Quantification of Flows Emerging From Small Pores in Plane Walls

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Abstract

Current membrane separation processes are limited in high production and high purity settings due to a trade-off between selectivity and permeance. Methods of creating nanoscale geometries in 2D materials are emerging and present an opportunity for fast, size selective mass transport that can be tailored to a wide array of applications. This thesis develops a method for quantifying flow through small pores in plane walls based on the behaviour of a solute dispersed in a downstream reservoir. This method is validated for a range of micropore diameters, for which flow rates can be calculated with confidence, and is shown to provide accurate results up to a Reynolds number of 17. From an approximate control volume analysis, the method is shown to apply for both single pores and arrays of pores, making it a suitable candidate for future studies measuring flow rates through microscopic areas of nanoporous atomically thin membranes.

Keywords

Nanoscale flows, micron scale flows, flow quantification, two dimensional polymers, graphene, membrane separation processes, solute dispersions, nanofabrication
Summary for Lay Audience

Membrane separation devices are used in a wide array of applications, most notably in water desalination/purification, carbon capture, fuel cells and drug delivery. By utilizing materials that permit selective transport, one is able to separate substances based on size, chemical composition or charge. An ideal material would allow fast, unobstructed flow of desirable species and completely reject the undesired. Current devices do not have this capability and have a trade-off between flow rate and undesired species rejection. Emergence of one atom thick materials that are partially permeable, present the opportunity to realize the concept of an ideal membrane. In order to develop devices using these materials that are able to carry out the desired separation processes, an understanding of fluid flow behaviour and transport properties through various materials must be established. The flows emerging from these pores are so small that they are not detectable by conventional means. The purpose of this thesis is to develop a method for quantifying these small flows emerging from individual pores. Although jets emerging from the pore itself cannot be measured, the movement of the fluid in a downstream reservoir caused by the jet can be quantified and related to the jet flow. The behaviour of a fluorescent dye downstream of the pore is used to extract the volume flow rate through the pore itself. The method created in this paper can be used to analyze flows through nanoscale geometries, providing a basis for future separation device designs.
Co-Authorship Statement

This thesis was written by Matia Edwards with edits and suggestions from supervisor Dr. Michael Boutilier. Experiments, image processing, data processing and experiment design was performed by Matia Edwards. The flow quantification method was developed in conjuncture with Dr. Michael Boutilier.

OpenFOAM simulations were completed by Dr. Michael Boutilier.

FIB drilling and SEM imaging was performed by Todd Simpson a Western’s Nanofabrication facility.
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## Nomenclature

- \( a \) rate of decay of normalized concentration far from the pore
- \( C \) concentration field
- \( c \) dimensionless concentration field
- \( C_{ms} \) microscope calibration factor
- \( CF \) flow rate calibration factor
- \( D \) solute diffusivity
- \( d \) pore diameter
- \( F_F \) “jet force” parameter proportional to momentum through a pore
- \( I(R), I(r, z) \) pixel grey intensity value
- \( I_{max} \) maximum pixel intensity in an image
- \( l \) effective path length
- \( LI(\%) \) microscope light intensity percentage
- \( M \) momentum flux through the pore
- \( m \) rate of decay of normalized intensity far from the pore
- \( \dot{m} \) mass flux through the pore
- \( Pe \) Peclet number
- \( Pt \) platinum
- \( Q \) volume flow rate
- \( Q_{sim} \) simulated volume flow rate
- \( Re \) Reynolds number
- \( R_0 \) Radial distance to the edge of a hemispherical plume
- \( R_t \) carbon nanotube radius
- \( Sc \) Schmidt number
- \( Si_Nx \) silicon nitride
- \( Si_O_2 \) silicon oxide
- \( t_{exp}(s) \) camera frame exposure time
- \( V \) average fluid velocity
- \( \nu(\theta) \) velocity component in ( ) direction
- \( z_{10} \) distance along the z axis to the 10% iso-intensity contour
- \( \Delta P \) pressure difference
- \( \Delta p \) dimensionless pressure gradient
- \( \mu \) fluid dynamic viscosity
- \( v \) fluid kinematic viscosity
- \( \rho \) fluid density

### Coordinate Systems

- \( X, Y, Z \) cartesian coordinate variables
- \( r, \theta, \phi \) cylindrical coordinate variables
- \( R, \theta, \phi \) spherical coordinate variables
- \( s, q \) oblate-spheroidal coordinate variables where \( r = \frac{1}{2}d\sqrt{(1 + s^2)(1 - q^2)} \)
  and \( z = \frac{1}{2}dqs \)
List of Abbreviations

AFM     atomic force microscope
APS     ammonium persulfate
Ar      argon
AR      allura red AC
BNNTs   boron nitride nanotubes
C       carbon
CH₄     methane
COOH    carboxylic acid
CO₂     carbon dioxide
Cu      copper
C₂₀H₁₂O₅ fluorescein
CNTs    carbon nanotubes
CVD     chemical vapour deposition
DI      deionized
EDS     energy dispersive X-ray spectroscopy
Fe      iron
FIB     focused ion beam
FOV     field of view
Ga      gallium
hBN     hexagonal boron nitride
He      helium
HfO₂    hafina
H₂      hydrogen
IPA     isopropyl alcohol
KCl     potassium chloride
LAP     laminar assembly polymerization
MgSO₄   magnesium sulfate
MOF     metal organic framework
NATM    nanoporous atomically thin membrane
O₂      oxygen
PIV     particle imaging velocimetry
PLA     polylactic acid
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>polymethyl methacrylate</td>
</tr>
<tr>
<td>Pt</td>
<td>platinum</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SiNx</td>
<td>silicon nitride</td>
</tr>
<tr>
<td>SiO₂</td>
<td>silicon dioxide</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>2DP</td>
<td>two-dimensional polymer</td>
</tr>
<tr>
<td>2D</td>
<td>two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>three-dimensional</td>
</tr>
<tr>
<td>μPIV</td>
<td>micro particle image velocimetry</td>
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Chapter 1

Introduction

Membranes are thin, semipermeable barriers between adjacent phases that moderate the transport of chemical species.\textsuperscript{1,2} This partial permeability is governed by the physical and chemical properties of the membrane material and has brought about separation processes based on selective mass transport.\textsuperscript{1–3} Scientific advancements and explorations of various membrane materials have caused separation applications to become increasingly prevalent in a wide range of industries. Some major examples include water desalination and purification,\textsuperscript{4–7} sustainable hydrogen fuel cells,\textsuperscript{8} natural gas purification, harvesting of various gasses from air, hemodialysis, and many more.\textsuperscript{3}

Ideally, membranes utilized in these applications should completely reject undesired species (highly selective), permit high flow rates of desired species (highly permeable) and exhibit physical and chemical fortitude.\textsuperscript{3} Current industrial practices are far from this idealized case and encounter performance and economic limitations in high purity and high production applications. These limitations arise due to an inherent trade-off between selectivity and permeability. This trade-off sees membranes that are highly permeable to desired species also being partially permeable to the undesired.\textsuperscript{1,3} Simultaneously, highly selective membranes are typically less permeable to desired species and require large energy inputs to overcome flow resistances. An example of this is reverse osmosis desalination, which uses a large pressure gradient to filter salt ions from water.\textsuperscript{9} Reverse osmosis processes show high selectivity but are extremely time and energy consuming (1.8-5 kWh/m\textsuperscript{3}).\textsuperscript{10,11} The inherent trade-off between permeability and selectivity, known as the Robeson limit for gasses, has inspired much research into transport properties of various membrane materials.\textsuperscript{12}

Liquid transport mechanisms across membranes vary based on the membrane morphology and operative length scale. For dense membranes or membranes lacking pores, permeance is related directly to ion transport rates within the membrane material itself. These processes are modeled by Fick’s Law of diffusion.\textsuperscript{1,13} Conversely, porous membranes have transport mechanisms based on pore size and electrostatic interactions where the rate of transport of a species is defined by its size in comparison to the pores...
and the thickness of the membrane itself. Rates at which species can pass through a membrane is inversely proportional to its thickness.\textsuperscript{1} Higher transport rates (permeance) are desirable for overcoming limitations in conventional membranes and for this reason investigations into thinner membrane materials are becoming pervasive.

