Research Probes (Model AC240TS-R3) and Opus (Model 240AC-NA). AFM images were obtained using the AC Air Topography mode, varying the set point and drive amplitude parameters until a clear image and line traces were obtained. Earlier images for PMMA graphene transfer samples were acquired with the following AFM settings: set point of 0.7 V, drive amplitude of 1 V, and gain of 10. The final parameters used for polymer-free graphene transfer samples were: a set point of 1.25 V, drive amplitude of 300 mV, and gain of 10. The set point may need to be decreased to obtain a clear image as the maximum sample height decreases. Wide images were taken at a Scan Size of 50 µm, 128 Points & Lines, and a Scan Rate of 0.36 Hz. Close-up images of the cavities
were taken at a window size of 10-15 µm. The AFM line trace, 3D surface plots, masks, and properties tools were used for image analysis. The line traces were measured horizontally through the center of the cavity. Visual identification through the camera and the height trace view was typically used to locate support cavities. The phase trace view was used as double confirmation when the height trace view was ambiguous.

**Figure 3.5:** AFM camera view of a 5 µm diameter cavity wafer with graphene monolayer.

**Figure 3.6:** Comparison of the (a) AFM height trace view and (b) phase trace view used for visual identification of a cavity. Sample E1 (3 layers of graphene on a 5 µm cavity) after PMMA removal.

To obtain the desired volume measurement, the Mask Panel was used to select the cavity area while calculated values were displayed in the Roughness panel (Figure 3.7). Initially, the circular (or occasionally elliptical) area was selected based on approximate visual of the deflected membrane seen in the height trace. Later, a methodical approach was developed to maintain consistency across AFM scans over time. After a clear AFM
image of the cavity edges was obtained, these edges on the height trace or phase trace view were outlined with an elliptical mask tool and the calculated area was recorded (Figure 3.8). Multiple traces were performed until an average area could be used as a guide for future cavity mask traces. For each image, the circular areas which were masked were aligned as best as possible with the cavity edges seen in the height trace and phase trace views and within a ±0.5 µm² range of the guide cavity area. A sensitivity analysis was performed for some control cavities to determine whether this range would be acceptable given variance in the mask position and size. We found that for pores with the average 28 µm² area, the calculated volume of the deflected membrane displayed a maximum 5% sensitivity when within 1 µm² of the average (Table 3.1). As the accepted deviation from the average is increased, the range of sensitivity increases and becomes nonzero more frequently. Sensitivity calculations are given in Appendix G. A height line trace across the center of the cavity was obtained using the section panel (Figure 3.9). Finally, the “PlanetEarth256” ColorMap was used in 3D generations of the cavity topography (Figure 3.10).

**Table 3.1:** Sensitivity ranges for various control cavities on Sample K1 (5 layers of graphene on 5 µm cavity) and deviances from average area. Scanning days after major processing events indicated in the “Experiment” column.

<table>
<thead>
<tr>
<th>Cavity</th>
<th>Experiment</th>
<th>Sensitivity range [%] (A = A_{avg} ± 2 µm²)</th>
<th>Sensitivity range [%] (A = A_{avg} ± 1 µm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Charged in 1 atm air continuously for 5 days</td>
<td>-1 to 7</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>-5 to 6</td>
<td>-5 to 3</td>
<td>-1 to 1</td>
</tr>
</tbody>
</table>
Figure 3.7: Modify Panel and Analyze Panel used for cavity area and volume calculations.

Figure 3.8: (a) Height and (b) phase trace views of the chosen cavity. (c) Cavity outline and resulting mask. Areas in red are excluded from the (d) “Masked Image” statistics.
3.5 Pressure Chamber

Two pressure chambers were used during this experiment to charge samples with gases. Various charging gases (from Praxair or Lindy) were tested to determine molecular
sieving ability. A large 2 ½ gallon high pressure pot was purchased from VEVOR for air and vacuum experiments. We noticed gas leakage and created our own handheld pressure chamber. Using OnShape, we designed a circular pressure chamber 7.62 cm in diameter and 1.27 cm tall. The pressure chamber was composed of a top and a bottom piece with a platform for the sample. This pressure chamber and the screws, nuts, and washers were provided by University Machine Services at Western University. Screws, an O-ring, and metal tubing minimized gas leaking. Further details are in Chapter 5.

![OnShape 3D rendition of the two pressure chamber parts.](image)

**Figure 3.11:** OnShape 3D rendition of the two pressure chamber parts.

### 3.6 Scanning Electron Microscope

A scanning electron microscope (SEM) uses an electron beam to capture the details on a sample surface. A beam of electrons is condensed through a series of lenses and focused onto the sample (Figure 3.12). The electron beam can also be controlled to change the magnification or area. Upon contact with the sample, electrons are released from the sample and collected on the secondary electron, backscatter, and X-ray detectors. The scatter patterns provide information of the sample surface and composition. 27
Figure 3.12: Schematic of the main SEM features.

The ZEISS 1540XB SEM at the Western University Nanofabrication Facility was used to produce high quality images of the samples. Nanopores introduced by FIB could be visible in the SEM but not in the AFM. SEM images were obtained at 1.00 kV, working distance of 4.6 mm, 100-50k magnification, and using InLens Signal A detector.

3.7 Focused Ion Beam

A Focused Ion Beam (FIB) is used to etch samples by hitting the sample surface with ions until the material sputters and is ejected from the bulk as secondary ions or neutral atoms (Figure 3.13). The ZEISS 1540XB FIB at the Western University Nanofabrication Facility was used to introduce nanopores in the samples. The nanopores were produced at 30 keV and 1 pA for various time periods for different materials and nanopore sizes. A period of 2 seconds was used to create ~30 nm diameter pores in the samples with PMMA, and 15 ms and 25 ms was used to create ~10 nm and 30 nm diameter pores respectively, in polymer-free samples. All FIB work (including ion bombardment) was performed with the ion beam at normal incidence to the sample surface.
3.8 Ion Bombardment

Similar to the FIB, ion bombardment uses ions to knock out single atoms from the sample surface. The ZEISS 1540XB FIB at the Western University Nanofabrication Facility was also used to perform ion bombardment. The parameters used were 20 pA at 10kV (defocused to about 1/2 µm), 50x50 micron implanted area to 16 µC/cm² ion fluence for an ion bombardment of $10^{14}$ ion/cm². The scanning time was scaled by 0.1 and 1.0 for ion bombardment of $10^{13}$ and $10^{15}$ ion/cm² respectively. The ion beam was at normal incidence to the sample surface.

3.9 LAMMPS

In parallel to the laboratory experimentation, molecular dynamics simulations were used to study liquid phase molecular advection-diffusion through graphene nanopores. Simulations were performed in LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). A graphene membrane with a single nanopore of various diameters ($D = 1, 2, 3, 4, 5, 7, 9$ nm) was simulated in between two fluid reservoirs (Figure 3.14). Pistons at either end were used to apply external pressure on the fluid molecules to produce a pressure difference across the membrane ($\Delta P = 0, 5, 10, 25, 50, 100, 150, 200, 300$ atm). Visual Molecular Dynamics (VMD) was used for results visualization. MATLAB (MATrix LABoratory) was used to create atoms, format VMD-compatible data files, and generate data plots.
**Figure 3.14:** Visual Molecular Dynamics (VMD) (a) front view of a 3 nm diameter pore in graphene (grey) with Type 1 argon (red, lower pressure side of the membrane) and Type 2 argon (blue, higher pressure side of the membrane) visible. (b) Side view of the argon membrane crossings at timestep $2.5 \times 10^6$ with 25 atm piston (black) pressure difference.
Chapter 4

4 Molecular Dynamics Simulation

In parallel to our laboratory experimentation, we developed a Molecular Dynamics (MD) simulation of fluid flow through graphene nanopores with diameters of 1-9 nm for water and argon fluid across applied pressure differences of 0-300 atm.

Continuum fluid mechanics models for advection and diffusion are typically used to estimate transport rates through graphene membranes and serve as the guide for membrane design efforts. Prior molecular dynamics simulations have shown that advection rates through graphene nanopores can deviate from the continuum model by factors of ~2.11 These deviations from continuum can be quantified with molecular dynamics and help recognize the limits of the models. These simulations can also be used to introduce correction factors and estimate species transport rates in separation applications.

In this chapter, we develop a continuum expression for mass advection-diffusion in creeping flow through an orifice plate of arbitrary thickness consistent with the finite volume solution to within 3%. However, deviations from the continuum fluid mechanics behavior are expected as the membrane pores reach <10 nm in diameter. We seek to understand how molecular advection-diffusion differs from continuum predictions as the graphene nanopore size decreases, and the limits of the continuum advection-diffusion expression.

4.1 Methodology

Visual Molecular Dynamics (VMD) was used to initialize the coordinates for the central graphene sheet (membrane) and two water reservoirs on either side using the Nanotube Builder and Solvation Box tools respectively. MATLAB was used to replicate the VMD graphene sheet into two additional graphene walls for use as pistons on each end of the simulation box, enclosing the water reservoirs. MATLAB was also used to remove graphene atoms from the center of the graphene sheet membrane. A circle centered in the
middle of the graphene sheet with diameters: 1, 2, 3, 4, 5, 7, and 9 nm was used to determine which atoms in the graphene sheet will be removed. Graphene atoms with their centers located within the circle area were removed to produce the nanopore. After these changes were made, MATLAB was finally used to format LAMMPS compatible data files for each system which were used to initiate the simulations. VMD was used to visualize the complete graphene membrane system and confirm successful molecular dynamics modeling once the simulation started running.

The simulation setup was validated for water flow since the advective flow results could be compared to those of Suk and Aluru (2013). Subsequently, this methodology was used to simulate argon flow. Interactions between argon atoms are well modelled by a simple Lennard-Jones potential whereas accurately modeling water interactions can be more difficult. We chose to simulate argon flow to focus on the transport physics with less concerns of anomalous behaviors arising from the choice of interaction potential. Figure 4.1 depicts the sequence for the MD simulations of argon flowing through graphene nanopore diameters of 1, 2, 3, 4, and 5 nm and applied pressures of 0-200 atm.

**Figure 4.1:** Flowchart of the MD simulation process for the final argon simulation.
The water MD Simulation started with atom generation in VMD. First a square graphene sheet of length, $W$, in the x and y directions, was created at $z = 0$ nm, where $W$ is at least three times the magnitude of the intended nanopore diameter, $D$. Next, $W^3$ solvation boxes composed of water molecules were generated on each side of the graphene sheet such that there was 0.34 nm (carbon atom diameter) of space in the z-direction between the graphene and the water. A length of 3D was used in the z-direction because, from the continuum solution, we found that the pressure reaches within 1.2% of the bulk value at 2.5 diameters away from the membrane. Spaces of 0.34 nm were used between species to ensure there was no atom overlap which could prevent the simulation from starting. Larger simulations contained an $W^3$ fluid reservoir on the high-pressure (HP) side of the membrane and a $W \times W \times \frac{1}{3} W$ (x y z) fluid reservoir on the low-pressure (LP) side of the membrane to improve computational ability (Figure 4.2). Finally, using MATLAB, the graphene sheet was duplicated to the ends of the water reservoirs to act as external pistons, leaving another space of 0.34 nm in between water and graphene.

Pores in the graphene sheet at $z = 0$ nm were created by removing all carbon atoms from the graphene lattice within a circle of diameter $D$. Information regarding the dimensions for each water simulation are given in Table 4.1. The atom data of this system was then reformatted to match the LAMMPS program data file. This data file requires an atom number, molecule number, charge, and coordinates for each atom as well as any bonds and angles between corresponding atoms. This file also required the boundaries for the system and the total number of atoms, bonds, and angles listed.
Figure 4.2: VMD side views of the (a) 1 nm and (b) 5 nm diameter nanopore water simulations.

Table 4.1: Material parameters for the water simulation.

<table>
<thead>
<tr>
<th>Nanopore diameter [nm]</th>
<th>Graphene dimensions [nm x nm]</th>
<th>Graphene number of atoms</th>
<th>Membrane atoms removed</th>
<th>HP water dimensions [nm x nm]</th>
<th>HP water atoms</th>
<th>LP water dimensions [nm x nm]</th>
<th>LP water atoms</th>
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<tr>
<td>1</td>
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<td>10 x 10 x 10</td>
<td>96603</td>
<td>10 x 10 x 10</td>
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<tr>
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<td>8928</td>
<td>752</td>
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<td>2436</td>
<td>27 x 27 x 27</td>
<td>1934253</td>
<td>27 x 27 x 9</td>
<td>639957</td>
</tr>
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</table>

Real units, full atom style, 0.06667 timestep, reflective boundary on z, periodic boundaries on x and y, simple cubic lattice, and SPC/E (simple point-charge extended) water model parameters were used for this simulation. This model assumes water molecules have three interaction-sites and are rigid in an isosceles triangle orientation. Interactions between the graphene membrane and pistons were assumed negligible. The
Lennard-Jones (LJ) pair coefficients used are listed in Table 4.2. Here, the LJ parameters: \( \varepsilon \) and \( \sigma \) describe the intermolecular interactions between two atoms. Epsilon, \( \varepsilon \), represents the potential well depth, and sigma, \( \sigma \), represents the distance between the atoms at which the potential is zero. Water molecule velocities were randomly sampled from a Maxwell-Boltzmann distribution at 300 K while the graphene membrane was fixed in place, and the carbon pistons were fixed in the x-y directions. Atom positions were adjusted to minimize system energy before beginning equilibration. A Nosé-Hoover thermostat was applied in an NVT ensemble using the SHAKE algorithm to ensure the equilibrium bond lengths and angles are maintained between the oxygen and hydrogen atoms. A temperature damp parameter of 100 timesteps was used. An NVE (microcanonical) ensemble was applied on the pistons and were set to be influenced in the z direction by the water molecules. This ensemble represents an adiabatic process where the system does not undergo changes in moles, volume, or energy. The system was evolved in this state for 1 ns to reach equilibrium before external forces were applied on the graphene pistons. Pressure differences of 0, 5, 10, 25, 50, 100, 150, 200 and 300 atm were created across the membrane by setting one piston to apply 1 atm of pressure on the water reservoirs and the other piston to provide the desired pressure difference. Water molecule crossings were recorded over time.

**Table 4.2:** Water simulation Lennard-Jones pair coefficients used in LAMMPS.

<table>
<thead>
<tr>
<th>( \varepsilon ) [kcal mol(^{-1})]</th>
<th>( \sigma ) [Å]</th>
<th>Species Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08500</td>
<td>3.436</td>
<td>C-O</td>
</tr>
<tr>
<td>0.15535</td>
<td>3.166</td>
<td>O-O</td>
</tr>
<tr>
<td>0.00000</td>
<td>0.000</td>
<td>All other interactions</td>
</tr>
</tbody>
</table>

In the case of argon, we created the membranes and pistons in the same way using VMD and MATLAB. This time, nanopores with diameters ranging from 1 to 5 nm were used. Aerial views of these nanopores can be found in Figure 4.3. However, due to short range
repulsive forces between atoms, it is unlikely that argon atoms will reach this outer diameter. We define an effective pore area open to transport, $A_e$, by considering both the carbon atoms and argon atoms as hard spheres of diameters $2^{1/6} \sigma_{C-C}$ and $2^{1/6} \sigma_{Ar-Ar}$, respectively. These are the separations distances where two like atoms interacting by a Lennard-Jones potential exert zero force on one another. The effective pore area was calculated by hit and miss Monte Carlo integration with $10^8$ randomly selected $(x, y)$ argon atom center points in a square of side length $D$ centered on the pore. Points falling more than $2^{1/6}(\sigma_{C-C} + \sigma_{Ar-Ar})$ from any carbon atom do not overlap with these atoms and are counted in the open area. The effective diameter, $D_e$, was then calculated as the diameter of a circle with the calculated effective pore area (Equation 4.1).

$$D_e = \sqrt{\frac{4A_e}{\pi}}$$ (4.1)

**Table 4.3**: Calculated effective pore diameters for each simulation.

<table>
<thead>
<tr>
<th>Nominal pore diameter, $D$ [nm]</th>
<th>Effective pore diameter, $D_e$ [nm]</th>
<th>Effective pore length, $L_e$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.48</td>
<td>2.2</td>
</tr>
<tr>
<td>2.00</td>
<td>1.63</td>
<td>1.4</td>
</tr>
<tr>
<td>3.00</td>
<td>2.65</td>
<td>1.2</td>
</tr>
<tr>
<td>4.00</td>
<td>3.72</td>
<td>0.5</td>
</tr>
<tr>
<td>5.00</td>
<td>4.79</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Figure 4.3: VMD aerial view of the graphene membrane with (a) 1 nm, (b) 2nm, (c) 3nm, (d) 4nm, and (e) 5 nm diameter pores.

Illustrations depicting the effective pore area are shown in Figure 4.4 where the area available for argon transport is shown in green, and the area occupied by $2^{1/6}\sigma_{c-c}$ carbon atoms in graphene is shown in gray with the atom centers and lattice structure shown in solid black. The size of one carbon atom is shown as a dotted black circle. The area occupied by an argon atom with diameter $2^{1/6}\sigma_{Ar-Ar}$ in contact with a carbon atom is shown as a dotted blue circle. The purple circle shows the circle of diameter $D$, within which all carbon atoms were removed to create the pore. The area that the center of an argon atom can occupy without overlapping with a carbon atom is the effective area, and is shown in green.
Figure 4.4: Geometry of (a) 1 nm, (b) 2 nm, (c) 3 nm, (d) 4 nm, and (e) 5 nm diameter pores illustrating the effective area available for transport (green).

The argon fluid reservoirs were created using the LAMMPS create_atoms command and a spacing of 0.34 nm was maintained between the reservoirs and the carbon materials. Dimensions for each species for the different nanopore sizes are provided in Table 4.4 and side views of the simulation set up are shown in Figure 4.5. Real units, full atom style, 0.06667 timestep, periodic boundaries, and face centered cubic lattice were used. Argon velocities were initialized from a Maxwell-Boltzmann distribution at 85 K was used. The system energy prior to equilibration. Nosé-Hoover n thermostat was to maintain NVT conditions. The pistons were free to move in the z-direction and interactions between the graphene membrane and pistons were assumed negligible. The Lennard-Jones pair coefficients used are listed in Table 4.5. The system equilibrated in this state for a period of 1 ns before the external forces were applied on the graphene pistons. Pressure gradients of 0, 5, 10, 25, 50, 100, 150 atm, and 200 atm were created across the membrane. After the equilibration, the argon molecules on each side of the membrane were tagged as Type 1 and Type 2 argon depending on which side it was
located on after this equilibration. The pressure difference was then applied through the pistons on either side of the membrane and the number of crossings of each argon type were recorded over time. Simulations for each nanopore size and applied pressure difference were kept running until the recorded argon crossings reached equilibrium or sufficient crossings were obtained.

**Table 4.4:** Argon simulation material parameters.

<table>
<thead>
<tr>
<th>Nanopore diameter [nm]</th>
<th>Graphene dimensions [nm x nm]</th>
<th>Graphene number of atoms</th>
<th>Membrane atoms removed</th>
<th>HP argon dimensions [nm x nm]</th>
<th>HP argon atoms</th>
<th>LP argon dimensions [nm x nm]</th>
<th>LP argon atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 x 5</td>
<td>1008</td>
<td>28</td>
<td>5 x 5 x 5</td>
<td>3249</td>
<td>5 x 5 x 5</td>
<td>3249</td>
</tr>
<tr>
<td>2</td>
<td>10 x 10</td>
<td>3936</td>
<td>270</td>
<td>10 x 10 x 20</td>
<td>50653</td>
<td>10 x 10 x 10</td>
<td>25326</td>
</tr>
<tr>
<td>3</td>
<td>10 x 10</td>
<td>3936</td>
<td>270</td>
<td>10 x 10 x 20</td>
<td>50653</td>
<td>10 x 10 x 10</td>
<td>25326</td>
</tr>
<tr>
<td>4</td>
<td>10 x 10</td>
<td>3936</td>
<td>270</td>
<td>10 x 10 x 20</td>
<td>50653</td>
<td>10 x 10 x 10</td>
<td>25326</td>
</tr>
<tr>
<td>5</td>
<td>27 x 27</td>
<td>8928</td>
<td>752</td>
<td>15 x 15 x 25</td>
<td>145824</td>
<td>15 x 15 x 15</td>
<td>87808</td>
</tr>
</tbody>
</table>

**Figure 4.5:** VMD side views after 1 timestep of the argon equilibration period for (a) 1 nm diameter and (b) 5 nm diameter simulations
Due to random molecular diffusion, argon molecules pass from left to right and from right to left across the nanopore during the simulations, regardless of which side is held at higher pressure. By tracking the net argon crossings through the nanopore over time, we obtain the net flow rate through the nanopore. By further tracking the total number of argon molecules that started on the high-pressure side and ended up on the low-pressure side, we can estimate the total rate of transport due to advection and diffusion from the high-pressure side to the low-pressure side. Similarly, by recording the number of crossings from the low-pressure side to the high-pressure side, we can estimate the total transport due to diffusion against advection. Thus, we are able to estimate the total flow rate and advection-diffusion rates from the same simulations. The advantage of doing this rather than monitoring advection-diffusion rates of another solute dispersed in the argon is that we obtain a far greater number of crossings in the simulation time for reduced statistical noise. Furthermore, considering argon diffusion within argon avoids variations in solute diffusivity with concentration.

### 4.2 Results and Discussion

As the simulation extended beyond the equilibration period, we observed reservoir mixing which increased with nanopore size and pressure difference. Cross-sectional views of a timestep in the middle of the simulations for each nanopore size are given in Figure 4.6 and Figure 4.7. The viscosity of argon, $\mu$ (Pa s), was calculated by Houghton’s approximation$^{28}$ relating viscosity and diffusivity as:

#### Table 4.5: Argon simulation Lennard-Jones pair coefficients.

<table>
<thead>
<tr>
<th>$\varepsilon$ [kcal mol$^{-1}$]</th>
<th>$\sigma$ [Å]</th>
<th>Species Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12029</td>
<td>3.395</td>
<td>C-Ar</td>
</tr>
<tr>
<td>0.23807</td>
<td>3.405</td>
<td>Ar-Ar</td>
</tr>
<tr>
<td>0.00000</td>
<td>0.000</td>
<td>All other interactions</td>
</tr>
</tbody>
</table>
\[ \mu = \frac{k_B T}{6 \mathcal{D}} n^{1/3} \]  

(4.2)

where \( n \) is the number density of argon (molecules/m\(^3\)), \( \mathcal{D} \) is the self-diffusivity of argon (m\(^2\)/s), \( k_B \) is Boltzmann’s constant, and \( T \) is temperature (K). The argon density was calculated to be \( 2.13 \times 10^{28} \) molecules/m\(^3\) from the 0 atm pressure difference simulation on the 5 nm pore. The self-diffusivity of argon was estimated as one-fourth the slope of the mean squared displacement in \( xy \) vs. time curve obtained for the same simulation (Figure 4.8). Displacement in \( z \) was excluded because the graphene more significantly constrains argon motion in \( z \). This resulted in a diffusivity of \( \mathcal{D} = 2.15 \times 10^{-9} \) m\(^2\)/s and a calculated viscosity of \( \mu = 2.52 \times 10^{-4} \) Pa s.

**Figure 4.6:** VMD cross sectional top view of (a) 1 nm, (b) 2nm, (c) 3nm, (d) 4nm, and (e) 5 nm diameter pores in graphene (grey) with Type 1 (red, located on the lower pressure side of the membrane after equilibration) and Type 2 (blue, located on the higher pressure side) argon mixing in the middle of the simulation after the equilibrium run.
**Figure 4.7:** VMD cross sectional side views of the (a) 1 nm, (b) 2 nm, (c) 3 nm, (d) 4 nm, and (e) 5 nm diameter pore simulations through graphene (grey) with Type 1 (red) and Type 2 (blue) argon visible. External piston (black) pressure is higher on the Type 2 argon side. Views were captured at timestep $2.5 \times 10^6$ with a 50 kPa pressure difference for the 4-nm diameter pore and 25 kPa pressure difference for every other pore.
**Figure 4.8:** Mean squared displacement of argon atoms in $xy$, $(\Delta x^2 + \Delta y^2)$, over time from the 0 atm pressure difference simulation for the 5-nm pore. Time zero, from which displacement are calculated, corresponds to timestep $2.0 \times 10^7$ from the start of equilibration. Diffusivity is calculated from the slope of this curve as $D = \text{slope}/4 = 2.15 \times 10^{-9}$ m$^2$/s.

Argon transport rates were calculated from the slope of crossings vs. time plots (Figure 4.9). Forward crossings included the Type 2 argon (blue colour in the previous cross sectional views) which started on the high-pressure side of the membrane after equilibration but ended up on the low-pressure side at the end of the timestep. Backward crossings included the Type 1 argon (red colour) which started on the low-pressure side of the membrane but ended up on the high-pressure side. Net crossings were the difference between the forward and backward crossings.
Figure 4.9: Time traces of cumulative argon crossings. Forward crossings are atoms found on the low-pressure side that started on the higher-pressure side. Backward crossings are atoms found on the high-pressure side that started on the low-pressure side. Net crossings are the difference between forward crossings and backward crossings.

The flow rate through an orifice plate in creeping flow is calculated from the expression developed by Dagan et al. They showed that a hydrodynamic resistance model taking the resistance to flow through an infinitesimal thickness orifice plate, obtained by Sampson, in series with that of Poiseuille flow, is accurate to 1% for the flow through a non-zero thickness orifice plate. Therefore, the average velocity through the pore (volume flow rate divided by pore area) is,

\[
V = \frac{D \Delta p}{\mu (6\pi + 3\frac{L^2}{D})}
\]  

(4.3)
Where, \( D \) is the nominal pore diameter, \( \Delta p \) is the pressure difference, \( \mu \) is the fluid viscosity, \( L \) is the pore length.

We constructed a similar expression for mass flow rate due to advection diffusion in creeping flow through an orifice plate that matches finite volume solution to within 3%. The dimensionless mass transfer rate Sherwood number, defined as,

\[
Sh = \frac{mD}{\mu \Delta p} \tag{4.4}
\]

is given approximately by,

\[
Sh = \frac{Pe}{1 - \exp \left[ -Pe \left( \frac{\pi L}{D} \right) \right]} \tag{4.5}
\]

where the Péclet number is defined as,

\[
Pe = \frac{mD}{\mu L} \tag{4.6}
\]

\( m \) is the mass flow rate, \( \Delta C \) is the concentration difference, and \( A \) is the pore area.

A comparison of the argon crossings, net flow rate, and directional flow rates are given in Figure 4.10. Forward crossings include the argon which moved from the high pressure reservoir, across the membrane, to the lower pressure reservoir. Backward crossings include the argon which moved in the opposite direction, and the net argon crossings define the forward minus the backward crossings. Net advection of argon (Figure 4.10b) is calculated from the slope of the net argon crossings over time for each pore size. We note that the determined advection-diffusion transport rates (Figure 4.10c) through the 5-nm pore are in agreement with continuum predictions for a zero-thickness orifice plate. Lower transport rates than predicted from continuum theory are found for smaller pores, with relative error increasing as pore size decreases. We observe that the net advection and advection-diffusion rates decrease for smaller pore diameters in a similar way to how continuum transport rates through orifice plates decrease with increasing plate thickness. We define an effective pore length as the thickness of an orifice plate needed for the
continuum advection-diffusion rate prediction of Equation 6 to match the simulated advection-diffusion rates presented in Figure 4.10c.

Performing numerical least squares fitting we obtain the effective pore lengths shown in Figure 4.11a, with the corresponding continuum model predictions presented in Figure 4.11b-c. Both the net advection and the species advection-diffusion rates are well approximated by using an effective pore length to correct for sub-continuum transport behavior at pore diameters larger than the molecule size. As the pore diameter increased, the effective pore length decreased providing less resistance to argon crossings.

![Figure 4.10: Mass transfer rates.](image)

(a) Example time traces of forward, backward, and net crossings, shown for the 4-nm pore with a 10 atm pressure difference applied. Flow rates are calculated as the slopes of linear fits (dashed lines) to these traces, using data following an equilibration period with the pressure difference applied. (b) Net argon flow rates for different pore diameters. Dashed curves are linear fits to guide the eye. (c) Forward and backward molecule flow rates. Forward flow rates are plotted at positive pressure differences whereas backward molecule flow rates are plotted at negative flow rates. Separate markers for crossings in either direction are shown for zero pressure difference. Error bars show standard error for the linear least squares fit to the trace of molecule crossings vs. time.
Figure 4.11: (a) Effective pore length for each pore diameter obtained from a numerical least squares fit to $Sh$ vs. $Pe$. Error bars show standard error for fit. Inset shows the definition of $D$ and $L$ for an orifice plate. (b) Péclet number calculated from MD simulation flow rates compared to the corresponding value from the orifice plate expression for the effective pore lengths plotted in panel (a). Solid line shows a slope of 1. (c) Sherwood number vs. Péclet number calculated from MD simulation flow rates. Solid lines show orifice plate equation values for the effective pore lengths plotted in panel (a).

As the pore diameter is reduced towards the diameter of a single carbon atom, the graphene nanopore no longer resembles a zero-thickness orifice plate, but instead appears more like a low aspect ratio orifice plate with an irregular pore shape. However, the effective pore lengths for ~1-3 nm pores exceed the thickness of graphene by several times (Figure 4.11a). The physical reason for this can be understood by examining the density of argon in the vicinity of the graphene. Away from the graphene surface, in the bulk fluid, the fluid atoms are randomly arranged in space. However, near the graphene membrane, the argon atoms form dense layers parallel to the graphene. These layers could be quantitatively displayed by comparing the local argon density to the bulk density in 0.5 Å slices (Figure 4.13). On both graphene membrane surfaces, the argon density peaked to 5 times that of bulk as a result of strong attractive forces between the argon and carbon atoms. The layer of argon neighboring the graphene is sufficiently dense that attractive forces between argon atoms create a second layer of argon farther
from the graphene. Several layers of argon, with diminishing density peaks can be identified in Figure 4.14.

**Figure 4.12:** Close-up of the argon spatial arrangement which becomes more uniform as the fluid approaches the graphene membrane.

**Figure 4.13:** Relative density compared to bulk computed for the 5-nm pore simulation, averaged over all pressure differences simulated, binning in slices 0.5 Å thick in \( z \). Inset illustrates an example \( z \) slice (not to scale).
Figure 4.14: Relative density compared to bulk computed for each of the 1 to 5 nm diameter pore simulations, binning in slices 0.5 Å thick in z.

Layering of fluid near graphene and carbon nanotube surfaces has been previously reported with similar magnitude relative density peaks and extent of layering away from the surface as we observe.\textsuperscript{1,19} Here, we find further argon layering within the graphene pore (Figure 4.15). We found the highest relative argon density at the pore edge in most cases and observed the overall highest relative density of argon in the 1 nm diameter nanopore simulation. This layering is so strong that in the 1 nm pore simulation that argon forms a ring shape within the pore and is virtually excluded from the center (Figure 4.15b). Similar transport in shells of fluid has been observed in molecular dynamics simulations of flow through carbon nanotubes\textsuperscript{20-31}, but here we see that this behavior occurs even for the low aspect ratio pores in graphene.

Wang and Hadjiconstantinou (2018)\textsuperscript{31} found that the strong attraction of the fluid to the graphitic surface effectively confines the fluid on the nanoscale. Fluid molecules move
within this dense layer but have a lower tendency to escape the layer into the bulk. Consequently, the fluid molecule diffusivity is effectively lower in these surface layers than in the bulk. Within a graphene nanopore, this would mean lower transport rates in the regions with dense layering. While the 5-nm pore has significant area in its center with density unaffected by the pore edge (Figure 4.15f), smaller pores have a layered structure throughout (e.g., Figure 4.15c). Having an effectively lower diffusivity over a portion of the pore area increases the transport resistance and reduces transport rates just as increasing the pore thickness increases resistance to transport. Fluid layering on the graphene surface (Figure 4.13) will similarly increase the access resistance for molecules to reach the pore. We found that the increased transport resistance due to these layers can be reasonably accounted for by introducing an effective pore length in continuum transport models.