Impermeable two-dimensional materials that can sustain defects of variable size and density without compromising their mechanical strength are emerging. These materials introduce the potential of producing ultrathin devices that support selective mass transport with minimal flow resistance.\textsuperscript{3,11,14,15} Furthermore, the development of fabrication methods for nanoscale geometries in these materials allows these devices to be tuneable to a wide range of applications and have the potential of filtration capabilities thus far unrealized commercially.

Graphene membranes containing a multitude of nanopores (i.e., holes with diameters between 0.1 and 1000 nm) demonstrate a water permeance five times higher than that of conventional ultra filtration devices.\textsuperscript{16} Simultaneously, investigations of ionic conductance across nanoporous graphene membranes have outlined the potential of applications rooted in electrodialysis, water purification and desalination processes because of observed size-based,\textsuperscript{17,18} cation/anion\textsuperscript{19} and inter-cation\textsuperscript{18} selectivity.

Nanoscale geometries have an impact on fluidics that is not well understood.\textsuperscript{20} In order to further the development of said devices, fluid flow behaviour and transport properties through nanoporous atomically thin membranes (NATM) must be investigated. Despite the potential, transport properties of uncharged liquids through individual nanopores in two dimensional materials are seldom explored experimentally. This scarcity is driven by the considerable challenges associated with resolving such minute flows.\textsuperscript{21} Current flow sensors have detection limits well higher than the flow rates through graphene nanopores predicted by molecular dynamics simulations.\textsuperscript{3,22} Also, measurement techniques such as particle image velocimetry (PIV) require tracers that are small enough to not be intrusive while being large enough to avoid noise associated with Brownian motion.\textsuperscript{23}

This limitation has caused research groups to become creative in their methods of investigating permeance of nanoporous materials. Recently, two related studies were published by Secchi et al.\textsuperscript{24,25} that individually developed ways to quantify flow rates
through nanocapillaries based on the behaviour of a solute or colloid tracer in a downstream reservoir. In the first study, the group observed tracer particles downstream of a nano-jet as they followed streamlines of the viscous entrainment of the jet. The streamlines revealed by the tracers correlate to a flow field defined by the Landau-Squire similarity solution and from this correlation, the group solved for the flow rate through the capillary. Similarly, in the second study, the group then used the same velocity field to derive a relation that predicts the concentration field of a solute tracer as dispersed by the jet. The relation allowed the flow rate through the capillary to be determined based on the shape of the solute dispersion. Although the group was able to develop a method for quantifying nanoscale flows, the method is inapplicable for investigating permeance of nanoporous membranes for separation devices.

This inapplicability arises due to a geometric difference between their capillary and a porous membrane. Secchi et al. were concerned with a flow that resembles a jet emerging from a tube into an infinite reservoir whereas porous membranes resemble an orifice plate in a semi-infinite reservoir. Although both are free jets, the flow fields are sufficiently different due to the presence of impermeability and viscous effects at the wall. The difference between the flow fields is illustrated in Figure 1.1. Secchi et al. velocity field includes flow through the plane where there is an impermeable wall in the orifice plate geometry. The difference between the flow fields causes different flow rates under similar pressures and a distinct concentration field. The difference between the flow fields is sufficient enough that a novel quantification method is required.
1.1 Research Objective

Thus far, there are very limited experimental studies exploring uncharged liquid behaviour through individual pores in atomically thin membranes. This scarcity is due to the considerable technical challenge of accurately exploring the aspects of fluid flow through individual pores because of their minute flow characteristics. The goal of this thesis is to develop and verify a method for quantifying volume flow rates through individual micropores in continuous membranes. The method is designed with nanopores in mind but focuses on the micron scale where results can be compared to analytical and numerical solutions with confidence. The intention is that in a future work the method can be used to measure permeance of nanoporous two-dimensional materials to identify favourable membrane materials and further the development of optimized selective mass transport devices. This study attempts to perform such permeance measurements but was unable to produce observable flows through nanoscale geometries. Despite this, some contribution is made towards achieving these measurements. A small portion of this thesis focuses on experimentation with various two-dimensional material hybrid structures and fabrication/polymerization methods to create nanoporous devices for flow experiments.
The method developed in this thesis draws much inspiration from that of Secchi et al.\textsuperscript{25} and aims to use the behaviour of a solute downstream of a pore to estimate the flow rate through the pore itself. Continuum fluid mechanics is accurate for uncharged liquid flows down to ~20 nm and for smaller pore sizes the plume will still be much larger than the pore. For such reasons, even though the method is developed for micron scale pores, it is expected to still provide accurate volume flow rate estimates at smaller scales.

This thesis has the overall goal of developing and verifying a method for quantifying volume flow rates through individual micropores in continuous membranes. From this overarching theme there stems a few subobjectives that this thesis addresses:

1. Designing a flow cell capable of developing experimental flows through porous materials.
2. Interfacing the flow cell with a microscope to observe the behaviour of a solute in the downstream reservoir.
3. Correlating image pixel intensities to solute concentration levels.
4. Developing a relationship between an observed concentration field and the influx of solute that can be used to estimate flow rates
5. Validating the method via comparison to simulation data (at the micron scale)
6. Fabricating NATM devices for flow experimentation

The following sections will discuss the development and validation of this method. Chapter 2 provides a literature review on current flow sensors, flow quantification methods used for NATM and analytical solutions of flows emerging from a hole in a plane wall. Chapter 3 describes the design process of the flow cell and experimental setup. Chapter 4 covers the experimental methods and introduces the acquired image datasets. Chapter 5 covers the development of the quantification method, estimating flow rates based on images of solute dispersions and comparing to simulation data. Chapter 6 discusses fabrication methods of porphyrin polymers and porous graphene membranes as well as the results of their flow experiments.
Chapter 2

Literature Review

For membrane process optimization, there is a need for investigations into the permeance of various membrane materials. The expected flow rates through single pores in nanostructured membranes are extremely low.

2.1 Current Flow Sensors

Flow rates as low as $10^{-9}$ nL/min have been estimated through nanocapillaries, whereas comparatively, current flow sensors have detection limits at least a full order of magnitude higher. Existing flow meters used in industrial applications typically operate based on a magnetic, mechanical, thermal or differential inducing premise.