**Figure 4.15:** Relative density of argon within pore. (a) Example averaging volume shown in green. The density at each radius is the average within a cylindrical shell 4 Å tall and 0.5 Å thick taken over all pressure differences simulated. Relative density plots are presented for (b) 1 nm, (c) 2 nm, (d) 3 nm, (e) 4 nm, and (f) 5 nm diameter pores.
**Figure 4.16**: Relative density of argon within pore. The density at each radius is the average within a cylindrical shell 4 Å tall and 0.5 Å thick.

To understand the argon behaviour near the nanopore, both relative densities taken in the radial and z-directions were considered in cylindrical shells from the center of the nanopore (Figure 4.17). By visualizing the data in both directions, it could be clearly seen that the argon adsorbs most strongly onto the graphene membrane at $z \approx \pm 0.3$ nm to form the first fluid layer on the carbon surface. Distinct fluid layers can be seen in both z directions, and in the negative r direction from the pore edge, each decreasing in relative density magnitude until it reaches bulk density in the z-direction, or the pore center. These plots illustrate the extent of dense argon layers where transport is inhibited and provide a visualization of how the pore aspect ratio effectively increases as the pore diameter is reduced.
Figure 4.17: Relative density averaged over 0.5 Å tall, 0.5 Å thick, cylindrical shells over all simulated pressure differences for (a) 1 nm, (b) 2 nm, (c) 3 nm, (d) 4 nm and (e) 5 nm diameter pores. The relative density range shown extends from 0 to 6, with segments averaging greater than 6 shown with the color at the top of the scale.

Figure 4.18: Relative density averaged over 0.5 Å tall, 0.5 Å thick, cylindrical shells. The relative density range shown extends from 0 to 6, with segments averaging greater than 6 shown with the color at the top of the scale.
4.3 Conclusion

We calculated argon advection-diffusion rates through graphene nanopores by molecular dynamics simulations. The results show agreement with continuum transport model predictions for 5 nm pore size but lower transport rates through smaller pores than predicted by continuum theory. Significant layering of argon within the pores and on the graphene surface was observed. Transport rates in such layers are lower than in the bulk fluid and are partly responsible for the reduced transport rates through graphene nanopores compared to continuum predictions. We showed that by including an effective pore length in the continuum models that accounts for the added resistance through these nanopores, the net advection and advection-diffusion rates could be reasonably corrected for sub-continuum effects. The extent of fluid layering is strongly dependent on the interaction potential between the fluid and the graphene as well as on the fluid temperature. We therefore expect transport rates and effective pore length to be sensitive to the specific fluid and operating temperature.
Chapter 5

5 Wafer and Pressure Chamber Fabrication

At the Western Nanofabrication Facility, we produced a platform to measure flow rates through pores in graphene and other two-dimensional materials. We had to ensure that the support configuration provided a sufficiently large graphene nanoballoon volume that would allow us to measure deflection changes as gas escapes on an AFM resolvable time scale. Furthermore, the arrangement had to limit the available flow area to improve measurement resolution while ensuring that the perforated membrane and corresponding sub-nanometer pore could be located for subsequent imaging. Arrays of circular microcavities were patterned on silicon wafers through photolithography. Multiple layers of graphene were individually stacked on the wafer and the sample was charged in a pressure chamber that we designed to limit any leakage. Our custom pressure chamber also allowed us to heat the sample under vacuum. Gas permeance was then measured through these nanoballoons as a function of the membrane deflection (outward or inward bulge).

5.1 Wafer Methodology

Understanding the limits of the random arrangement of cavities in the polycarbonate membrane support material, we opted to create uniform arrangements of cavities on an Si wafer support platform. We chose the cavity dimensions such that the size of the nanoballoon would deflate at a rate which could be measured. Noting that Koenig et al. (2012)\textsuperscript{7} used cavities of 5-7 μm diameters with depths of 250-500 nm and Wang et al. (2015)\textsuperscript{2} used cavities of 3-5 μm diameters with depths of 400-1000 nm, we opted to create 3 μm, 5 μm, and 10 μm diameter cavities in our support material with different cavity spacing. Creating a variety of patterns at once would maximize potential of creating one pattern which would perform well as a graphene membrane support in our experiments. Since, a deep reactive ion etch (DRIE) was used to deepen the cavities which had a 1:1 depth to diameter resolution, we chose a depth of 3 μm.
A large enough cavity volume would allow us to record permeance over a significant time period using the AFM. Due to the greater volume (as a result of increased depth) compared to Koenig and Wang, we expect the nanoballoon deflection to be AFM resolvable.

5.2 Mask Design

We used AutoCAD to create a photomask pattern (Figure 5.1) on a 4-inch diameter circle to represent the Si wafer. Arrays of 3 µm, 5 µm, and 10 µm cavities with 56.6 µm and 183.8 µm spacing (center-to-center) were arranged in the AutoCAD design in 9500 µm² squares. The squares with the smallest diameters were arranged in the center of the design while the largest diameters were arranged near the edges because etching accuracy was higher near the center of the wafer as opposed to the edges. A few rows of square holes were included on the side of each individual array in reference to the shape used in Bunch (2008). It was found that the centers of the chips were the best areas for imaging and graphene transfer (edges were either taped down or used as tweezer holds) so the square cavities were not used. Furthermore, the photolithography resolution was 1-2 µm so there was minimal difference between square and circular cavities in reality.

Figure 5.1: (a) AutoCAD layout and (b) legend of the different cavity sizes and spacing for each die on the Si wafer. The colours in AutoCAD represent different cavity spacing.
Figure 5.2: Close-up of the (a) 3 µm, (b) 5 µm, and (c) 10 µm diameter cavity patterns on individual wafers with 183.8 µm spacing and (d) 3 µm, (e) 5 µm, and (f) 10 µm diameter cavity patterns with 56.6 µm spacing.

5.3 Wafer Fabrication

The photomask was printed on a 5x5 inch square glass by Front Range PhotoMask. We took a 4-inch diameter Si/SiO$_2$ wafer (100 mm Si, 500 nm SiO$_2$ and <100> crystal orientation) using wafer tweezers and placed it (mirror side up) in a large glass dish. The wafer was submerged in shallow hydrofluoric acid (HF) and the dish was agitated for 2 minutes to etch the SiO$_2$ layer down to 200-300 nm. Next, the wafer was submerged in a DI water bath. The wafer was removed, rinsed with DI water from a tap, and dried with an air gun. An Ellipsometer (from Woollam) was used to measure the SiO$_2$ layer thickness. We created three wafers with 283, 283.8, and 223.0 nm SiO$_2$ layers respectively. The wafers were then placed in the Spin Rinse Dryer. The hydrofluoric acid etch rate for SiO$_2$ was found to be approximately 120 nm/min. The wafers were placed in a DI water bath and then rinsed with DI water via tap. The wafer was dried with an air nozzle and then placed in a Teflon wafer cassette and brought to the Spin Rinse Dryer.
(semitool by Rhetech ST-240D) for cleaning. Once the cycle finished, the cassette was placed in the HMDS oven (Yield Engineering YES-3TA) for dehydration for 10-15 minutes. Next, the wafer was placed, mirror side up, on a CEE 200 spinner and spin coated with S1805 photoresist at 3000 RPM. The wafer was then baked on a hotplate (from Thermoscientific, SuperNuova) at 113°C for 3 minutes and loaded into the mask aligner (Neutronix-Quintel NXQ4006). The photomask was loaded and the wafer was exposed to the pattern. Next, the wafer was transferred to a large empty glass dish and submerged in MF 319 developer. The dish was agitated for 2 minutes and the wafer was transferred to a DI water bath. After agitating for 2 minutes, the wafer was placed back into the Spin Rinse Dryer. Successful mask printing was confirmed visually under a microscope (ZEISS Axioskop) and a final cleaning cycle was performed in the Spin Rinse Dryer.

Next, the wafers were sent to University of Toronto for deep reactive ion etching (DRIE) to deepen the cavity depths. A 1:1 diameter to depth ratio was the maximum possible depth so we chose to use a depth of 3 µm for the entire wafer. The oxide layer was used as a protective mask for the DRIE process and then removed. A protective photoresist was applied to prepare for dicing. The wafers were diced into small ~1 cm² wafer chips using a Dicing Saw and kept in place with dicing tape. We labeled the individual wafers to record the cavity size and spacing and then removed the photoresist (PR) from each wafer chip using acetone and isopropyl alcohol (IPA). The wafers were sprayed with IPA until the PR was removed, the colour of the surface was used for visual confirmation (any purple colour indicated PR while the Si wafer was grey). Next, each wafer was placed in two consecutive acetone baths and agitated for ~10 seconds each. Immediately after, the wafers were placed in two consecutive IPA baths and agitated for 5–10 seconds each. The chips were then dried on both sides using an air gun. For deeper cleaning, especially for the smaller cavities, we performed O₂ plasma etching (TRION TG390/420 M technology) on the chips for ~20 minutes. We found that the wafers with 5 µm diameter cavities were the easiest to locate using the AFM while providing the largest number of pores per area.
5.4 Wafer Characterization

The individual wafer dies were cleaned by subsequently sonicating in acetone and IPA baths for 5 minutes each followed by blow drying with air to prevent residue deposition. The wafers were then viewed with a Zeiss Axioscope optical microscope revealing pinprick holes in the wafer aside from the intentionally created cavities (Figure 5.4). We believe that these unintentional holes could have been the result of damage to the photomask pattern during photolithography or during the O₂ plasma etching.

![Figure 5.3](image1.png)

**Figure 5.3:** Optical microscope images of wafers with (a) 3 µm, (b) 5 µm, and (c) 10 µm diameter cavities with 56.6 µm face-centred cubic (FCC) spacing.

![Figure 5.4](image2.png)

**Figure 5.4:** Optical microscope images of wafers with (a) 3 µm, (b) 5 µm, and (c) 10 µm diameter cavities with 183.8 µm FCC spacing. (d) 3 µm, (e) 5 µm, and (f) 10 µm cavities. Pinprick holes outside of the cavities are visible.
Figure 5.5: SEM image of a wafer with 5 µm diameter cavities and 56.6 µm spacing.

5.5 Pressure Chamber Design

Using OnShape, we designed a two-piece pressure chamber for charging the graphene nanoballoon sealed cavities that can be placed on a hot plate to increase gas charging rates if desired. The bottom piece has a flat platform for sample placement and a depression for an O-ring. The top piece has a depression to increase the volume of the chamber and an opening for the gas inlet/outlet. Holes along the edge of each piece are used as openings for the nuts and screws which will clamp the pieces together and prevent gas leakage. The pressure chamber was fabricated by University Machine Services at Western University. Screws, nuts, and washers were provided by University Machine Services while the rest of the pieces were purchased from McMaster-Carr. Metal tubing was used later to further minimize the probability of fluid leakage. OnShape schematics of the individual pieces are shown in Figure 5.6.
Figure 5.6: OnShape schematic of the (a) top and (b) bottom pieces of the pressure chamber.

Figure 5.7: Custom pressure chamber (a) closed and (b) open with Si wafers inside.
Chapter 6

6  Nanoballoon Experiment

To test the membrane performance of CVD grown graphene, we will generally follow the nanoballoon experimental techniques demonstrated in Koenig et al. (2012)\(^7\). Multilayer graphene is used to reduce the permeance of defects in CVD graphene. We will transfer multilayer graphene onto cavities in various support substrates and charge the resulting sealed microcavities with various gases until a pressure difference is represented as elastic membrane deflection in the positive or negative directions. This deflection will be monitored by AFM (Figure 6.1) as a function of time to determine the leak rate through intrinsic CVD grown graphene defects before and after nanopore introduction. We expect to see gradually decreasing height traces as the gas escapes from the microcavity and we will record the microcavity volume as a function of time. We use Equation 6.1, derived by Koenig et al. (2012)\(^7\), to determine the gas molar flow rate out of the cavity \(\frac{dn}{dt}\) from the volume leak rate \(\frac{dV_b}{dt}\) obtained from the AFM images.

\[
\frac{dn}{dt} = \frac{1}{RT} \left[ P_{atm} + \frac{3KE\omega}{c^3\pi^3a^{10}}V_0V_b^2 + \frac{4KE\omega}{c^3\pi^3a^{10}}V_b^3 \right] \frac{dV_b}{dt} \tag{6.1}
\]

where \(R\) is the universal gas constant, \(T\) is the temperature (295.15 K), \(P_{atm}\) is the atmospheric pressure, \(K\) and \(c\) are constants (3.09 and 0.524 respectively, for graphene), \(E\) is the Young’s modulus (1 TPa for graphene), \(\omega\) is the thickness (0.34 nm per layer of graphene), \(a\) is the radius of the suspended graphene (also the radius of the wafer cavity), \(V_0\) is the volume of the cavity \((\pi a^2H\text{, where } H = 3 \mu m\text{ is the cavity depth})\), and \(V_b\) is the initial bulge volume. A complete derivation of this equation is provided in Appendix A.
Figure 6.1: (a) Representation of the AFM graphene deflection measurement. Maximum deflection decreases over time as gas molecules escape. (b) After Cavity 2 on Sample L1 (5 layers of graphene on a 5 µm diameter cavity on Si wafer) was charged for 2 days in 1 atm air pressure, the sample was removed from the pressure chamber and left at SATP. AFM height traces after 0, 72, 168, and 216 h in SATP are shown. (c) Cavity 2 volume as a function of time is recorded. The volume leak rate $\frac{dV_b}{dt}$ is obtained from the slope.

After measuring membrane deflection with various charging gases in stacked multilayer graphene, we will introduce a 10-30 nm FIB hole and repeat the membrane deflection testing and AFM measurement to confirm high permeance (Figure 6.2). Next, we will transfer a final layer of graphene to seal the FIB nanopore and test the membrane deflection to confirm sealing. Finally, a nanopore will be produced using ion bombardment in the graphene monolayer suspended over the FIB nanopore. It is expected that bombarding the microcavity area with ions will produce a pore in the single graphene layer as opposed to the multilayer stack surrounding the FIB nanopore. In this way, we ensure that any measured permeance above the background 6-layer graphene leakage is through the small area of graphene over the FIB generated hole. This will allow us to measure more highly permeable areas of graphene than would be possible if the graphene over the entire microcavity had this high permeance. The large cavity diameter allows for sufficient deflection of the nanoballoon to resolve the inflated height
by AFM, while the FIB hole restricts the flow to a smaller area, limiting the deflation rate so that higher permeances can be measured.

**Figure 6.2:** Schematic of the intended fabrication method. (a) Graphene is transferred over a cavity in the support material until (b) a multilayer graphene stack is achieved. Nanoballoon gas charging and leak rate measurements will be performed before and after (c) a FIB hole is introduced. (d) A final graphene layer is transferred to seal the previous FIB nanopore and nanoballoon charging and deflection will be tested. (e) Finally, we aim to create a single sub-nanometer pore using ion bombardment in the single graphene layer over the previous FIB generated hole.

### 6.1 Polycarbonate Track Etch Membranes

We first tried polycarbonate track etch membrane (PCTEM) filters (from Sterlitech) as a support substrate due to the commercial availability and familiar handling. We ordered PCTEM filters with cavity diameters of 0.2 µm, 5 µm, and 10 µm. These cavities have a conic structure (smaller diameter on the surface, larger diameter in the bulk material), go through the entire membrane, and are randomly arranged throughout the material. The PCTEM filters have a smooth (shiny) surface on one side and a rougher (matte) surface on the other side. We transferred 0-3 layers of graphene onto each side of the membranes to create sealed microcavities and determined cavity coverage with SEM imaging. Further fabrication details and early steps are written in Appendix B. Concerns regarding pore geometry and coverage led us to develop our own support platform (Chapter 5).
6.1.1 Results

We found that during graphene transfer, the PCTEM with 5 μm diameter cavities provided the best adhesion for multiple layers of graphene. However, large pieces of graphene were difficult to maintain as tears would occur during handling in the transfer process. Furthermore, as the number of layers increased from 1-n layers, the area of n-layer graphene would decrease.

Using 1 layer of graphene on the smooth side of a 5 μm diameter cavity PCTEM, no covered pores could be found. Next, we stacked 2 layers of graphene on the smooth side and used an AFM to produce the following images:

![Figure 6.3: Wide AFM images of (a) covered and uncovered cavities in Sample 1A and (b) uncovered cavities in Sample 1B (2 layers of graphene on PCTEM with 5 μm cavities). Close-up images of the covered cavities in (c) Sample 1A and (d) 1B.](image)

To create a higher coverage percentage, we stacked three layers of graphene on both sides of a PCTEM with 5 μm diameter cavities and imaged it with an SEM. The two sides provided a range of covered and uncovered cavities and different graphene appearances. It was difficult to relocate cavities since the random arrangement provided no coordinate system and the number of uncovered cavities was high even with three layers of graphene.
6.1.2 Obstacles

We noticed that during graphene transfer, the graphene pieces would tear during handling stages. This could have been due to the high surface tension on the water-air interface during transfer making it difficult to achieve large areas of graphene coverage on the PCTEM, especially when trying to stack multiple layers. While the transfers had many tears, graphene was successfully suspended over some pores in the PCTEM. The coverage was low and it was even harder to transfer onto the rough side of PCTEM. As a result, the probability of creating sealed volumes was low due to the coverage rate and the fact that the PCTEM needed to be sealed on both sides with graphene to create the microcavities. The random arrangement of pores made it difficult to repeat experiments on an isolated area and we were also worried that the pore location and oblique angles could cause interconnectivity in the bulk. Furthermore, due to the conical shape of the cavity through holes, and possible connections, we would not be able to calculate the exact cavity volume. These obstacles, and the possibility of inherent polycarbonate permeability limiting the low permeance resolution, led us to create a custom Si support platform (Chapter 5).

**Figure 6.4:** SEM images of covered and uncovered cavities with 3-layer graphene on the (a, b) matte side and (c, d) shiny side of a 5 µm cavity PCTEM.
6.2 PMMA Facilitated Graphene Transfer

Using the Si wafers which have controlled cavity geometry and lower permeability, we first tried a polymethyl methacrylate (PMMA) supported graphene transfer onto the support substrate. More fabrication details are included in Appendix C. This polymer acted as a protective layer and a support for the graphene during transfer. This bond limited (but did not eliminate) significant graphene tears during the copper etching and rinsing steps. Concerns with polymer residue and tearing due to surface tension, pushed us to use a polymer free transfer technique which will be described in the next section.

6.2.1 Results

We created a 3-layer graphene stack using a PMMA support layer and transferred it onto an Si wafer (E1) with 5-µm diameter cavities. Complete cavity coverage was observed after the PMMA was removed. The sample was placed in 1 atm air pressure for 2 days and then vacuum for 2 days with AFM measurement after each 2-day interval. We noticed that the chosen microcavity (Cavity E1-5) did not deflate completely within this time frame while other cavities reached maximum negative deflection in the same time. This suggested that Cavity E1-5 could seal to vacuum.

Next, the sample was placed in a pressure chamber under vacuum for 19 days. After this period, the sample was removed and placed in ambient conditions. Daily AFM images were obtained at the same time each day for 12 days. It was found that while the cavity still had positive deflection after 2 days under vacuum, after 19 days under vacuum the cavity reached maximum negative deflection and remained stable for ~10 days at SATP.
Figure 6.5: AFM topography of Cavity 5 on Sample E1 (3 layers of graphene on 5 µm diameter cavity) demonstrating positive membrane deflection after a 2-day charging period with 1 atm air. After a 2-day vacuum period, positive deflection is still observed. After a 19-day vacuum period, maximum negative deflection occurs.

Figure 6.6: Volume changes in Cavity 5 on Sample E1 (3 layers of graphene on 5 µm diameter cavity) as a function of time. Sample E1 is placed at SATP and measured each day after a 19-day period under vacuum.

Table 6.1: Flux rate for Cavity 15 on Sample E1 (3 layers of graphene on 5 µm diameter cavity) over 2 days under continuous 1 atm air pressure.

<table>
<thead>
<tr>
<th>Range [days]</th>
<th>Cavity</th>
<th>Initial bulge volume [µm³]</th>
<th>Volume deflation rate [µm³/s]</th>
<th>Gas flow rate [mol/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-12</td>
<td>5</td>
<td>-1.4</td>
<td>5.95x10⁻⁷</td>
<td>3.46x10⁻²³</td>
</tr>
</tbody>
</table>
To further test the cavity sealing, we placed the sample in 1 atm air pressure continuously for 15 days. The sample was removed at the same time each day for AFM measurements before it was returned to the pressure chamber. We found that the pressure differences across the membranes reached mechanical equilibration within 2 days in air pressure. Using Equation 6.1 and the slope obtained for Cavity E1-15, we determine the air permeance to be $7.43 \times 10^{-22}$ mol/s.

**Figure 6.7:** AFM topography of (a) Cavity 15 and (b) Cavity 19 on Sample E1 (3 layers of graphene on 5 µm diameter cavity) under continuous charging with 1 atm air. These cavities equilibrated within 2 days.
Figure 6.8: Volume changes in Cavity 15 and 19 on Sample E1 (3 layers of graphene on 5 µm diameter cavity) as a function of time. Sample E1 is placed in 1 atm air pressure continuously for 15 days with daily removal for AFM imaging.

Table 6.2: Flux rate for Cavity 15 on Sample E1 (3 layers of graphene on 5 µm diameter cavity) over 2 days under continuous 1 atm air pressure.

<table>
<thead>
<tr>
<th>Range [days]</th>
<th>Cavity</th>
<th>Initial bulge volume [µm³]</th>
<th>Volume deflation rate [µm³/s]</th>
<th>Gas flow rate [mol/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-2</td>
<td>15</td>
<td>-0.93</td>
<td>1.52x10⁻⁵</td>
<td>7.43x10⁻²²</td>
</tr>
</tbody>
</table>

6.2.2 Obstacles

We found that despite the protective PMMA layer, the graphene was still subject to tearing during handling in the transfer process. There were also concerns that possible PMMA residue could affect the graphene membrane permeability and the accuracy of the resulting gas permeance calculation. This residue could also affect the sealing ability of the final graphene layer and have different height levels in different areas. The gas transport would be affected by surface adsorption and there is a chance the polymer could migrate and plug the fabricated nanopores or graphene defects we intended to measure. Other PMMA removal techniques, including the use of a 400°C quartz tube furnace, can still be subject to polymer residue. Therefore, we decided to adopt a cleaner polymer-free graphene transfer technique.
6.3 Polymer-free Graphene Transfer

Adapted from Zhang et al. (2016)\textsuperscript{25}, the polymer-free graphene transfer process used hexane as a second liquid layer to decrease the surface tension on the graphene. The graphene was rinsed on the water-hexane interface which has a lower surface tension (45 mN/m) compared to the water-air interface (72.8 mN/m). Using this method, we produced two samples with 5 layers of graphene on 5 µm diameter cavities. The first sample (using wafer L1) was created by directly stacking 5 layers of graphene onto an Si wafer, where the sample was air dried and annealed under vacuum at 200°C for 1 hour after each layer. The second sample (using wafer K1) was created by stacking layers of graphene on a Gr/Cu piece until a total of 5 graphene layers was achieved. The copper was then etched and the 5-layer graphene stack was transferred onto an Si wafer, air dried, and annealed under vacuum at 200°C for 1 hour. Sample L1 was used as a control for testing gas permeance through 5 layers of CVD grown graphene, while Sample K1 was used for additional control tests, FIB processing, and ion bombardment. Further fabrication details are available in Appendix D. Continuous areas of suspended graphene on the Si wafer could then be identified with an SEM and directly targeted for FIB processing.

6.3.1 Sample L1 Results

We charged Sample L1 with 1 atm air for 14 days to ensure microcavity equilibration. We then left the sample at SATP (Standard Ambient Temperature and Pressure) and measured the deflation of Cavity 2 over 15 days. We found that the cavity reached minimum deflection in about 10 days. The slow deflation time suggested that the graphene layers were well adhered and permeable to air. Using the slope obtained from Figure 6.10, we determine an air permeance of $-1.57 \times 10^{-23}$ mol/s which is ~50-fold smaller leakage than achieved with Cavity E1-15 using the PMMA transfer. This shows that we are able achieve an effective seal with the polymer-free graphene transfer method. Furthermore, it is a direct measurement of the inherent permeance of five-layer CVD graphene and provides a lower bound on the resolvable permeance by this measurement technique imposed by leakage through the graphene.
**Figure 6.9:** AFM topography of Cavity 2 on Sample L1 (5 layers of graphene on 5 µm diameter cavity) topography over time at SATP after a period of charging with 1 atm air for 14 days. The cavity deflates within 10 days and remains stable for 5 more days.

**Figure 6.10:** Volume changes in Cavity 2 on Sample L1 (5 layers of graphene on 5 µm diameter cavity) as a function of time. Sample L1 is placed at SATP after charging in 1 atm air pressure for 14 days.
Table 6.3: Flux rates over 15 days for Cavity 2 on Sample L1 (5 layers of graphene on 5 µm diameter cavity) at SATP after charging at 1 atm air pressure for 14 days.

<table>
<thead>
<tr>
<th>Range [days]</th>
<th>Cavity</th>
<th>Initial bulge volume [µm³]</th>
<th>Volume deflation rate [µm³/s]</th>
<th>Gas flow rate [mol/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-15</td>
<td>2</td>
<td>0.34</td>
<td>-3.70x10⁻⁷</td>
<td>-1.57x10⁻²³</td>
</tr>
</tbody>
</table>

Subjecting the sample to increasing helium gas charging pressures caused Cavity L1-1 to inflate (Figure 6.11) and Cavity L1-2 (Figure 6.12) to deflate by the time it reached the AFM for imaging. Higher pressures produced greater maximum levels of positive deflection in Cavity L1-1 as expected but greater maximum levels of negative deflection in Cavity L1-2. This negative deflection is due to the helium gas escaping from the microcavity very quickly after removal from the pressure chamber, leaving vacuum behind since the larger air molecules pass through the graphene defects at a lower rate. Since defects in graphene have a wide size distribution, and there is likely a small number of defects over each 5 µm cavity\textsuperscript{23}, the gas permeance and molecule size cut-off can vary from cavity to cavity. Here we find one cavity (L1-1) that with low helium permeance and low air permeance and another (L1-2) with high helium permeance but low air permeance. Thus, the graphene over Cavity L1-2 is selectively permeable to helium over air. These measurements demonstrate gas selectivity through defects in five-layer CVD graphene.

![Figure 6.11: AFM topography of Cavity 1 on Sample L1 (5 layers of graphene on 5 µm diameter cavity) topography over time with increasing helium charging pressures. The cavity is charged for a day at each pressure and measured with AFM. This cavity](image-url)
demonstrates low permeance to helium. It is observed to have an air equivalent sealing limit.

**Figure 6.12:** AFM topography of Cavity 2 on Sample L1 (5 layers of graphene on 5 µm diameter cavity) topography over time with increasing helium charging pressures. The cavity is charged for a day at each pressure and measured with AFM. This cavity is highly permeable to helium and demonstrates helium/air selectivity. Helium fills the cavity during charging and escapes after removing from the pressure chamber. Air is unable to replace the helium in the cavity, leaving behind a vacuum and a negative deflection in the graphene membrane.

**Figure 6.13:** Volume changes in Cavity 1 and 2 on Sample L1 (5 layers of graphene on 5 µm diameter cavity) as a function of pressure. Sample L1 is charged at 1 day intervals with helium gas and increasing pressures.
**Figure 6.14:** Visual explanation for the negative deflection in Cavity L1-1 after charging in helium gas. (a) The microcavity is charged with helium and reaches equilibrium. (b) After removal from the pressure chamber, the sample is exposed to air and helium quickly permeates through the membrane due to the pressure difference. (c) Since the air cannot permeate through the membrane, the helium atoms leave behind a vacuum in the microcavity and the suspended graphene displays negative deflection.

Assuming an elapsed time of 15 minutes between removal from the pressure chamber and complete AFM imaging, and using a conservative initial bulge volume of 0.25 \( \mu m^3 \) (minimum AFM resolvable height), we calculated the following lower limit gas permeance for helium out of Cavity L1-2.

**Table 6.4:** Flux rates for Cavity 2 on Sample L1 (5 layers of graphene on 5 \( \mu m \) diameter cavity) at SATP after subjection to various pressures of helium charging assuming an elapsed time of 15 minutes during removal from the pressure chamber and complete AFM imaging.

<table>
<thead>
<tr>
<th>Time elapsed [min]</th>
<th>Cavity</th>
<th>Initial bulge volume [( \mu m^3 )]</th>
<th>Volume deflation rate [( \mu m^3/s )]</th>
<th>Gas flow rate [mol/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>15*</td>
<td>2</td>
<td>0.25*</td>
<td>-2.78\times10^{-4}</td>
<td>-1.16\times10^{-20}</td>
</tr>
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</table>

* conservative estimates to determine the lower limit gas permeance.

After helium, we tested Cavity L1-2 deflection behavior under 25 kPa argon charging. After charging the sample for 1 day, Sample L1 was left at SATP and measured
regularly. We observed Cavity L1-2 inflated on the AFM after charging with argon even though it did not inflate with helium previously. Thus, the argon leakage rate through the graphene over Cavity L1-2 is much lower than that of helium. The graphene over Cavity L1-2 is selective to helium over both argon and air. Helium has a kinetic diameter of 0.26 nm whereas argon has a kinetic diameter of 0.34 nm. The molecules in air are even larger, with kinetic diameters of oxygen and nitrogen of 0.346 and 0.364 nm, respectively. The molecule size cut-off for this micron-scale graphene membrane is therefore between 0.26 nm and 0.34 nm.

We note that the argon pressurization test was performed starting from the vacuum state immediately after the helium test, with negative deflection of the membrane. Over the 24 h charging time, the membrane went from having negative deflection to being slightly inflated. The fact that the membrane deflection did not return to a negative value when the membrane was exposed to SATP indicates that the leakage rate for argon is similar to that for air. Unfortunately, the membrane became damaged before further pressurization tests could be performed, so the argon flux could not be calculated.

**Figure 6.15:** AFM topography on Cavity 2 on Sample L1 (5 layers of graphene on 5 µm diameter cavity) topography over time at SATP after charging for 1 day in 25 kPa argon. The cavity slowly deflates over time.
Figure 6.16: Volume changes in Cavity 2 on Sample L1 (5 layers of graphene on 5 µm diameter cavity) as a function of time after charging under 25 kPa argon pressure for 1 day.

6.3.2 Sample K1 Results

Using Sample K1, we tested charging under SF₆ gas at various pressures to determine the general ability of the suspended membranes to hold pressure. We found that after charging in SF₆ at 80 kPa for 21 hours, the deflation rate of the 5 µm diameter cavity would be -2.97x10⁻²² mol/s. We noticed that the time to reach maximum deflation (equilibrium at SATP) required approximately 84 hours whereas the sample charged in SF₆ for only 21 hours.

Figure 6.17: AFM topography of Cavity 0 on Sample K1 (6 layers of graphene on 5 µm diameter cavity) topography over time at SATP after charging for 21 hours in 80 kPa SF₆.
**Figure 6.18:** Volume changes in Cavity 0 on Sample K1 (6 layers of graphene on 5 µm diameter cavity) as a function of time after charging under 80 kPa SF₆ pressure for 21 hours.

**Table 6.5:** Flux rates over 72 hours for Cavity 0 on Sample K1 (6 layers of graphene on 5 µm diameter cavity) at SATP after subjection to 80 kPa SF₆ pressure charges for 21 hours.