Development of smaller fluidic devices require sensors with higher sensitivity. The most common sensor used for miniaturized flows are thermal sensors. Thermal flow sensors can operate on various similar principles that include extracting flow velocity based on heat transferred to or from a thermal resistor. The generic device consists of two thermal resistors submerged in a flow channel and held at a defined temperature gradient: one resistor at the ambient temperature and the other heated via electrical current. As the fluid flows within the measurement region, heat is drawn from the heated resistor and the corresponding cooling effect is measured and counteracted by increasing the current. The current needed to maintain the temperature gradient is proportional to the cooling effect and thus the mass flow rate of the fluid. These devices are widely available for small and large applications and at the smallest scale have resolutions of 7 nL/min, significantly higher than the expected flow rates through individual pores in NATM. Wang et al. discuss flow rates through single NATM pores of $1E-8$ molecules/ns-Pa or $2E-9$ nL/min.

Outside of available flow sensors, multiple research groups have developed methods for characterizing flow through microfluidic channels. Noeth et al. developed a measurement technique based on the deflection of an SU-8 cantilever proportional to the pressure gradient applied by the moving fluid (Fig. 2.1a). The deflection is measured by the reflection of a laser off an adhered aluminum pad. The movement of the laser is detected by a photo diode and is used to extract applied pressure and subsequently flow rate. The devices made in the study had resolutions of 3-6 nL/min. A promising
improvement compared to their thermal counterparts but still not expected to detect the flows of interest. Similarly, Stern et al.\textsuperscript{33} developed a method that takes measurements based on the Doppler shift of light caused by the motion of bubbles in a microfluidic channel (Fig. 2.1b), providing a velocity resolution of 2.15 nL/min. Although this is an improvement, it is still not applicable at the scale of interest due to its reliance on the presence of bubbles that would alter transport mechanisms in the NATM.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Schematics of experimentally developed flow sensor concepts (a) Cantilever\textsuperscript{21} (b) Doppler\textsuperscript{33} a) From [Noeth N, Keller SS, Boisen A. Fabrication of a cantilever-based microfluidic flow meter with nL min \textsuperscript{-1} resolution. Journal of Micromechanics and Microengineering. 2011;21(1). doi:10.1088/0960-1317/21/1/015007] © IOP Publishing. Reproduced with permission. All rights reserved. b) Reproduced from [33] MDPI Publishing. Open access Creative Commons CC BY 4.0 Licence}
\end{figure}

Another prominent method for flow measurements in microfluidic settings is micro particle image velocimetry (μPIV). This process seeds flow fields with particles of neutral buoyancy that move with the fluid, the presence of the particles making the motion of the fluid visible.\textsuperscript{34,35} Acquiring multiple images of the moving particles allows for a velocity
field to be inferred using spatial correlation image processing algorithms.\textsuperscript{34} The application of PIV at the micro scale, although similar in principle, exhibits three main distinctions from the macro: the illumination method, particle selection and image interpretation. In macro-PIV the field of view (FOV) is illuminated by a laser sheet that defines the measurement plane whereas, due to the small geometry, μPIV illuminates the entire volume using a double pulsed laser. Resolving flow in microscale geometries requires the use of tracers with diameters small enough to not impact the overall flow but large enough to avoid noise associated with Brownian motion (200 nm-2 μm).\textsuperscript{35–37} μPIV provides the capability of characterizing a flow in a microfluidic device provided the apparatus is compatible with a microscope. As geometries shrink, difficulties with flow visualization arise. Nanochannels and pores themselves are much too small to resolve optically. Simultaneously, the smaller geometries require smaller tracer particles that increase the noise associated with particle wall interactions and Brownian motion.\textsuperscript{37}

The discussed limitations in resolving fluid flow at such small scales have hindered experimental explorations of flows through NATMs. These explorations are required to understand the aspects of fluid behaviour through atomically thin membranes that will lead to advancements in membrane separation processes. Research groups are beginning to avoid the limitations by developing creative methods of analyzing flow through porous membranes without the use of typical flow sensors and characterization methods.

2.2 Experimental Flow Characterization

Methods for experimentally exploring ionic and gas transport across nanoporous materials are being developed and have been used to identify membrane structures that have potential in separation applications. Such developments have been less prevalent for liquid phase processes.

2.2.1 Ionic transport

Motivated by applications in DNA analysis and water desalination, multiple groups examine ionic transport across graphene membranes driven by voltage\textsuperscript{6,7}, concentration and pressure gradients.\textsuperscript{6,7} Ionic conductance of graphene membranes of varying pore size and count are often characterized using methods like the one outlined by Garaj et al.\textsuperscript{28} in 2010. This method (Fig. 2.2) suspends graphene over a 200 nm square aperture in a
silicon nitride membrane. Graphene membranes are advantageous for creating such devices as the van der Waals forces between the membrane and most substrates are sufficient to hold the membrane in place. Previous studies suspend graphene membranes on silicon oxide or silicon nitride membranes in the construction of devices that were able to sustain pressure differences up to 5 bar.\(^{16,23}\) The suspended membrane is placed in a fluidic cell separating two ionic solution-containing reservoirs. Ag/AgCl electrodes are placed across the membrane in contact with the ionic solutions. The conductance of the graphene membranes can be quantified by applying a voltage difference across the membrane and measuring the ionic flux from one reservoir to the other. Considering the reservoirs are completely sealed from one another, any flux from one reservoir to the other can be attributed to ionic transport through the graphene membrane. The recorded current-voltage relationships (Fig. 2.2b) can be used to calculate for the ionic conductance through individual pores in the membrane. The group uses the method to measure conductance across pores ranging from 2-23 nm in diameter and present a near linear relationship between pore diameter and conductance.

In 2013 and 2015, O’Hern et al.\(^{17,19}\) utilized a similar method to outline both size-based and charge-based separation capabilities of porous graphene. In their studies, the group creates nanofiltration devices by suspending porous graphene over a polycarbonate track etch membrane. Transport of various hydrated molecules (KCl, Allure Red AC (AR), MgSO\(_4\)) across the device, as driven by a concentration gradient, is measured via
conductance and UV visible spectroscopy. The group illustrates a constraint on selectivity attributed to the presence of natural defects in chemical vapour deposition (CVD) graphene and in the 2015 study, employ a hafnia (HfO$_2$) coating to block intrinsic defects. The studies show different transport mechanisms that arise for varying pore diameters. At the lowest etch durations there is a slight cation/anion selectivity which disappears in membranes exposed for longer periods of time. At this point, steric effects dominate the diffusion process where permeance of salt ions (hydrated ion diameter $\sim$ 0.66 nm) gradually increased with pore diameter whilst retaining AR molecule selectivity (hydrated ion diameter $\sim$ 1 nm). One device in the study with pore diameters $\sim$0.5 nm at areal densities $\sim$$10^{12}$ cm$^{-2}$ exhibited ion rejection and water permeance consistent with molecular dynamics simulations,$^{3,9}$ suggesting the feasibility of such membranes to be utilized in sized-based desalination and purification processes.$^{6,7}$

Another group, Rollings et al.$^{18}$, used a similar conductance method to explore the cation/anion selectivity capabilities of lower-diameter pores in graphene membranes originally encountered by O’Hern et al. in 2013.$^{17}$ The group utilized both electric potential and concentration gradients to drive flow through singular graphene pores with sizes in the range of 3-200 nm. The study identified cation selectivity based on short circuit current values consistent with the transport of cations down the concentration gradient. The group further demonstrated inter-cation selectivity, showing strong conductance distinctions between monovalent and divalent cations. The results of this study suggest that porous graphene membranes have potential applications in electrodialysis.

These studies outline a few of many potential applications of nanoporous devices and provide insight that will assist in the design of NATM flow devices.

2.2.2 Gas Transport

The measurement of ion transport across membranes has become relatively standard but there are still challenges associated with resolving flows of uncharged substances, that cannot be quantified based on conductance through single pores. Characterizations of gas phase flows through graphene membranes are conducted by recording deflation rates of nanoballoons. Bunch et al.$^{29}$ describe the creation of graphene nanoballoons to examine the
permeance of various gasses through monolayer graphene. The balloons were created by suspending graphene membranes over pre-etched wells in silicon dioxide wafers. Van der Waals force between the graphene and SiO$_2$ seal the chamber, creating a confined volume of ~μm$^3$. This confined volume is initially at atmospheric pressure. The group found that the internal pressure could be increased by placing the chamber in an elevated external pressure environment for prolonged periods of time and allowing the internal pressure to equilibrate via leakage through the walls of the SiO$_2$ substrate. Upon removal from the high pressure, the elevated internal pressure of the chamber causes the surface of the graphene membrane to bulge and stretch like the surface of a balloon as depicted schematically and as an atomic force microscope (AFM) image in Figure 2.3.

Figure 2.3 a) Schematic of a sealed graphene nanoballoon post inflation where the pressure gradient is nonzero b) AFM image (tapping mode) of a multilayer graphene nanoballoon. Reprinted (adapted) with permission from [Bunch JS, Verbridge SS, Alden JS, et al. Impermeable atomic membranes from graphene sheets. Nano Lett. 2008;8(8):2458-2462. doi:10.1021/nl801457b]. Copyright 2008 American Chemical Society.

Koenig et al.$^{30}$ expanded upon this process in 2012 by introducing nanopores in bilayer graphene nanoballon membranes via repeated UV/ozone etching. This periodic etching yielded membranes where a single pore dominated the transport. After the pores were introduced, the deflection of the membrane was measured versus time using an AFM. Molecular selectivity of the pores was demonstrated by carrying out the inflation with various gasses. Differences in deflection decay rates for H$_2$, CO$_2$, Ar and CH$_4$ quantified molecule selectivity. After etching, the experiments with the smaller molecules (CO$_2$ &
H₂) showed higher leak rates than the larger molecules suggesting size-based molecular selectivity. This measurement technique assisted in outlining membrane materials and structures that are favorable for gas separation applications.

2.2.3 Liquid Transport

A few studies evaluate uncharged liquid transport across nanopores in graphene\textsuperscript{16,23} and porphyrin based two-dimensional polymers (2DPs)\textsuperscript{31} by inducing pressure-driven flows across membranes containing trillions of pores and averaging flow rates to estimate individual pore transport characteristics. Surwade et al.\textsuperscript{23} present a method which uses oxygen plasma etched graphene membranes with varying pore size and densities. The membranes were adhered to the caps of vials by first transferring to silicon nitride substrates and subsequently epoxying them to the lids. The vials were filled with deionized (DI) water and inverted (Fig. 2.4a), putting the water in contact with the membrane for transport and creating a gravity driven flow. Membranes of different pore size and density were inverted for 24-hour periods and the change in mass was recorded. The experiment showed the magnitude of water transport was proportional to the increasing defect ratio (Fig 2.4b). A similar experiment was conducted using porphyrin-based 2DPs of various thicknesses suspended on porous (200 nm pore diameter) anodic aluminum oxide and nylon microfiltration mesh filters.\textsuperscript{31} Pressures ranging from 0-5 bar were applied across said devices, one of which, with a 300 nm layer of porphyrin polymer, boasted a water permeance of 840.1 L m\textsuperscript{-2} h\textsuperscript{-1} bar\textsuperscript{-1} and a dye rejection rate of 99.8%. This permeance was shown to be highly dependent on thickness and geometry of the membrane.\textsuperscript{31}

![Figure 2.4](image)

**Figure 2.4** a) Schematic of Surwade et al.\textsuperscript{23} flow experiment; graphene is suspended over a 5 um hole in a SiNx membrane and adhered to the top of a vial, said vial filled with water and inverted in an oven at 40°C. b) Water loss
over a 24-hour period as estimated by mass of the vial based on the ratio of Ramen spectrum peaks (I_D/I_G) that correlate with defect density. From [23]. Reproduced with permission from Springer Nature.

Celebi et al.\textsuperscript{16} conducted a similar experiment using bilayer graphene to avoid transport attributed to defects in single layer graphene sheets. The study uses graphene membranes containing randomly distributed pores ranging from 50-1000 nm and demonstrated a difference in permeation onset for membranes with one side versus both sides wetted. Permeation is unfavourable for one side wetted membranes due to capillary force acting at the graphene opening and would in some cases take multiple bars of pressure for flow to commence. This flow onset pressure is lowered to 250 mbar for one case by prewetting both sides. This impact of wetting the membrane is an important consideration in the design of future experiments. A device in this study with 50 nm pores and 4.6\% porosity demonstrated the potential of NATM in increasing the energy efficiency of separation processes by displaying a water permeance 5 times higher than conventional ultrafiltration membranes (Fig. 2.5a). The group went on to estimate the flow per pore (Fig. 2.5b) by dividing its overall flow rate by its estimated number of pores and is shown to agree with Sampson’s model within a reasonable degree of error.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.5.png}
\caption{a) Celebi et al.\textsuperscript{16} comparison of measured permeance of water through 50 nm pores in graphene membranes to other ultrafiltration membranes. b) Water flow rates per pore measured in the same study compared to Sampson’s model (dashed line). Used with permission of AAAS, from “Ultimate Permeation Across Atomically Thin Porous Graphene.” Celebi K, Buchheim J, Wyss RM, et al. Science (1979). 2014}
\end{figure}
The issue with estimation of liquid transport rates through single pores from investigations of liquid transport mechanisms mentioned thus far is that the membranes used contain trillions of pores which are not uniform in size nor distribution. Using many pores without uniformity to estimate the characteristics of transport in singular pores results in ambiguity when relating to an average pore diameter.