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<tbody>
<tr>
<td>12-84</td>
<td>0</td>
<td>2.1</td>
<td>-3.61x10⁻⁶</td>
<td>-2.97x10⁻²²</td>
</tr>
</tbody>
</table>

**Focused Ion Beam**

After confirmation that the membrane seals to air, we sent Sample K1 to the Western University Nanofabrication Facility for FIB processing (Figure 6.19). An area with high graphene coverage was identified with SEM and marked for FIB nanopore introduction (Figure 6.20a). Since the Si wafer cavity arrangement and spacing are known, the FIB could be automated to create one 10 nm or 30 nm diameter pore in each cavity area (Figure 6.20b-c).
**Figure 6.19:** FIB drilling to create a nanopore in the suspended multilayer graphene.

**Figure 6.20:** Illustration of the (a) FIB area identification markers, (b) 10 nm FIB nanopores created in Si wafer cavities, and (c) 30 nm FIB nanopores created in Si wafer cavities.

Using the SEM, we identified the nanopore in the suspended graphene membranes (Figure 6.21, all SEM images located in Appendix F). Adjacent cavities which were not FIB processed (do not have a nanopore) were used as “controls” for comparison. Cavity locations in the Si wafer array were also recorded relative to a corner in case the noticeable features could not be found with different imaging tools.
Figure 6.21: SEM images of (a) Cavity 11 and (b) Cavity 16 on Sample K1 (5 µm diameter cavity) with a 10-nm and 30-nm diameter nanopore, respectively (circled).

We placed the sample under 1 atm air pressure for 4 days and measured both the controls and FIB cavities daily before returning the sample to the pressure chamber. Control cavities demonstrated good sealing as shown with clear graphene deflection where the nanoballoons held pressure (Figure 6.22). This also showed that the charging gas could permeate into the cavity via pressurization. Cavities which underwent FIB drilling were not observed in an inflated state by AFM. We expected that deflation occurred too quickly to be measured by AFM. Since the permeance of the FIB hole is higher than can be measured by this technique, it will not affect the measured permeance through the final layer of graphene to be placed over the hole.
Figure 6.22: AFM topography of control and FIB processed cavities on Sample K1 (5 layers of graphene on 5 µm diameter cavity) topography over time with continuous 1 atm air pressure. (a) Cavity C is a control cavity which had no FIB processing and displays clear positive graphene deflection after 2 days in air pressure. (b) Cavity 11 has a 10-nm diameter FIB nanopore and does not display positive graphene deflection.

Figure 6.23: Volume changes in control (Cavity C) and FIB cavities (Cavity 11) on Sample K1 (5 layers of graphene on 5 µm diameter cavity) as a function of time while charging under 1 atm air pressure continuously. Cavity C had no FIB processing and Cavity 11 has a 10-nm diameter FIB nanopore.

Final Graphene Layer Transfer

A final layer of graphene was transferred onto the wafer to seal the FIB nanopores (Figure 6.24). The sample was then subjected to 1 atm air pressure for 6 days, with removal for AFM imaging before returning to the pressure chamber. It was shown that the control cavities which did not have FIB nanopores were air sealing and some cavities with FIB nanopores showed possible inflation post graphene layer transfer. It was also
indicated that graphene damage was a possibility after transferring the final layer as shown by the increase in “bumps” surrounding the cavity.

**Figure 6.24:** Transfer of the final graphene layer to seal the FIB nanopore.

**Figure 6.25:** AFM topography of Cavity 16 on Sample K1 (6 layers of graphene on 5 µm diameter cavity) topography over time with continuous 1 atm air pressure after transfer of a final (6th) graphene layer. Cavity 16 has a 30-nm diameter FIB nanopore and displays inflation.

**Figure 6.26:** Volume changes in Cavity 16 on Sample K1 (6 layers of graphene on 5 µm diameter cavity) as a function of time while charging under 1 atm air pressure
continuously after transfer of a final (6\textsuperscript{th}) graphene layer. Cavity 16 has a 30-nm diameter FIB nanopore and displays inflation.

**Table 6.6:** Flux rates over 5 days for Cavity 16 on Sample K1 (6 layers of graphene on 5 μm diameter cavity) while charging under 1 atm air pressure continuously after transfer of a final (6\textsuperscript{th}) graphene layer. Cavity 16 has a 30-nm diameter FIB nanopore.

<table>
<thead>
<tr>
<th>Range [hours]</th>
<th>Cavity</th>
<th>Initial bulge volume [μm(^3)]</th>
<th>Volume deflation rate [μm(^3)/s]</th>
<th>Gas flow rate [mol/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-5</td>
<td>16</td>
<td>-0.43</td>
<td>1.83x10(^{-6})</td>
<td>7.87x10(^{-23})</td>
</tr>
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**Ion Bombardment**

The final step of our experiment involved ion irradiation on the FIB cavities with the intention of introducing subnanometer pores at the weakest point of the graphene monolayer. It was theorized that the subnanometer pores would be created in the single layer graphene as opposed to the surrounding 6-layer graphene (Figure 6.27). Control cavities were also bombarded with ions for comparison to confirm or deny this concept. Three ion fluences (10\(^{13}\) ion/cm\(^2\), 10\(^{14}\) ion/cm\(^2\), and 10\(^{15}\) ion/cm\(^2\)) were tested to determine which setting would provide us with targeted monolayer pore introduction. However, the cavities which underwent 10\(^{15}\) ion/cm\(^2\) ion fluences were not observed inflated under any circumstances. We determined that fluences of 10\(^{15}\) ion/cm\(^2\) and higher caused significant damage to the multilayer graphene and could not be used for our purposes. We will further discuss the 10\(^{13}\) ion/cm\(^2\) and 10\(^{14}\) ion/cm\(^2\) findings.

**Figure 6.27:** Illustration of the predicted nanopore introduced by ion bombardment.
Starting with $10^{13}$ ion/cm$^2$ ion fluence and using air as the charging gas, we placed the sample in a pressure chamber at 1 atm continuously for 4 days, with removal for AFM imaging before returning to the pressure chamber. We found that slight positive deflection occurred in some control cavities bombarded at $10^{13}$ ion/cm$^2$ fluence while the cavities with FIB nanopores did not inflate. These control cavities with 6 layers of graphene were air sealing and retained low permeance even after ion bombardment such that the nanoballoon could inflate and hold pressure long enough for AFM measurement. The FIB cavities which underwent ion bombardment at $10^{13}$ ion/cm$^2$ fluence were highly air permeable, suggesting that a small pore could have been created by ion bombardment in the suspended graphene monolayer.

**Figure 6.28:** AFM topography of control and FIB processed cavities on Sample K1 (6 layers of graphene on 5 µm diameter cavity) topography over time with continuous 1 atm air pressure after ion bombardment at $10^{13}$ ion/cm$^2$ fluence. (a) Cavity O is a control cavity which had no FIB processing and displays clear positive deflection after 2 days in air pressure. (b) Cavity 4 and (c) Cavity 12 have a 10-nm diameter FIB nanopore and do not display positive graphene deflection.
Figure 6.29: Volume changes in control (Cavity O) and FIB cavities (Cavity 4 and 12) on Sample K1 (6 layers of graphene on 5 µm diameter cavity) as a function of time while charging under 1 atm air pressure continuously and ion bombardment at $10^{13}$ ion/cm$^2$ fluence. Cavity O has no FIB processing while Cavity 4 and Cavity 12 have a 10-nm diameter FIB nanopore.

Assuming an elapsed time of 15 minutes between removal from the pressure chamber and complete AFM imaging, and using a conservative AFM resolvable initial bulge volume of 0.25 µm$^3$, we calculated the following lower limit gas permeances for air out of Cavity K1-4 and K1-12.

Table 6.7: Flux rates for Cavity 4 and Cavity 12 on Sample K1 (6 layers of graphene on 5 µm diameter cavity) while charging under 1 atm air pressure continuously and after ion bombardment at $10^{13}$ ion/cm$^2$ fluence. Assuming an elapsed time of 15 minutes during deflation and a conservative initial bulge volume of 0.25 µm$^3$. Cavity 4 and Cavity 12 have a 10-nm diameter FIB nanopore.

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<tbody>
<tr>
<td>4</td>
<td>0.25*</td>
<td>-2.78x10^{-4}</td>
<td>-1.16x10^{-20}</td>
<td></td>
</tr>
<tr>
<td>15*</td>
<td>0.25*</td>
<td>-2.78x10^{-4}</td>
<td>-1.16x10^{-20}</td>
<td></td>
</tr>
</tbody>
</table>

* conservative estimates to determine the lower limit gas permeance.
The cavities were also investigated under helium charging. No inflation was detected in any of the control or FIB cavities. This same behavior was measured for a cavity without ion bombardment and could therefore be a result of intrinsic defects in the graphene as opposed to ion damage. After charging in air pressure for 2 days, we left the sample at SATP and tested the deflation period for Cavity K1-O (ion bombarded at $10^{13}$ ion/cm$^2$ fluence, no FIB processing). The cavity remained stable for at least 5 days with negligible (~10 nm) deflection change. We determined air sealing with 6-layers of graphene and a low air permeance of $-4.92 \times 10^{-22}$ mol/s.

**Figure 6.30**: AFM topography of Cavity O on Sample K1 (6 layers of graphene on 5 µm cavity) at SATP over 5 days after charging in air pressure for 2 days. Cavity O is a control which did not have FIB processing but was ion bombarded at $10^{13}$ ion/cm$^2$ fluence.

**Figure 6.31**: Volume changes in Cavity O on Sample K1 (6 layers of graphene on 5 µm diameter cavity) as a function of time at SATP after charging at 1 atm air pressure for 2
days and ion bombardment at $10^{13}$ ion/cm$^2$ fluence. Cavity O is a control which did not have FIB processing but was ion bombarded at $10^{13}$ ion/cm$^2$ fluence.

**Table 6.8:** Flux rates over 5 days for Cavity O on Sample K1 (6 layers of graphene on 5 $\mu$m diameter cavity) at SATP after charging at 1 atm air pressure for 2 days and ion bombardment at $10^{13}$ ion/cm$^2$ fluence. Cavity O is a control which did not have FIB processing.

<table>
<thead>
<tr>
<th>Range [hours]</th>
<th>Cavity</th>
<th>Initial bulge volume [$\mu$m$^3$]</th>
<th>Volume deflation rate [$\mu$m$^3$/s]</th>
<th>Gas flow rate [mol/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-120</td>
<td>O</td>
<td>0.95</td>
<td>-9.94x10^{-6}</td>
<td>-4.92x10^{-22}</td>
</tr>
</tbody>
</table>

Using $10^{14}$ ion/cm$^2$ ion fluence, the sample was placed in a pressure chamber under 1 atm air continuously for 4 days, with removal for AFM imaging before returning to the pressure chamber. The inflation rate of the control cavity with 6 layers of graphene was much lower after $10^{14}$ ion/cm$^2$ bombardment than after $10^{13}$ ion/cm$^2$ bombardment. The membrane may have partially deflated between being removed from the pressure chamber and being imaged by AFM. This would mean that $10^{14}$ ion/cm$^2$ irradiation increases the permeance of 6-layer graphene over the inherent value due to intrinsic defects. Again, the FIB holes sealed with a final layer of graphene that underwent ion bombardment (this time at $10^{14}$ ion/cm$^2$ fluence) were highly air permeable, suggesting that a small pore could have been created by ion bombardment in the suspended graphene monolayer. Thus, we find that while 1 layer graphene can be perforated with air preamble pores at only $10^{13}$ ion/cm$^2$ bombardment, the permeance of 6-layer graphene remains unchanged by $10^{13}$ ion/cm$^2$ bombardment, but increases significantly with $10^{14}$ ion/cm$^2$ irradiation.
**Figure 6.32:** Control and FIB processed cavities on Sample K1 (5 µm diameter cavity) topography over time with continuous 1 atm air pressure after ion bombardment at $10^{14}$ ion/cm$^2$ fluence. (a) Cavity F is a control cavity which had no FIB processing and displays clear positive deflection after 2 days in air pressure. (b) Cavity 3 and (c) Cavity 15 have a 10-nm and 30-nm diameter FIB nanopore, respectively, and do not display positive graphene deflection.

**Figure 6.33:** Volume changes in control (Cavity F) and FIB cavities (Cavity 3 and 15) on Sample K1 (5 µm diameter cavity) as a function of time while charging under 1 atm air pressure continuously after ion bombardment at $10^{14}$ ion/cm$^2$ fluence. Cavity F had no FIB processing while Cavity 3 and Cavity 15 have a 10-nm and 30-nm diameter FIB nanopore, respectively.
Table 6.9: Flux rates over 4 days for control and FIB processed cavities on Sample K1 (5 \(\mu m\) diameter cavity) while charging at 1 atm air continuously after ion bombardment at \(10^{14}\) ion/cm\(^2\) fluence. Cavity F is a control which did not have FIB processing while Cavity 3 and Cavity 15 have a 10-nm and 30-nm diameter FIB nanopore, respectively.

<table>
<thead>
<tr>
<th>Range [days]</th>
<th>Cavity</th>
<th>Initial bulge volume [(\mu m^3)]</th>
<th>Volume deflation rate [(\mu m^3/s)]</th>
<th>Gas flow rate [mol/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-4</td>
<td>F</td>
<td>0.95</td>
<td>8.70x10(^{-7})</td>
<td>3.60x10(^{23})</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.95</td>
<td>3.47x10(^{-7})</td>
<td>1.54x10(^{23})</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>0.95</td>
<td>2.28x10(^{-7})</td>
<td>9.43x10(^{24})</td>
</tr>
</tbody>
</table>

6.3.3 Conclusions

We developed a technique to measure the gas permeance of \(~10\) nm diameter areas of graphene based on the method of Bunch et al. (2008)\(^6\) and Koenig et al. (2012)\(^7\) for measuring the gas permeance of micron-scale areas of graphene. This enables measurement of nanoscopic areas of more permeable materials than were previously possible. While we have tested it on perforated areas of single layer graphene, we anticipate being able to measure other atomically thin materials in future work. To do this, the nanomaterial would be depositing over the FIB generated hole in a multi-layer graphene nanoballoon and the same inflation test would be performed.

Using a polymer-free transfer procedure, we stacked 5 layers of CVD graphene over 5 \(\mu m\) diameter, 3 \(\mu m\) deep wells in a silicon wafer. We charged the wells with various gases under pressure, then tracked the membrane deflection over time by AFM. We successfully measured the intrinsic He, air, and SF\(_6\) permeance of 5-layer CVD grown graphene. Defects in CVD graphene have a wide size distribution and their density means that a small number will exist in the area of 5-layer graphene over these microcavities. Thus, the gas permeance and molecule size cut-off will vary from membrane to membrane over the sample. One cavity provided a strong seal for both helium and air while another showed high helium permeance with low air and argon permeance. The helium permeance in Cavity L1-2 exceeded the measurement limit of 1.16x10\(^{20}\) mol/s
while the air permeance was found to be $1.57 \times 10^{-23} \text{ mol/s}$ for air. This corresponds to a helium/air selectivity of 740 through defects in 5-layer graphene. Based on the membrane’s selectivity to helium over argon, we determined that the molecule size cut-off for the Cavity L1-2 membrane was between 0.26 nm (helium kinetic diameter) and 0.34 nm (argon kinetic diameter). Figure 6.34 summarizes our gas permeance measurements.

We used FIB milling to create ~10 or ~30 nm holes in the 5-layer graphene nanoballoons and found that they provided lower resistance to gas flow than could be measured by the AFM technique. We sealed the holes with a final layer of graphene and perforated that area by ion bombardment. The 6 layers of graphene around the FIB hole were found to remain sealed after $10^{13}$ ion/cm$^2$ bombardment but increased in permeance after $10^{14}$ ion/cm$^2$ bombardment. Single layer graphene, on the other hand, became highly air permeable at only $10^{13}$ ion/cm$^2$ bombardment. This demonstrates that the measurement technique we developed successfully isolates gas flow to the graphene area over the FIB drilled hole and that low dosage ion bombardment can be used to perforate that area without compromising the seal of the surrounding nanoballoon.

Future work will use this method to explore the gas selectivity created by ion bombardment and other treatments. The method will further be applied using other two-dimensional materials to seal the FIB hole in the graphene nanoballoon. Here, the graphene nanoballoon structure is essential because it allows measuring materials that cannot be suspended over micron-scale areas or that would be too permeable on that scale to be measured by AFM before deflating.
Figure 6.34: Comparison of gas permeance for He, air, and SF₆ across graphene membranes in samples E1, K1, and L1. (Inset) Close-up of the air permeance values. All cavities measured have a diameter of 5 µm. Sample E1 (crosses) was created using PMMA-supported graphene transfer and has 3 layers of graphene. Samples K1 (circles) and L1 (squares) were created using PMMA free graphene transfer and have 6 and 5 layers of graphene, respectively. Open circles indicate FIB processed and/or ion bombarded cavities, specific processing indicated. Arrows indicate the possibility for greater permeance (a lower limit point).
Chapter 7

Final Conclusions

In this chapter, we will summarize the main findings from this paper, the contributions made, and further steps required in the future of atomically thin membrane technology.

7.1 Molecular Advection-Diffusion Through Graphene Nanopores

We created LJ liquid argon molecular dynamics simulations and calculated argon advection-diffusion rates through graphene nanopores by molecular dynamics simulations. The results agree with continuum transport model predictions for 5 nm pore size but demonstrated lower transport rates at <5 nm pore size. These lower values were partly due to argon adsorption on the graphene and nanopore surface. The amount of argon adsorption or surface layering depended on fluid-graphene interaction potential and fluid temperature. Transport rates in these argon adsorption layers can cause reduced transport rates as a result of higher nanopore entrance resistance. We showed that this resistance can be accounted for in the continuum models by using an effective pore length.

7.2 Gas Permeance Measurements Through Micron-Scale Graphene Membranes

Experimentally, we tested various graphene transfer techniques and developed a reliable method for producing multilayer graphene nanoballoons from CVD graphene based on a previously developed polymer free biphasial technique. Furthermore, we successfully created a silicon platform for testing various atomically thin materials with potential for membrane technologies. This platform provided arrays of individual cavities which could be methodically identified such that experiments could be repeated on the same micrometer area of suspended 2D material over time and using different equipment. The ease of identification also allowed for targeted nanopore introduction by Focused Ion Beam (FIB) and then isolation of the measurement area on the micrometer scale such that the nanopores could be located within the cavity area for imaging and testing. The
cavities in the silicon wafer held sufficient volume, allowing for the detection of suspended membrane deflection as a result of pressure differences across the material. The relatively large cavity volume in comparison to the membrane deflected “nanoballoon” volume provided a flow rate through the membrane which was on a time and height scale resolvable on an Atomic Force Microscope (AFM). We developed an AFM calculation method for volume and area analysis on the Si platform. The deflected membrane nanoballoon volume could be calculated by identifying the cavity area under the AFM image views. Then, using the AFM tools and statistics panels, these values as well as topographical representations of the membrane could be obtained with low sensitivity.

The platform allowed us to create and localize nanopores in the suspended membrane material and test the processed cavity under various gas and pressure conditions. While pristine graphene is impermeable to gases, we used graphene grown from Chemical Vapour Deposition (CVD) techniques which contains graphene defects. Using multilayer graphene stacks, these defects could be isolated and provide selectivity. We measured selectivity and gas permeance through defects in graphene membranes with at least 5 layers. The graphene membranes demonstrated $1.57 \times 10^{23}$ mol/s air permeance, $2.97 \times 10^{22}$ mol/s SF$_6$ permeance, and a lower $1.16 \times 10^{-20}$ mol/s He limit. We calculated a lower limit due to the unresolvable time scale of the helium gas flow. We also observed a molecule size cut-off range of 0.26-0.34 nm demonstrated by a helium-air and argon-air selectivity during testing. We quantified the helium-air selectivity to be 740. Additionally, we varied the levels of gas permeance by creating pores with Focused Ion Beam (FIB) processing and ion bombardment. Cavities with 6 layers of graphene, with and without FIB fabricated nanopores, still presented air permeance after ion bombardment at $10^{13}$ and $10^{14}$ ion/cm$^2$ ion fluences. Exceeding this created too much damage in the cavities to hold pressure. We also determined that charging gas kinetic diameter and pressure have a proportional influence on gas permeance.

7.3 Recommendations and Future Work

The unresolvable flow rates, due to gases escaping on a time scale too small for the AFM measurement, could potentially be remedied with the introduction of smaller nanopores
or a greater support cavity length. This cavity length was limited by the 1:1 cavity diameter to depth ratio possible through Deep Reactive-Ion Etching (DRIE) but could be increased to 5 µm as opposed to the 3 µm used. We found that the 5 µm diameter cavity was the best to work with for suspending multilayer graphene stacks.

Some difficulties we encountered with using the custom Si platform included lack of visibility as more layers of graphene were used or if the cavity size was too small or the cavity spacing was too large. As graphene was stacked, the material would become more opaque or features on the graphene would make the uniform cavity pattern on the platform less visible and harder to use. If the cavity sizes were too small, the cavities would be comparable to small features on the sample (debris or crumpled graphene), making the pattern hard to distinguish and use. The same issue was possible with cavities which were too spread apart (183.8 µm spacing), with greater space between the cavities, the pattern would be harder to identify. Solutions to this could include using a minimum cavity diameter of 5 µm, a spacing of ~50 µm, and better wafer and graphene cleaning steps with storage as soon as possible to limit exposure to floating particles in the air. Additional improvements to the wafer fabrication would be to include a visible grid outline and etched coordinates where the cavities occur at line intersections, each with a unique identifier. This would help with identification if the grid lines could be used in addition to recognizing the uniform cavity arrangement.

While the potential of graphene membranes could not be fully recognized in this research alone, it served as a good starting point in developing suitable measurement and fabrication techniques for future advancement. Larger areas of suspended graphene and various conditions including fluid type, temperature, and pressures, could be further explored to understand the limits of atomically thin graphene membrane technologies. Furthermore, graphene membrane performance could be analyzed for fluid mixtures, long-term integrity, and scale-up economics.
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Appendix A: Cavity Leak Rate Equation Derivation

Figure A. 1: Illustration of the cavity parameters after positive membrane deflection due to gas charging. Both variables, $P$ and $V_b$, change over time as gas leaks out of the cavity.

Starting with the ideal gas law,

$$n = \frac{P(V_o + V_b)}{RT} \quad (A. 1)$$

where $n$ is the number of moles, $P$ is the pressure, $R$ is the universal gas constant, $T$ is the temperature (295.15 K), $V_o = \pi a^2 H$ is the volume of the cavity, $a$ is the radius of the cavity, $H$ is the depth of the cavity, $V_b = c\pi a^2 \delta$ is the volume of the bulge, $c$ is a constant (0.524 for graphene), and $\delta$ is the maximum height of the deflected membrane.

Taking the derivative, we obtain an expression for the gas molar flow rate out of the cavity ($\frac{dn}{dt}$ [mol/s]),

$$\frac{dn}{dt} = \frac{1}{RT} \frac{d[P(V_o + V_b)]}{dt} \quad (A. 2)$$
Hencky’s solution for thin membrane deflection as a result of a pressure difference across the membrane, relates the volume of the deflected membrane “bulge” \(V_b\) and the pressure difference across the membrane \(\Delta P\) to the membrane deflection \(\delta\):

\[
\Delta P = \frac{K E w \delta^3}{a^4}
\]  

where \(K\) is a constant (3.09 for graphene), \(E\) is the Young’s modulus (1 TPa), and \(w\) is the membrane thickness (0.34 nm per layer of graphene).

Understanding that \(P = P_{atm} + \Delta P\) and \(\delta = \frac{V_b}{c \pi a^2}\), Equation 1 and 2 become,

\[
\frac{dn}{dt} = \frac{1}{RT} \frac{d}{dt} \left[ (P_{atm} + \Delta P) (V_0 + V_b) \right]
\]  

\[
\Delta P = \frac{K E w}{a^4} \left( \frac{V_b}{c \pi a^2} \right)^3 = \frac{K E w}{c^3 \pi^3 a^{10}} V_b^3
\]  

Substituting Equation A. 5 into Equation A. 4 we get,

\[
\frac{dn}{dt} = \frac{1}{RT} \frac{d}{dt} \left[ (P_{atm} + \frac{K E w}{c^3 \pi^3 a^{10}} V_b^3 (V_0 + V_b) \right]
\]  

\[
\frac{dn}{dt} = \frac{1}{RT} \frac{d}{dt} \left[ (P_{atm} V_0 + P_{atm} V_b + \frac{K E w}{c^3 \pi^3 a^{10}} V_0 V_b^3 + \frac{K E w}{c^3 \pi^3 a^{10}} V_b^4) \right]
\]

\[
\frac{dn}{dt} = \frac{1}{RT} \left[ P_{atm} \frac{dV_b}{dt} + \frac{3 K E w}{c^3 \pi^3 a^{10}} V_0 V_b^2 \frac{dV_b}{dt} + \frac{4 K E w}{c^3 \pi^3 a^{10}} V_b^3 \frac{dV_b}{dt} \right]
\]

\[
\frac{dn}{dt} = \frac{1}{RT} \left[ P_{atm} + \frac{3 K E w}{c^3 \pi^3 a^{10}} V_0 V_b^2 + \frac{4 K E w}{c^3 \pi^3 a^{10}} V_b^3 \right] \frac{dV_b}{dt}
\]  

where \(\frac{dV_b}{dt} \ [\mu m^3/s]\) is the volume flow rate.
Appendix B: Polycarbonate Track Etch Membranes

Figure B. 1: Position of the glass slides for silane deposition.

Figure B. 2: (a) A PCTEM on top of a graphene on copper piece on top of a glass slide. (b) A silanated slide is placed on top of the stack in (a). (c) The silanated slide with PCTEM and graphene on copper piece adhered to it. (d) PCTEM on top of a graphene on copper piece on top of a pool of water on a glass slide.

Figure B. 3: The graphene transfer process using PCTEMs as the support substrate. (a) The Gr/Cu piece on PCTEM is placed in APS and etched. (b) After etching the sample is (c) rinsed in DI water and (d) ethanol before (e) removal.

Figure B. 4: AFM images of single layer graphene on PCTEM with 5 μm cavities. (a) Various cavities, (b) partially covered cavity, (c) height line trace along (b).

Figure B. 5: AFM topography of graphene covered cavities on Sample 1A (2 layers of graphene on PCTEM with 5 μm cavity) where clear negative deflection is displayed in Cavity 2.

Fabrication

Approximately 1cm² pieces of monolayer graphene on copper (Graphenea) were cut using razor blades. These pieces were held with tweezers and dropped parallel into a dish of ammonium persulfate solution (APS-100 Copper Etchant, Transene) such that the copper side floats on the etchant surface. The piece was pre-etched for 2 minutes to remove unwanted graphene on the backside of the copper resulting from CVD growth. After this cleaning step, the graphene on copper (Gr/Cu) piece was transferred using a glass slide to three consecutive deionized (DI) water baths and rinsed for 5 min, 2 min, and 2 min respectively. Next, the Gr/Cu was removed and air dried. Four glass slides were cleaned on both sides with acetone, ethanol, and two rounds of DI water. Dispenser bottles were used to spray sheets of each liquid on the glass surface. The glass slides were then immediately dried off with nitrogen gas using a tube and nozzle. All four glass slides were placed in a large plastic petri dish side by side (Figure B. 1). A micropipette was used to measure 200 μL of chlorotrimethylsilane (≥ 99.0%, Sigma-Aldrich) which was dropped evenly on the exposed areas of the petri dish, avoiding contact with the glass slides. The petri dish lid was placed on top and a timer was set for 4 minutes to allow the
silane to deposit onto the top surface of the glass slides. After 4 minutes, the glass slides were removed and placed in a clean petri dish. A pre-etched piece of Gr/Cu is placed on a new glass slide with the graphene side facing up. Next, a polycarbonate track etched membrane (PCTEM) filter (5 µm pores, 25 mm diameter, from Sterlitech), which has a shiny and a matte side, was placed on top with the shiny side facing up. A silanated glass slide is placed on top of the Gr/Cu and PCTEM stack, with the silanated side of the slide touching the PCTEM. Next, a small glass pipette is rolled at least 8 times with force across the glass slides to press the Gr/Cu and membrane together. The top slide is removed with the Gr/Cu and polycarbonate membrane adhered to it. Weigh paper could be placed between the graphene and the glass slide to prevent sticking and encourage adherence to the PCTEM and silanated slide.

A second glass slide is placed on a flat surface, and DI water is pooled at one end. The silanated slide with the Cu/Gr/membrane stack (in that order) is brought carefully to the water pool surface until the membrane floats with the Gr/Cu underneath (Cu facing the water). If the Cu/Gr/membrane successfully floats on the pool of water, the pool is carefully poured into an APS bath and allowed to etch until there is no more visible copper. After this point, it is “over-etched” for 2 minutes. The membrane is then transferred from the APS bath to three consecutive DI water baths for 5 minutes each using a glass slide. The membrane sample is then transferred into a beaker filled with distilled water. The distilled water is diluted with ethanol until the membrane sinks. Then the membrane is removed with tweezers and air dried. If the Gr/Cu turns significantly dark at any point the sample has failed and a new one must be made. Multiple layers of graphene were stacked by repeating the process on the same polycarbonate membrane sample. Up to 3 layers of graphene were stacked on the shiny side of the PCTEM before up to 3 layers of graphene were stacked on the matte side.
Figure B. 1: Position of the glass slides for silane deposition.

Figure B. 2: (a) A PCTEM on top of a graphene on copper piece on top of a glass slide. (b) A silanated slide is placed on top of the stack in (a). (c) The silanated slide with PCTEM and graphene on copper piece adhered to it. (d) PCTEM on top of a graphene on copper piece on top of a pool of water on a glass slide.
Figure B. 3: The graphene transfer process using PCTEM as the support substrate. (a) The Gr/Cu piece on PCTEM is placed in APS and etched. (b) After etching the sample is (c) rinsed in DI water and (d) ethanol before (e) removal.

**Results**

Using 1 layer of graphene on a 5 μm diameter cavity PCTEM, no covered pores could be found. However, some partially covered pores and tears in the AFM scanning direction could be seen. These tears suggested that the AFM probe was exerting too much force on the graphene resulting in damage, indicating that our scan settings needed to be adjusted.

Figure B. 4: AFM images of single layer graphene on PCTEM with 5 μm cavities. (a) Various cavities, (b) partially covered cavity, (c) height line trace along (b).
Stacking 2 layers of graphene on the shiny side of a PCTEM with 5 µm diameter cavities produce the following AFM images:

![AFM images of Cavity 1 and Cavity 2](image)

**Figure B. 5:** AFM topography of graphene covered cavities on Sample 1A (2 layers of graphene on PCTEM with 5 µm cavity) where clear negative deflection is displayed in Cavity 2.
Appendix C: PMMA Facilitated Graphene Transfer

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**Fabrication**

CVD grown graphene on copper was ordered from Graphenea with a 60 nm layer of PMMA on top. Approximately 1cm² pieces of the PMMA/Gr/Cu material were cut using razor blades. These pieces were held with tweezers and dropped on top of ammonium persulfate solution (APS-100 Copper Etchant, Transene) such that the copper side was floating on the solution surface. (Figure C. 1) The copper was etched for ~15 minutes until it visually disappeared. After this point, the piece was “over-etched” for 2 minutes to ensure any residual copper was removed. The PMMA/Gr was then scooped using a glass slide into two consecutive DI water baths and allowed to rinse for 5 minutes each. Multilayer graphene stacks were created by scooping the PMMA/Gr piece with a Gr/Cu piece such that the graphene layers were in contact. The piece was then air dried and repeated until the desired number of layers was achieved (PMMA/Gr/Gr../Cu). Finally, the copper was etched away and placed in two consecutive DI water baths. An Si wafer chip was used to scoop the piece out of the final bath and air dried. The sample was then annealed on a hotplate for 30 minutes in air at 180˚C. Eventually, the PMMA layer was removed by submerging the sample in acetone at 50˚C for 1 hour followed by an IPA
bath for 1 hour. Note that the acetone beaker was placed in a heated water bath on a preheated hot plate.