In 2016, Secchi et al.\textsuperscript{24} recognized a similar limitation in the exploration of water flow through carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs) and set out to develop a method for characterizing such flows. The group developed a method for obtaining flow rates of pressure driven transport thorough singular nanotubes by observing the viscous effects imparted by nano-jets on a reservoir containing colloid tracers. A similarity solution to the Navier-Stokes equations called the Landau-Squire Jet found by Squire\textsuperscript{26} in 1951 is used to assist in the analysis. The solution shows a jet emerging from the capillary drives a laminar “entrainment” flow beside the jet through viscous interactions. The velocity field can be described in rotationally symmetric spherical coordinates \((r, \theta)\) based solely on the momentum flux imparted by the jet or “jet force” \((F_P)\) that is proportional to the capillary fluid velocity.

\[

v_R = \frac{F_p \cos \theta}{4\pi \mu}, \quad v_\theta = -\frac{F_p \sin \theta}{8\pi \mu R}, \quad F_P = \alpha \mu R \bar{V}, \quad \bar{V} = \frac{Q}{\pi R_1^2}\quad (1)

\]

Where, \(v_R, v_\theta\) are the spherical components of velocity, the origin is taken as the tube tip, \(\mu\) is fluid dynamic viscosity, \(\alpha\) is a numerical coefficient corresponding to the nanocapillary geometry, \(R_1\) is the radial dimension of the capillary, \(Q\) is the fluid flux and \(\bar{V}\) is the average fluid velocity through the capillary.

Due to its miniature nature, the flow from the jet itself cannot be resolved optically using \(\mu\)PIV without encountering the limitations previously discussed. To avoid the need to pass colloid particles through CNTs, Secchi et al.\textsuperscript{25} decided instead to seed the reservoir around the jet where the entrainment of particles can be measured via \(\mu\)PIV. The dependence of the velocity field on the jet force presented the opportunity to extract capillary flow characteristics from the bulk flow field. The group used an optical microscope to record the behaviour of the tracer particles near the tip of a nanotube and extracted a velocity field using classical particle velocimetry techniques.
The experimental setup used to perform said experiment is shown in Figure 2.6 and consists of a CNT adhered to the tip of a pulled glass pipette filled with water. The pipette is placed in a reservoir created out of two microscope slides and a polymer membrane to connect them; the reservoir contains 500 nm polystyrene tracers in DI water. A pressure gradient was applied across the CNT creating the Landau-Squire jet,\textsuperscript{26} where the movement of tracers was recorded by a microscope oriented perpendicular to the flow. A velocimetry algorithm was then used to extract velocity fields downstream of CNTs with radii ranging from 23-50 nm at various pressures and is shown to agree with Landau-Squire predictions. The force parameter, and equivalently, the velocity of the fluid in the tube can be extracted based on the dependence of the bulk flow on jet force. This method was used to identify the vastly different transport in CNTs versus BNNTs.

The same group further used the peculiarities of the Landau-Squire plume to probe the flow properties inside nanocapillaries in 2017. The group use the velocity field defined by the Landau-Squire\textsuperscript{26} similarity solution to derive a relation for the concentration field produced by a jet containing a fluorescent solute tracer (fluorescein dye). The relation
estimates the shape of a dye plume downstream of a nanocapillary based on the effective jet Peclet number.

\[ Pe = \frac{F_p}{4\pi \mu} \]  

(2)

Figure 2.7 shows iso-concentration profiles and simulations of expected plumes for various Peclet numbers; the increasing jet force, as expected, creates plumes extending farther from the jet origin.

\[ \text{Figure 2.7 a) Simulated [25] concentration profiles at various pressures for a 240 nm CNT b) Plume like shapes of concentration profiles for various Peclet numbers. Reproduced from [25] no licence required.} \]

The study recreates this scenario experimentally where a dye mixture is dispersed into a downstream reservoir through a CNT. The result is a dye plume created through the convection of the pressure driven flow and the natural molecular diffusion of the dye from areas of high to low concentration. Plumes are imaged with an epifluorescence capable microscope (Fig. 2.8a) where the relative concentration of the fluid at any location can be extracted through pixel intensity values. Intensity profiles at various pressures are shown in Figure 2.8b. Plume shapes can be extracted from images based on longitudinal and lateral dimensions of iso-intensity contours (Fig. 2.8c). The shape provides a basis of relating the bulk flow to the capillary flow by relating the shape of intensity profiles to those produced by the concentration field relation. Force parameters extracted through this method agree with simulation data and the group’s previous velocimetry technique (Fig. 2.9). This agreement suggests the plume method can be used in future investigations to extract flow information in this geometry. These methods were
used to identify the enhanced permeance of CNTs in comparison to BNNTs and provide much inspiration for the experimental methods developed in this thesis.

As mentioned in the introduction, the second of these studies is used as inspiration for the development of an adapted measurement technique for taking permeance measurements of porous membranes (unlike the one above). The concentration field in the downstream reservoir will be used to reveal information about the flow field through the pore in a plane wall rather than from a tube tip. Several researchers provide analytical solutions for
the flow field expected from an orifice in a plane wall and one presents an approximate concentration field in the low Reynolds number (Re) limits that will be useful in the development of this method.

2.3 Analytical solutions
Recent studies outline intriguing methods for measuring nanoscale flow rates by imaging the larger scale flows they induce and fitting continuum solutions. The use of such solutions by Secchi et al.\textsuperscript{24,25} to resolve nanocapillary flow are accompanied by studies concerned with viscous effects of impinging stagnation points,\textsuperscript{38} and laser induced microjets for additive manufacturing.\textsuperscript{39,40} The majority of the cited works consist of submerged jet flows into an infinite reservoir and are analyzed using the previously discussed Landau-Squire solution.\textsuperscript{26} Unlike these studies, the jet from a singular nanopore in a membrane and its entrainment flow, although similar geometrically, cannot be adequately represented using this solution. The resultant flow field is more aptly described as a submerged flow emerging from a circular orifice in a plane wall and in this section that geometry will be considered for a range of Reynolds numbers.

This problem is originally investigated for the low Reynolds number limit by Sampson\textsuperscript{41} in 1891 who explored the pressure driven flow from an infinitesimally thick orifice plate. Sampson solved the reduced Stokes equations in the oblate-spheroidal coordinate system (Fig. 2.10) which is related to the axisymmetric cylindrical coordinates by

$$r = \frac{1}{2} d \sqrt{(1 + s^2)(1 - q^2)} \quad \text{and} \quad z = \frac{1}{2} ds q s,$$

where curves of constant $q$ are also conveniently streamlines. Here Sampson solved the velocity field,

$$v_r = \frac{3}{2} V \frac{q^2 s}{s^2 + q^2} \sqrt{\frac{1 - q^2}{1 + s^2}}, \quad v_z = \frac{3}{2} V \frac{q^3}{s^2 + q^2}, \quad V = \frac{\Delta p d}{6 \pi \mu},$$

where cylindrical velocity components ($v_r, v_z$) beyond the hole are defined by the applied pressure difference ($\Delta p$) and hole diameter ($d$). An advection-diffusion equation for this velocity field containing a solute tracer is presented by Atwal et al.\textsuperscript{42} as,

$$Pe q^2 \frac{\partial c}{\partial s} = \frac{\partial}{\partial s} \left[ (1 + s^2) \frac{\partial c}{\partial s} \right] + \frac{\partial}{\partial q} \left[ (1 - q^2) \frac{\partial c}{\partial q} \right].$$
where \( Pe = \frac{v_d}{D} \), \( c = \frac{C - c_{\text{low}}}{c_{\text{high}} - c_{\text{low}}} \) is the dimensionless concentration in terms of high and low concentration values \((c_{\text{low}}, c_{\text{high}})\) and the dimensional concentration value \((C)\). \( D \) is the diffusivity of the species. Atwal et al.\(^{42}\) consider a case analogous to solute transport across a membrane system where the concentration of the downstream reservoir far from the orifice is zero \((c(q, s\to\infty)=0)\), the concentration far from the orifice on the upstream side is constant \((c(q, s\to-\infty)=1))\) and the wall in non-porous areas is impermeable \((\frac{\partial c}{\partial q}|_{q=0} = 0)\). The group applies a Legendre integral transform and truncating the resultant series solution to a single term provides an analytical approximation for the concentration field of,

\[
c(q, s) = \frac{\exp\left(\frac{Pe}{4} \arctan(s)\right) - \exp\frac{\pi Pe}{8}}{\exp\left(\frac{\pi Pe}{8}\right) - \exp\frac{\pi Pe}{8}}
\]