![Diagram](image)

**Figure C. 1:** The (a) etching, (b) scooping, (c) rinsing, and (d) stacking (onto a new Gr/Cu piece) steps in the PMMA-facilitated graphene transfer process.

**Results**

Stacking 3 layers of graphene (with a layer of PMMA on top) on a 3-µm and 5-µm diameter cavity wafer produced low yield for complete cavity coverage. However, it seemed that the 3-µm diameter cavities demonstrated greater potential since it had partially covered pores. We later discovered that it was difficult to identify the 3-µm diameter cavities once graphene had been transferred because the cavities were comparable to other features on the sample and easily confused.
We created a 3-layer graphene (plus PMMA) stack on a new wafer (E1) with 5-µm diameter cavities which demonstrated greater cavity coverage. We produced AFM images in ambient conditions, after annealing, and after charging with 1 atm air pressure. We expected to measure negligible membrane deflection with the PMMA layer aiding graphene sealing. With the PMMA removed, we expected to measure outward membrane deflection at positive pressure differences, and inward membrane deflection at negative pressure differences (Figure C. 3).

**Figure C. 3:** Expected membrane deflections with (a) the PMMA boundary layer and without PMMA under (b) zero, (c) positive, and (d) negative pressure differences.
We found positive membrane deflection after the anneal step, and negative deflection after 1.5 weeks in SATP conditions. This suggested that there could have been water trapped in the microcavities after graphene transfer which then vaporized during the heating step, causing the nanoballoons to expand. Then given enough time, the vapour slowly diffused out of the nanoballoon. The inflation was found to be on the same order as with gas pressure as tested in later experiments, giving confidence to the idea that trapped water could have vaporized.

Figure C. 4: AFM topography of graphene covered cavities on Sample E1 (3 layers of graphene on 5 µm cavity) before and after annealing.

After a 10-day period, the sample was subjected to air pressure. We found that many cavities demonstrated negative deflection even after 2 days of pressurization. Next, we removed the PMMA layer with a 1 hour, 50°C acetone bath followed by a 1 hour IPA bath at room temperature. The sample was then charged in air pressure for 2 days, allowed to rest in ambient conditions for 3 days, and finally subjected to vacuum for 2 days. It was found that only some cavities responded to the pressure changes as demonstrated by seemingly random recorded deflection directions (Figure C. 6). However, it was clear in Cavities E1-1 and E1-2 that greater flux rates were demonstrated after PMMA removal. Without the PMMA layer, the system was more permeable and demonstrated responsive graphene deflection to both air pressure and vacuum (Figure C. 7). This showed that the PMMA layer provided a good seal for the system and while the
PMMA removal process likely left residue, sufficient amounts of PMMA was removed to allow gas flow through the support cavities.

Figure C. 5: AFM topography of (a) Cavity 1 and (b) Cavity 2 on Sample E1 (3 layers of graphene on 5 µm cavity) demonstrating clear graphene deflection after PMMA removal.

Figure C. 6: AFM topography of various cavities on Sample E1 (3 layers of graphene on 5 µm cavity) after 2 days of vacuum.
Figure C. 7: Volume change overtime at SATP for Cavities 1, 2, and 5 on Sample E1 (3 layer graphene on 5 µm cavity). Pressure charging periods are labeled. The sample is charged in air pressure from Days 3-5 and 10-12. The sample is under vacuum from Days 12-14. PMMA removal is indicated on Day 9. AFM images are taken between these periods.

Using Cavity 2 as a reference, we concluded that Cavities 5, 6, and 8 were not responding to pressure changes. The positive deflection after vacuum could have been due to extra graphene material bunched up over the cavity with sufficient defects such that no pressure difference could be maintained across the graphene. This hypothesis was tested by subjecting the sample to longer periods of vacuum to determine whether a pressure difference was maintained across Cavities 5, 6, and 8 or if the deflection was caused by excess material. The sample was placed in a pressure chamber under vacuum for 19 days. After this period, the sample was removed and imaged in ambient conditions with the AFM. It was found that the samples which had a positive membrane deflection prior to the vacuum period, had a negative deflection after the 19 days in vacuum and remained stable for ~10 days at SATP. This suggested that there was a much better seal on some cavities which could not be achieved by graphene alone. This may have been the result of PMMA residue on the graphene providing a greater seal.
Figure C. 8: AFM topography of (a) Cavity 5 and (b) Cavity 6 on Sample E1 (3 layers of graphene on 5 µm cavities) showed negative deflection after a longer vacuum period.

Figure C. 9: AFM topography of Cavity 8 on Sample E1 (3 layers of graphene on 5 µm cavity) showed negative deflection after longer vacuum period.
**Figure C. 10:** Volume changes in Sample E1 (3 layers of graphene on 5 \( \mu \text{m} \) cavities) over time at SATP after a 19-day period under vacuum.

**Table C. 1:** Flux rates after to 19 days under vacuum.

<table>
<thead>
<tr>
<th>Range [days]</th>
<th>Cavity</th>
<th>Initial bulge volume [( \mu \text{m}^3 )]</th>
<th>Volume deflation rate [( \mu \text{m}^3/\text{s} )]</th>
<th>Gas flow rate [mol/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>21-31</td>
<td>5</td>
<td>-1.5</td>
<td>5.81x10^{-7}</td>
<td>3.52x10^{-23}</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>-1.6</td>
<td>4.75x10^{-7}</td>
<td>3.00x10^{-23}</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>-1.7</td>
<td>2.26x10^{-7}</td>
<td>1.49x10^{-23}</td>
</tr>
</tbody>
</table>

We also tested the effects of heating under vacuum. We placed the sample under vacuum in a custom pressure chamber which could be placed on a hot plate at 150°C. The sample was taken out each day for AFM measurement and returned to the chamber for storage under heated vacuum. We found that the samples reached maximum negative deflection within one day and remained stable for 15 days.
Figure C. 11: AFM topography of (a) Cavity 19 and (b) Cavity 21 on Sample E1 (3 layers of graphene on 5 μm diameter cavity) showing equilibration within 1 day. Samples remained stable for 15 days under continuous vacuum at 150°C.
Figure C. 12: AFM topography of (a) Cavity 20 and (b) Cavity 27 on Sample E1 (3 layers of graphene on 5 µm diameter cavity) showing equilibration within 5 days and stability for 15 days under continuous vacuum at 150°C.

Figure C. 13: Volume changes for cavities on Sample E1 (3 layers of graphene on 5 µm diameter cavity) before and after daily subjection to a heated (150°C) vacuum.
**Focused Ion Beam**

Two PMMA supported graphene on copper stacks were sent to the Western University Nanofabrication Facility for nanopore drilling. We planned to drill nanopores in the PMMA/Gr.../Cu stacks and then etch the copper before transfer onto an Si wafer. We decided to create an array of 30 nm diameter FIB nanopores with 5 µm spacing to ensure that one and only one nanopore would align with the 5-µm diameter suspended graphene area on a support cavity regardless of orientation. A 200x200 µm² area of the PMMA/Gr.../Cu stack was drilled with the FIB to produce 1600 dots (1 pA at 2 seconds per hole). Markers were used to identify the location of the FIB area.

![FIB area identification markers, Si wafer cavities, FIB nanopores in the PMMA/Gr.../Cu stack, overlap of cavities and nanopores.](image)

**Figure C. 14:** Illustration of the (a) FIB area identification markers, (b) Si wafer cavities, (c) FIB nanopores in the PMMA/Gr.../Cu stack, and (d) overlap of cavities and nanopores.

![SEM images of the FIB nanopores in the PMMA/Gr.../Cu stack](image)

**Figure C. 15:** SEM images of the FIB nanopores in the PMMA/Gr.../Cu stack

After etching the copper, the first PMMA/Gr/Gr/Gr piece (Sample #1) tore during handling and was unusable. Sample #2 was successfully transferred onto an Si wafer and the PMMA was removed. However, upon SEM imaging, it was found that there were...
significant tears around the FIB area. Additionally, while 4 cavities were near the FIB area, the ones which had successfully introduced nanopores were already torn.

**Figure C. 16:** SEM images of the FIB area with (a) indicators and (b) four nearby cavities.

**Figure C. 17:** SEM images of (a) Cavity 1 with a tear and nanopore (circled), (b) Cavity 2 with a tear and located outside the FIB nanopore area, (c) Cavity 3 completely uncovered (broken), and (d) Cavity 4 with a tear and a nanopore (circled).
Introducing nanopores in the PMMA/Gr…/Cu prior to transfer onto an Si wafer made it difficult to ensure that there would be a continuous area of suspended graphene (no tears) surrounding the nanopore. Since the quality check was only possible at the end of the intensive fabrication process, it was very time consuming and expensive when the sample would fail either during graphene rinsing or transfer onto the wafer. As a result, we opted to perform FIB processing directly on the wafer to overcome these issues.
Appendix D: Polymer-free Graphene Transfer

Table D. 1: Flux rates in Sample L1 (5 layers of graphene on 5 µm cavity) over 14 days after daily subjection to 1 atm air pressure. ................................................................. 127

Table D. 2: Flux rates on Sample K1 (5 layers of graphene on 5 µm cavity) with daily subjection to 1 atm air pressure after final (6th) layer graphene transfer. Cavities C and D were not FIB processed, while Cavities 9 and 16 have 10 and 30 nm FIB pores, respectively. ........................................................................................................................................... 133

Table D. 3: Flux rates on Sample K1 (5 layers of graphene on 5 µm cavity) after ion bombardment at $10^{15}$ ion/cm² fluence and continuous 1 atm air pressure for 4 days. Cavity V did not have FIB processing while Cavity 5 had a 10 nm FIB pore. ............ 134

Figure D. 1: The (a) etching, (b) 2-liquid phase, (c) scooping, and (d) rinsing steps of the polymer-free graphene transfer process. Transfer onto (e) another Gr/Cu piece to form multilayer graphene stacks or (f) the support substrate as the final step. ....................... 124

Figure D. 2: AFM images of partially covered cavities on (a) Sample N1 (annealed) and (b) Sample O1 (not annealed). Both samples had one layer of graphene on 5 µm cavities. ................................................................. 125

Figure D. 3: AFM images of partially covered 5 µm diameter cavities on (a-c) Sample N1 and (d-f) Sample O1. Sample O1 had noticeably more coverage in comparison. ............ 125

Figure D. 4: AFM topography of (a) Cavity 1 and (b) Cavity 2 on Sample L1 (5 layers of graphene on 5 µm cavity) after daily charging in 1 atm air pressure. .............. 126

Figure D. 5: Volume changes in Sample L1 (5 layers of graphene on 5 µm cavity) with daily subjection to 1 atm air pressure. ................................................................. 127

Figure D. 6: AFM topography of various cavities on Sample L1 (5 layers of graphene on 5 µm cavities) under 25 kPa (a) SF₆, (b) CH₄, and (c) N₂ gas. A broken cavity is displayed in Cavity 2. ................................................................. 128

Figure D. 7: AFM topography of control Cavity C on Sample K1 (5 layers of graphene on 5 µm cavity) at SATP after charging at 1 atm air pressure for 2 days. The control cavity did not undergo FIB processing. ................................................................. 129

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Figure D. 9: AFM topographical timeline of control Cavity C on Sample K1 (5 layers of graphene on 5 µm cavity) over the inflation and deflation experiments. ...................... 130
Figure D. 10: AFM topography of (a) Cavity C and (b) Cavity D on Sample K1 (5 layers of graphene on 5 μm cavity) after 3 days of vacuum and then 1 day of 1 atm air pressure.

Figure D. 11: Volume changes in control cavities on Sample K1 (5 layers of graphene on 5 μm cavity) after 3 days of vacuum and then 1 day of 1 atm air pressure.

Figure D. 12: Transfer of the final graphene layer to seal the FIB nanopore.

Figure D. 13: AFM topography of (a) Cavity C, (b) Cavity D, (c) Cavity 9, and (d) Cavity 16 on Sample K1 (5 layers of graphene on 5 μm cavity) after final (6th) graphene layer is transferred. Cavities C and D have not been FIB processed while Cavities 9 and 16 have 10 and 30 nm FIB pores, respectively.

Figure D. 14: Volume changes on Sample K1 (5 layers of graphene on 5 μm cavity) with daily subjection to 1 atm air pressure before and after final (6th) layer graphene transfer. Cavities C and D were not FIB processed, while Cavities 9 and 16 have 10 and 30 nm FIB pores, respectively.

Figure D. 15: AFM topography of (a) Cavity V and (b) Cavity 5 on Sample K1 (5 layers of graphene on 5 μm cavity) after ion bombardment at $10^{15}$ ion/cm$^2$ fluence and continuous 1 atm air pressure for 4 days. Cavity V did not have FIB processing while Cavity 5 had a 10 nm FIB pore.

Figure D. 16: Volume changes on Sample K1 (5 layers of graphene on 5 μm cavity) after ion bombardment at $10^{15}$ ion/cm$^2$ fluence and continuous 1 atm air pressure for 4 days. Cavity V did not have FIB processing while Cavity 5 had a 10 nm FIB pore.

Fabrication

We first measured ~3.4227 g of solid ammonium persulfate (ACS reagent, ≥ 98.0%, Sigma-Aldrich) and dissolved it in 150 mL of DI water to produce 0.1 M ammonium persulfate solution (APS). This was placed in a glass dish and we prepared ~1 cm$^2$ pieces of monolayer graphene on copper (Graphenea). These pieces were floated on the APS solution and a thin, ~5 mL layer of hexane (Hexanes Optima, Fisher Chemical) was slowly added on top using a pipette and bulb. The dish was covered with a petri dish lid and allowed to etch for about 2 hours until visual confirmation of complete copper removal. A second petri dish was filled with DI water with a thin film of 5 mL hexane on top. The graphene piece was scooped out of the APS bath using a glass slide (Zhang recommended an angle of 40°) and transferred into the hexane/DI-water dish. The sample typically sits at the water-hexane interface which limits tearing due to the lower surface
tension as opposed to water-air. The sample was rinsed for 30 minutes. Multiple layers of graphene are achieved by scooping the graphene piece out of the final water bath with additional Gr/Cu pieces or by repeated scooping onto a single Si wafer. Following transfer onto the desired substrate (Gr/Cu or Si), the piece was air dried. Later samples were placed under vacuum in a custom-made pressure chamber for 30 minutes which was then placed on a hot plate at 200°C for 1 hour. Pressure chamber fabrication details are in Chapter 5. We tried the vacuum and hot plate anneal step after each layer of graphene for some samples and after the final graphene layer in a multilayer stack for other samples.

**Figure D. 1:** The (a) etching, (b) 2-liquid phase, (c) scooping, and (d) rinsing steps of the polymer-free graphene transfer process. Transfer onto (e) another Gr/Cu piece to form multilayer graphene stacks or (f) the support substrate as the final step.

**Results**

We noticed that there was less graphene tearing using the polymer-free transfer technique and larger pieces of graphene were possible during graphene transfer. Due to difficulty with perfect stacking, the area of n-layer graphene still decreased as n increased. We first tested the level of coverage for 1 layer of graphene on 5 µm cavity pores with and
without the annealing step. The first sample (N1) was placed under vacuum and then annealed at 200°C. Using AFM imaging, we were unable to find completely covered support cavities. Cavities that were partially covered typically had multiple tears in the graphene. The second sample (O1) was not heated under vacuum, and only air dried. While we could not find completely covered cavities with the AFM, we noticed that the partially covered cavities had significantly fewer tears, suggesting that the annealing step could be creating defects in the graphene.

![AFM images of partially covered cavities on (a) Sample N1 (annealed) and (b) Sample O1 (not annealed). Both samples had one layer of graphene on 5 µm cavities.](image)

**Figure D. 2:** AFM images of partially covered cavities on (a) Sample N1 (annealed) and (b) Sample O1 (not annealed). Both samples had one layer of graphene on 5 µm cavities.

![AFM images of partially covered 5 µm diameter cavities on (a-c) Sample N1 and (d-f) Sample O1. Sample O1 had noticeably more coverage in comparison.](image)

**Figure D. 3:** AFM images of partially covered 5 µm diameter cavities on (a-c) Sample N1 and (d-f) Sample O1. Sample O1 had noticeably more coverage in comparison.

Next, we produced two samples with 5 layers of graphene on 5 µm diameter cavities. The first sample (L1) was created by directly stacking 5 layers of graphene onto an Si wafer, where the sample was air dried and annealed under vacuum at 200°C for 1 hour after each
layer. The second sample (K1) was created by stacking layers of graphene on a Gr/Cu piece until a total of 5 graphene layers was achieved. The copper was then etched and the 5-layer graphene stack was transferred onto an Si wafer, air dried, and annealed under vacuum at 200℃ for 1 hour. Sample L1 was used as a control for testing flow rate through unprocessed cavities under various conditions, while Sample K1 was used for FIB processing and ion bombardment.

Next, we produced two samples with 5 layers of graphene on 5 µm diameter cavities. The first sample (L1) was created by directly stacking 5 layers of graphene onto an Si wafer, where the sample was air dried and annealed under vacuum at 200℃ for 1 hour after each layer. The second sample (K1) was created by stacking layers of graphene on a Gr/Cu piece until a total of 5 graphene layers was achieved. The copper was then etched and the 5-layer graphene stack was transferred onto an Si wafer, air dried, and annealed under vacuum at 200℃ for 1 hour. Sample L1 was used as a control for testing flow rate through unprocessed cavities under various conditions, while Sample K1 was used for FIB processing and ion bombardment.

To determine whether the time scale for gas flow through our graphene nanopore would be AFM resolvable, we tested various charging gases on our first 5-layer graphene sample, L1, which was annealed between each layer. First, we charged the sample under air pressure (1 atm) for 10 days and measured the deflection daily before storing the sample under air pressure.

Figure D. 4: AFM topography of (a) Cavity 1 and (b) Cavity 2 on Sample L1 (5 layers of graphene on 5 µm cavity) after daily charging in 1 atm air pressure.
Figure D. 5: Volume changes in Sample L1 (5 layers of graphene on 5 µm cavity) with daily subjection to 1 atm air pressure.

Table D. 1: Flux rates in Sample L1 (5 layers of graphene on 5 µm cavity) over 14 days after daily subjection to 1 atm air pressure.

<table>
<thead>
<tr>
<th>Range [days]</th>
<th>Cavity</th>
<th>Initial bulge volume [µm³]</th>
<th>Volume deflation rate [µm³/s]</th>
<th>Gas flow rate [mol/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-14</td>
<td>1</td>
<td>-0.6</td>
<td>1.83x10⁻⁶</td>
<td>8.14x10⁻²³</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-0.32</td>
<td>9.97x10⁻⁷</td>
<td>4.20x10⁻²¹</td>
</tr>
</tbody>
</table>

Sulfur hexafluoride (SF₆ at 25 kPa), methane (CH₄ at 25 kPa), and nitrogen (N₂ at 20 kPa) were tested as charging gases in that order. We note that these pressurization tests were performed starting from the vacuum state immediately after the helium test, with negative deflection of the membrane. Over the charging periods for each gas, the membrane did not display noticeable deflection change. This suggested very low permeance levels of these gases but unfortunately, the membrane became damaged before further pressurization tests could be performed, so the respective flux could not be calculated.
Figure D. 6: AFM topography of various cavities on Sample L1 (5 layers of graphene on 5 µm cavities) under 25 kPa (a) SF\textsubscript{6}, (b) CH\textsubscript{4}, and (c) N\textsubscript{2} gas. A broken cavity is displayed in Cavity 2.

**Sample K1**

**Focused Ion Beam**

To further test the deflation rate of the control cavities, the sample was placed under air pressure for 2 more days (to completely recharge the cavity) and then removed. The sample was placed at SATP and AFM images of control cavity C were recorded continuously until complete nanoballoon deflation (Figure D. 7). It was found that the control cavity deflated completely in <6 hours but remained stable for 5 days at a maximum deflection of ~50 nm. This showed that cavities without FIB nanopores could hold pressure much longer than those which underwent FIB drilling.
Figure D. 7: AFM topography of control Cavity C on Sample K1 (5 layers of graphene on 5 µm cavity) at SATP after charging at 1 atm air pressure for 2 days. The control cavity did not undergo FIB processing.

Figure D. 8: Volume changes in control Cavity C on Sample K1 (5 layers of graphene on 5 µm cavity) at SATP after charging at 1 atm air pressure for 2 days.
**Figure D. 9:** AFM topographical timeline of control Cavity C on Sample K1 (5 layers of graphene on 5 µm cavity) over the inflation and deflation experiments.

After charging with positive pressure differences, we subjected sample K1 to vacuum for 3 days and observed the deflection change. The control cavities were very responsive to pressure chambers, they demonstrated clear negative deflection as predicted after vacuum and re-inflated under 1 atm air pressure within 1 day (Figure D. 10).

**Figure D. 10:** AFM topography of (a) Cavity C and (b) Cavity D on Sample K1 (5 layers of graphene on 5 µm cavity) after 3 days of vacuum and then 1 day of 1 atm air pressure.
Figure D. 11: Volume changes in control cavities on Sample K1 (5 layers of graphene on 5 µm cavity) after 3 days of vacuum and then 1 day of 1 atm air pressure.

Final Graphene Layer Transfer

A final layer of graphene was transferred onto the wafer to seal the FIB nanopores (Figure 6.24). The sample was then subjected to 1 atm air pressure for 6 days, with removal for AFM imaging before returning to the pressure chamber. It was shown that the cavities which did not have FIB nanopores (control cavities) were permeable to air and some cavities with FIB nanopores showed possible inflation post graphene layer transfer. It was also indicated that graphene damage was a possibility after transferring the final layer as shown by the increase in “bumps” surrounding the cavity.

Figure D. 12: Transfer of the final graphene layer to seal the FIB nanopore.
Figure D. 13: AFM topography of (a) Cavity C, (b) Cavity D, (c) Cavity 9, and (d) Cavity 16 on Sample K1 (5 layers of graphene on 5 µm cavity) after final (6th) graphene layer is transferred. Cavities C and D have not been FIB processed while Cavities 9 and 16 have 10 and 30 nm FIB pores, respectively.

Figure D. 14: Volume changes on Sample K1 (5 layers of graphene on 5 µm cavity) with daily subjection to 1 atm air pressure before and after final (6th) layer graphene transfer.
Cavities C and D were not FIB processed, while Cavities 9 and 16 have 10 and 30 nm FIB pores, respectively.

**Table D. 2:** Flux rates on Sample K1 (5 layers of graphene on 5 µm cavity) with daily subjection to 1 atm air pressure after final (6th) layer graphene transfer. Cavities C and D were not FIB processed, while Cavities 9 and 16 have 10 and 30 nm FIB pores, respectively.

<table>
<thead>
<tr>
<th>Range [days]</th>
<th>Experiment</th>
<th>Cavity</th>
<th>Initial bulge volume [µm³]</th>
<th>Volume deflation rate [µm³/s]</th>
<th>Gas flow rate [mol/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-7</td>
<td>After 5 days at 1 atm (air) after graphene transfer</td>
<td>C</td>
<td>-1.2</td>
<td>2.71x10⁶</td>
<td>1.46x10⁻²²</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D</td>
<td>-1.4</td>
<td>1.12x10⁶</td>
<td>6.50x10⁻²³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td>0.075</td>
<td>1.02x10⁶</td>
<td>4.23x10⁻²³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16</td>
<td>-0.43</td>
<td>1.83x10⁶</td>
<td>7.87x10⁻²³</td>
</tr>
</tbody>
</table>

**Ion Bombardment**

We also tested ion bombardment at 10¹⁵ ion/cm² fluence. We found no inflation under any circumstance and concluded that this level created too much damage for the membranes to hold pressure.

**Figure D. 15:** AFM topography of (a) Cavity V and (b) Cavity 5 on Sample K1 (5 layers of graphene on 5 µm cavity) after ion bombardment at 10¹⁵ ion/cm² fluence and
continuous 1 atm air pressure for 4 days. Cavity V did not have FIB processing while Cavity 5 had a 10 nm FIB pore.

**Figure D. 16:** Volume changes on Sample K1 (5 layers of graphene on 5 µm cavity) after ion bombardment at $10^{15}$ ion/cm$^2$ fluence and continuous 1 atm air pressure for 4 days. Cavity V did not have FIB processing while Cavity 5 had a 10 nm FIB pore.

**Table D. 3:** Flux rates on Sample K1 (5 layers of graphene on 5 µm cavity) after ion bombardment at $10^{15}$ ion/cm$^2$ fluence and continuous 1 atm air pressure for 4 days. Cavity V did not have FIB processing while Cavity 5 had a 10 nm FIB pore.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0-4</td>
<td>V</td>
<td>-0.23</td>
<td>-8.68x10$^{-7}$</td>
<td>-3.62x10$^{-23}$</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>-0.27</td>
<td>-3.47x10$^{-7}$</td>
<td>-1.46x10$^{-23}$</td>
</tr>
</tbody>
</table>
Appendix E: Gas Permeance Comparison

Table E. 1: Comparison of gas permeance for He, air, and SF$_6$ across graphene membranes in Samples E1, K1, and L1. Sample E1 was created using PMMA-supported graphene transfer while Samples K1 and L1 were created using PMMA free graphene transfer. All samples contained 5 µm diameter cavities while Sample E1, L1, and K1 have 3, 5, and 6 graphene layers, respectively. Details regarding the transfer, FIB, and ion bombardment are in the “Fabrication details” column.

<table>
<thead>
<tr>
<th>Charging gas</th>
<th>Kinetic diameter [nm]</th>
<th>Gas flow rate [mol/s]</th>
<th>Cavity</th>
<th>Fabrication details</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.26</td>
<td>4.19x10$^{-21}$</td>
<td>L1-2</td>
<td>PMMA free (PF)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.13x10$^{-21}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.03x10$^{-20}$</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>1.07x10$^{-20}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air (O$_2$ and N$_2$)</td>
<td>0.346-0.364</td>
<td>7.43x10$^{-22}$</td>
<td>E1-15</td>
<td>PMMA supported</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.57x10$^{-23}$</td>
<td>L1-2</td>
<td>PF</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.87x10$^{-23}$</td>
<td>K1-16</td>
<td>PF, 30 nm FIB pore</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.92x10$^{-22}$</td>
<td>K1-O</td>
<td>PF, $10^{13}$ ion/cm$^2$ (fluence)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.43x10$^{-24}$</td>
<td>K1-15</td>
<td>PF, 30 nm, $10^{14}$ ion/cm$^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.54x10$^{-23}$</td>
<td>K1-3</td>
<td>PF, 30 nm, $10^{14}$ ion/cm$^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.60x10$^{-23}$</td>
<td>K1-15</td>
<td>PF, 30 nm, $10^{14}$ ion/cm$^2$</td>
</tr>
<tr>
<td>SF$_6$</td>
<td>0.55</td>
<td>2.97x10$^{-22}$</td>
<td>K1-0</td>
<td>PF</td>
</tr>
</tbody>
</table>
Appendix F: SEM Images of the FIB Nanopores

Figure F. 1: SEM image of Cavity 1 on Sample K1 (5 layers of graphene on 5 µm cavity) (15 ms, 10 nm pore diameter). Nanopore is circled......................................................... 137

Figure F. 2: SEM image of Cavity 2 (5 layers of graphene on 5 µm cavity) (15 ms, 10 nm pore diameter). Nanopore is circled................................................................. 137

Figure F. 3: SEM image of Cavity 3 (5 layers of graphene on 5 µm cavity) (15 ms, 10 nm pore diameter). Nanopore is circled................................................................. 138

Figure F. 4: SEM image of Cavity 9 (5 layers of graphene on 5 µm cavity) (15 ms, 10 nm pore diameter). Nanopore is circled................................................................. 138

Figure F. 5: SEM image of Cavity 10 (5 layers of graphene on 5 µm cavity) (15 ms, 10 nm pore diameter). Nanopore is circled................................................................. 139

Figure F. 6: SEM image of Cavity 11 (5 layers of graphene on 5 µm cavity) (15 ms, 10 nm pore diameter). Nanopore is circled................................................................. 139

Figure F. 7: SEM image of Cavity 12 (5 layers of graphene on 5 µm cavity) (15 ms, 10 nm pore diameter). Nanopore is circled................................................................. 140

Figure F. 8: SEM image of Cavity 15 (5 layers of graphene on 5 µm cavity) (25 ms, 30 nm pore diameter). Nanopore is circled................................................................. 140

Figure F. 9: SEM image of Cavity 16 (5 layers of graphene on 5 µm cavity) (25 ms, 30 nm pore diameter). Nanopore is circled................................................................. 141

Figure F. 10: SEM image of Cavity 17 (5 layers of graphene on 5 µm cavity) (25 ms, 30 nm pore diameter). Nanopore is circled................................................................. 141
**Figure F. 1:** SEM image of Cavity 1 on Sample K1 (5 layers of graphene on 5 µm cavity) (15 ms, 10 nm pore diameter). Nanopore is circled.

**Figure F. 2:** SEM image of Cavity 2 (5 layers of graphene on 5 µm cavity) (15 ms, 10 nm pore diameter). Nanopore is circled.
**Figure F. 3:** SEM image of Cavity 3 (5 layers of graphene on 5 µm cavity) (15 ms, 10 nm pore diameter). Nanopore is circled.

**Figure F. 4:** SEM image of Cavity 9 (5 layers of graphene on 5 µm cavity) (15 ms, 10 nm pore diameter). Nanopore is circled.
**Figure F. 5:** SEM image of Cavity 10 (5 layers of graphene on 5 µm cavity) (15 ms, 10 nm pore diameter). Nanopore is circled.

**Figure F. 6:** SEM image of Cavity 11 (5 layers of graphene on 5 µm cavity) (15 ms, 10 nm pore diameter). Nanopore is circled.
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**Figure F. 9:** SEM image of Cavity 16 (5 layers of graphene on 5 \( \mu \)m cavity) (25 ms, 30 nm pore diameter). Nanopore is circled.

**Figure F. 10:** SEM image of Cavity 17 (5 layers of graphene on 5 \( \mu \)m cavity) (25 ms, 30 nm pore diameter). Nanopore is circled.
Appendix G: AFM Volume Calculation Sensitivity Analysis

Due to variance in the manual drawing of the cavity mask across AFM images, a sensitivity analysis was performed to determine how much error the positioning of the drawn circle can produce in the ultimate volume calculation for each cavity.

Table G. 1: Sensitivity calculations compared to the baseline (closest value to the determined average area) for various control cavity AFM facilitated mask areas and volume calculations. Experiment column describes the major sample processing event after which these measurements take place.

<table>
<thead>
<tr>
<th>Cavity</th>
<th>Experiment [Day]</th>
<th>Area (µm²)</th>
<th>Volume (µm³)</th>
<th>Sensitivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>FIB (1)</td>
<td>27.7</td>
<td>1</td>
<td>Baseline</td>
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<tr>
<td></td>
<td></td>
<td>29.2</td>
<td>0.99</td>
<td>-1</td>
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<td>29.1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>FIB (6)</td>
<td>27.4</td>
<td>1.5</td>
<td>Baseline</td>
</tr>
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<td>27</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>28.4</td>
<td>1.5</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>FIB (1)</td>
<td>30</td>
<td>0.46</td>
<td>Baseline</td>
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<tr>
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<td>0.47</td>
<td>2</td>
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<td></td>
<td></td>
<td>29</td>
<td>0.47</td>
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<td></td>
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<td>26.4</td>
<td>0.79</td>
<td>1</td>
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Sensitivity was calculated between a new masked area to the baseline (average area value) as a ratio of the difference in volume and the difference in area.

<table>
<thead>
<tr>
<th>D</th>
<th>Ion (0)</th>
<th>28.1</th>
<th>0.02</th>
<th>Baseline</th>
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</thead>
<tbody>
<tr>
<td></td>
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<td>28.8</td>
<td>0.018</td>
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<td></td>
<td>29.8</td>
<td>0.0087</td>
<td>-1</td>
</tr>
</tbody>
</table>
Curriculum Vitae

Name: Anika Wong

Post-secondary Education and Degrees:
University of Alberta
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