\((5)\)
In 1952 Squire\textsuperscript{43} considers a similar geometry under a higher Reynolds number limit where the flow emerging from the orifice is a jet. Squire found an analytical similarity solution in cylindrical coordinates of the form,

\begin{align*}
v_r &= \frac{\phi(\theta)}{R}, \quad v_\omega = \frac{f(\theta)}{R}, \quad \frac{P}{\rho} = \frac{g(\theta)}{R^2} \quad (6)
\end{align*}

which when substituted into the Navier-Stokes equations result in a single differential equation in terms of \( f \) where,

\begin{align*}
\frac{df}{d\theta} &= \frac{1}{2\nu} f^2 + f \cot \theta + 2\nu \left[ \frac{a_2 \cos}{\sin^2 \theta} \frac{1}{2} \right] \quad (7)
\end{align*}

\( a, a_1, a_2 \) are integration constants and \( \nu \) is the kinematic viscosity of the fluid. Squire\textsuperscript{43} solved this differential equation neglecting the no slip condition where \( a = a_1 = a_2 \) giving,

\begin{align*}
f &= \frac{2a(1-c)}{\sin \theta \sqrt{1-2acot\left(\frac{\sqrt{1-2a}}{2} ln(1+cos)\right)-1}} \quad (8)
\end{align*}

The fluid velocity field can be derived from the expression for \( f \). As Squire outlines, this solution contains a tangential velocity component adjacent to the wall that does not satisfy a no slip boundary condition. He also states that the solution has a zero-mass flux across the wall and can be more adequately described as the consequence of a jet force at the pore location like his Landau-Squire solution presented in 1951 where there is no wall present.\textsuperscript{26} This force parameter (\( F_P \)) is calculated by integrating the \( z \) momentum transfer across a hemispherical shell centered at the flow origin giving total momentum flux (\( M \)) and \( F_P = \frac{M}{\rho \nu^2} \).

Schneider\textsuperscript{44} proposed another theoretical approach which satisfies the no slip condition at the wall and separates the flow into two regimes, the inner jet, and the outer entrainment flow. He later modified this solution\textsuperscript{45} to address the impact of the outer flow on the inner flow. He\textsuperscript{44,45} and Stern\textsuperscript{46} explored the asymptotics of the problem and found that the momentum flux imparted by the jet dissipates at distances sufficiently far from the orifice due to the jet force being counteracted by the negative pressure of the fluid over the wall. Meaning that at high distances from the jet source, the flow cannot be approximated by momentum flux and that only the mass flux is important and in this area, the Stokes approximation is applicable.
Recently, Gusarov addresses this peculiarity in the development of two separate analytical similarity solutions for momentum flux\textsuperscript{47,48} and mass flux\textsuperscript{48} dominated flows from a hole in a plane wall. In the momentum flux case, he assumes a similar form to Squire\textsuperscript{43} where the velocity field is in the form of Eqn. 6 and the governing equations reduce to the single differential in Eqn. 7. Alternatively, he showed that choosing $a = 2a_1 = 2a_2$ can be used for accounting for both finite momentum flux and no slip at the wall. Solving under this assumption gives,

\[
\frac{f}{v} = \left\{ \frac{2\alpha\beta}{\gamma} \left( \cos \frac{\theta}{2} \right)^{\gamma-1} \sin^2 \frac{\theta}{2} F \left( \alpha+1, \beta+1; \gamma+1; \cos^2 \frac{\theta}{2} \right) - \left( \cos \frac{\theta}{2} \right)^{\gamma-1} \left[ 2 - (2+\gamma) \sin^2 \frac{\theta}{2} \right] F \left( \alpha, \beta; \gamma, \cos^2 \frac{\theta}{2} \right) \right\}
\]

(9)

where $F$ is the hypergeometric function, $2\alpha = 2 - \sqrt{1+a} + \sqrt{1+2a}$, $2\beta = 2 - \sqrt{1+a} - \sqrt{1+2a}$, and $\gamma = 1 - \sqrt{1+a}$. The constant $b$ is calculated for a given value of $a$ by enforcing the impermeable wall condition, that $f(\pi/2) = 0$. Different values of $a$ correspond to different values of momentum flux. Unfortunately, neither solution corresponds to a flow where there is a constant, non-zero mass flux. Despite this, Gusarov did see reasonable agreement with numerical solutions for flow through a hole at $Re \gtrsim 30$.\textsuperscript{47} He further conjected that the effective force parameter $(FP)$ presented in Squire’s solution\textsuperscript{43} is proportional to $Re^2$, providing a basis for relating the two flows by taking $Re \approx \sqrt{\frac{M}{\rho y^2}}$. Streamlines of Squire’s\textsuperscript{43} versus Gusarov’s\textsuperscript{47} similarity solution are compared in Figure 2.11. Streamlines far from the jet origin line up well and have higher correlation for larger momentum fluxes (Fig 2.11c). Streamline differences are understandably considerable close to the wall where one solution considers no slip while the other does not.
Figure 2.11 Example streamlines from Squire [42] (solid lines) and Gusarov [46] (dashed lines) solutions for a) \(\sqrt{(M/\nu \rho^2)} = 50\) b) =200 and c) =1000

Gusarov’s second similarity solution considers a low Reynolds number jet dominated by mass flux in the Stokes approximation. He proposes a solution for the velocity field of the form,

\[
v_R = \frac{\phi(\theta)}{R^2}, \quad \nu_\theta = \frac{f(\theta)}{R^2}, \quad \frac{p}{\rho} = \frac{g(\theta)}{R^3}
\]

(10)

Substituting into the Stokes equations and solving under the non-slip \(\phi \left( \theta = \frac{\pi}{2} \right) = 0\) and impermeability of the wall for an infinitesimally small hole \(f \left( \theta = \frac{\pi}{2} \right) = 0\) for \(R > 0\) boundary conditions yields,

\[
\phi(\theta) = A \left[ (3 \cos^2 \theta - 1) \ln \left( \frac{1 + \cos \theta}{1 - \cos \theta} \right) - 6 \cos \theta \right] - B \cos^2 \theta
\]

(11)

and \(f(\theta) = 0\) where A and B are integration constants. Gusarov\(^4^8\) found that solutions where \(A = 0\) agree with numerical solutions of the flow field for low Reynolds numbers (Re \(\leq 10\)), corresponding to a velocity field where

\[
v_R = B \frac{\cos^2(\theta)}{R^2} \quad \text{and} \quad \nu_\theta = 0
\]

(12)

It remains uncertain whether Gusarov’s momentum flux solution accurately approximates flow from pores with non-zero mass flux and whether the mass flux and momentum flux solutions are adequate for describing micro/nanoscale orifice plate flows...
over the relevant range of Reynolds number. The solutions discussed provide a basis for understanding the flow in question and will be utilized in subsequent chapters to analyze flows within the different Reynolds number regimes.
Chapter 3

Experiment Design

With motivation rooted in membrane separation process optimization, this thesis set out to develop a method for measuring flows through pores in plane walls. The method is created by producing flows where an aqueous solute mixture is passed through a micron scale pore and the behaviour of the solute is recorded from a cross stream point of view. A fluorescent dye is selected as the solute to allow for pixel intensity values in recorded images to be related to the concentration field of the solute dispersion. This concentration field is used to reveal the volume flow rate of the liquid through the pore. The overall process uses microscope images of a solute dispersion downstream of a pore to estimate the volume flow rate through the pore itself and can be applied to various porous materials.

The method was developed using a series of micron scale flows. a set up capable of both creating the flows and allowing them to be imaged was needed. This section outlines the design of the experiment including a few physical and process iterations that led to successful flow experiments. The design process draws much inspiration from the studies presented by Secchi et al.\textsuperscript{24,25} in that a fluidic cell will be designed that simultaneously facilitates flow through a nanoporous medium and interfaces with a microscope for quantification purposes.

As in any design process, it is important to first outline the requirements of the product. The requirements for optimal functionality of this device are as follows:

The first and most important is to be capable of inducing a flow through a pore in a membrane which emulates conditions outlined in analytical solutions previously discussed. The similarities between the experimental flow field and solutions that can be replicated numerically provide a basis for verifying the capabilities of the measurement system and provide a tool for quantifying flow characteristics in individual pores. From this requirement stems a few others such as the ability to interface with atomically thin membranes and facilitating variable pressure gradients across the membrane. It also suggests that the process should allow images to be captured of the flow field for
characterization purposes. Finally, the device should allow for the membrane to be removed after flow experiments so that images of the pore may also be captured. This is important to verify that the membrane did not fail during the experiment and to allow for exact pore geometries to be linked to flow fields.

3.1 Substrate Selection

To create the orifice plate geometry, silicon nitride TEM grids were selected because of their commercial availability and ability to contain micron scale pores of various sizes. Another important consideration for NATM permeance measurements post calibration is that membranes of atomic thickness must be suspended on substrates to ensure structural integrity. The silicon nitride TEM grids not only provide the desired geometry for calibration and validation of the method but can be used to support NATM. Previous studies suspend graphene membranes on silicon oxide or silicon nitride membranes where the van der Waals forces between the two were able to sustain pressure differences up to 5 bar.\textsuperscript{16,23} Wang et al.\textsuperscript{3} demonstrate the ability of suspending CVD graphene membranes over apertures ranging from 200 nm to 3 μm and show lower burst pressures for smaller diameter supports and Surwade et al.\textsuperscript{23} suspend graphene membranes over 5 μm apertures. For the reasons discussed, and to allow for the subsequent imaging of pores, silicon nitride TEM grids were selected as the appropriate substrate. TEM grids were purchased from Norcada in pore diameters of 6, 3 and 1 μm (Product numbers NTPR003D-C6, NTPR005D-C3, A-C1 respectively) and a 50 μm copper TEM grid from SPI Supplies (#2885C). Microscope images of the pores in the substrates can be seen in Figure 3.1. The 30 μm pore is square in shape and is made using the 6 μm TEM grid with the silicon nitride window broken out.
Figure 3.1 a) 1 μm diameter hole in a 50 nm thick silicon nitride membrane b) 3 μm diameter hole in a 200 nm thick silicon nitride membrane c) 6 μm diameter hole in a 200 nm thick silicon nitride membrane d) 50 μm diameter hole in a copper TEM grid.

The general geometry of the SiNx TEM grids is illustrated in Figure 3.2 where a 3 mm diameter 200 μm thick silicon oxide substrate is coated with a thin (50-200 nm) silicon nitride layer which spans an aperture in the oxide. The nitride layer contains an individual pore and is designed for imaging samples under TEM but can withstand pressure differences up to 3 bar for the thinnest film.
3.2 Initial Design

Now that the interfacing with the nanomaterials and the orifice plate geometry had been considered, the design of the flow cell concerned itself only with interfacing with a 3 mm diameter TEM grid. The idea was to create a flow cell that interfaces directly with an optical microscope (Zeiss AXIO Imager A2) that uses a ElveFlow MK1 pressure controller (uncertainty ± 0.5 mbar) to apply a pressure gradient across a porous medium. A schematic of this idea is displayed in Figure 3.3.
A preliminary design was created and is shown in Figure 3.4. It consists of two reservoirs created by sandwiching an acrylic substrate in between two microscope slides attached with epoxy. The reservoirs are separated by an acrylic wall containing a ~2 mm diameter hole lined with a viton O-ring, Tubing connectors clamp a gasket around 1/16\textsuperscript{th} inch tubing that interfaces with the syringe pump (Fig. 3.4c). The TEM grid is held in place using acrylic clamps and threaded inserts (Fig 3.4b).

*Figure 3.3* Diagram of the proposed experimental set up. Drawing inspiration from previous studies, fluidic cell housing a nanoporous medium that interfaces with a constant pressure source and a microscope.
Testing with this and a few closely related subsequent iterations outlined four major areas for improvement:

- Elimination of leakage at connections to the syringe pump
- Developing a more efficient manner of interfacing TEM grid that eliminates leakage around the grid while still allowing removal
- Implementing geometry changes that facilitated the wetting of both sides of the membrane. First iterations of the cell caused air bubbles to be trapped between the upstream fluid and the membrane. This wetting was a persistent challenge throughout the duration of the experiment.
- Interfacing the device with the microscope which avoids issues associated with limited working distances of high magnification microscope lenses to allow for the flow field to be within the focal plane

3.3 Design and Process Modifications

3.3.1 Physical Cell Iterations

The issue of eliminating leakages between the cell and syringe pump was easily fixed by using IDEX flangless fittings from Cole Parmer (RK-02014-95) and introducing threads to the existing designs. The working distance issue was overcome both by finding long
working distance objective lenses and by switching the upper side of the cell to a microscope slide cover instead of a slide (~6x thinner).

Interfacing the TEM grid with the cell in a way that was watertight, removable, and facilitated wetting of the upstream side proved to be a more difficult task. Figure 3.5 shows a progression of methods for connecting the TEM grid to the flow cell and depicts ideas ranging from the original clamp (Fig. 3.5a), taping the grid onto an insert for the cell (Fig. 3.5b) and taping and coating the grid into the cell (Fig. 3.5c). There were many other concepts that explored alternative methods of setting up and carrying out the flow experiments compared to the original concept. A cell that used clips or magnets to hold the grid in place (Fig 3.6a) allowed for the upstream side of the cell to be primed prior to attaching the sample, thus ensuring the wetting of the upstream side of the grid. The two major drawbacks with this idea were the interference in the microscope FOV introduced by the material of the clip and that the leakage around the grid was still present at elevated pressures. Another iteration had adhered the grid to a 3D printed nozzle tip with epoxy (Fig. 3.6b) and primed the cell by drawing liquid backwards through the grid using a vacuum line (Fig. 3.6c). In this case the priming was unsuccessful and contamination of samples with epoxy was common.

Revisiting and modifying prior methods revealed the most effective way to interface the flow cell and TEM grid was to tape it over the orifice in the between reservoirs and seal the tape using JB Weld MarineWeld (Fig. 3.5c). The combination of tape and marine weld resulted in devices that withstood pressures up to 2 bar and the combination could be easily removed with heat after the flow experiments. It is also important to note that the success of this method may be attributed to altering cell material. The material was switched from the original acrylic to polylactic acid (PLA) to allow for rapid prototyping of cells via filament FDM 3D printing. The PLA cells were effective for pressures up to 500 mbar. Although the cell was printed with a solid fill, above 500 mbar they began to leak through the cell wall into the other reservoir and out of the cell itself. Treatments of the PLA parts such as dunking in acetone were explored but eventually a resin 3D printer (FormLabs Form3) was purchased, and the cell material was changed to FormLabs GREY v4 resin.
Figure 3.5 Methods for interfacing TEM grids with the fluidic cell. a) The original clamping method. b) Taping to an insert that is removable and fits into the flow cell after taping. c) The method used in later discussed flow experiments that tapes grids into the fluidic cell and seals the tape edges with JB Marine Weld.
3.3.2 Wetting the Membrane

A persistent challenge with the development of this process was developing a way to eliminate air bubbles in-between the upstream fluid and the reservoir. The inability to completely wet the upstream side of the membrane meant that the fluid in neighboring reservoirs was not in contact and that surface tension forces similar to the ones discussed by Celebi et al.\textsuperscript{16} were encountered at the pore opening and required large pressure gradients to clear. The high pressures often caused a failure in other locations of the cell and in the case that they did not, the permeating gas would take an extremely long time to fully clear and simultaneously provided interference in the measurement region by introducing bubbles (Fig 3.7). Various methods of priming the original cell were explored such as priming with a needle directly against the TEM grid (Fig 3.8a) and using fluids
with lower surface tensions such as isopropyl alcohol (IPA) and ethanol but eventually it was evident that the overall geometry of the cell needed to be altered. The new design contained a swept feature that forces air out of the cell during priming (Fig. 3.8b). This design was adequate for a few of the larger pore size TEM grid calibration studies (50 μm, 30 μm and 6 μm pores) but was limited in facilitating flow in smaller diameter samples. The wettability of the silicon nitride TEM grids was visualized by placing a droplet of water on its surface. Visibly (Fig. 3.9a), the droplet of water showed a large contact angle with the surface, indicating that the TEM grid was hydrophobic. Trials exposing the grids to UV ozone and air plasma evidently altered the overall wettability of the surface and lowered the fluid contact angle of the exposed substrates. Figure 3.9b shows the much-reduced contact angle of a water droplet on a SiNx TEM grid after exposure to UV ozone (20 min exposure in Bioforce ProCleaner). Although the contact angle improvement is not quantified, the post exposure substrate is clearly more hydrophilic than the original.
Figure 3.7 Bubbles introduced in the camera FOV as air passes through (and around) a 6 μm pore TEM grid, indicating an air bubble was adjacent to the membrane after priming and the membrane was not successfully wetted.

Figure 3.8 a) An alternative priming method using a needle to attempt to remove air bubbles and wet the upstream side of membranes. b) The final flow cell design that is used in the later flow experiments. Internal swept features facilitate priming.
3.4 Final Design

The iterative design changes led to a device where a TEM grid is taped, and marine weld sealed over an orifice separating two reservoirs. The upstream reservoir has a curved profile to facilitate priming without air bubbles and the downstream reservoir is sealed by a microscope slide on the under side and a slide cover on top. This allows for lower working distance objective lenses to focus on the flow field generated inside the device. The cell material is 3D printed using a resin printer with GREY v4 resin which facilitates rapid prototyping and is chemically inert to incident substances. Post printing, the cells were rinsed in IPA and water to remove residual resin before curing in a FormLabs FormCure curing station for 30 minutes of UV exposure at 60 °C. The final product is depicted in Figure 3.11. The detailed process of setting up and carrying out flow experiments will be discussed in the Methods section.
Figure 3.10 a) Photograph and b) CAD image of the final flow cell design.
Chapter 4
Methods

4.1 Flow Experiments

Flow experiments are carried out for the purposes of developing and validating a method of quantifying submerged flows emerging from orifices in a plane wall. The process outlined for preparation, priming, image acquisition etc. was designed iteratively with decreasing pore diameters and some portions needed for smaller pores are not necessary for the larger. The flows for developing the method are set up and run for bare TEM grids of pore diameters ranging from 1-50 μm.

4.1.1 Preparation and Assembly

The process begins with preparation of the fluids. The solute tracer used in the experiments is a fluorescent dye (fluorescein Sigma Aldrich F2456 CAS-2321-07-5). The dye, with excitation wavelength ~475 nm, is imaged with Zeiss FITC epifluorescence and produces high contrast images (in comparison to AR in brightfield) that were suitable for extracting information about the downstream concentration field as driven by fluid advection. A 1.5 mM fluorescein solution is prepared in DI water. Agitation is necessary for complete dissolution due to the low solubility limit of the dye in water. After mixing, the dye solution is filtered using a 0.45 μm syringe filter to remove any debris or precipitate dye particles that could potentially cause blockage. The solution, along with a comparable volume of pure DI water are degassed in a desiccator for at least 2 h prior to flow experiments. The fluid reservoir vials are prepared in specific volumes so that they contain approximately the same volume after the cell is primed to mitigate impacts of hydrostatic pressure.

While the fluids are being degassed, the components of the cell are prepared for assembly. The cell body, microscope slide, cover slip and tubing connectors are all scrubbed with residue free soap and sonicated for 5 minutes in both IPA and water. The components are then blown dry and stored in a covered petri dish prior to assembly. The TEM grid (with or without the NATM) is placed in a UV ozone cleaner to increase the hydrophilicity of the SiNx substrate as discussed in section 3.3.2. TEM grids with no
membrane were placed in a vertical orientation (held upright by tweezers or tape) in the cleaner to maximize ozone exposure.

The next step in the process is to assemble the flow cell. Kapton tape is prepared by punching a 2 mm diameter hole in two strips of approximately 3 cm length. The TEM grid is stuck onto the tape from its downstream side by touching the tape to the grid while the hole in the tape is aligned concentrically with the pore in the TEM grid. The tape with the grid on it is then stuck onto the flow cell body so that the grid aligns with the orifice in the upstream side of the fluidic cell. The tape is cut with a razor blade and folded around the protruding part of the cell body (Fig. 4.1a). A second layer of tape is applied prior to coating the area with marine weld. More marine weld is applied to the top and bottom of the cell where the slides are applied (Fig. 4.1b) to seal the downstream side of the cell and leave an observation window that interfaces with the microscope for imaging of the ensuing concentration fields. The cell is placed in an enclosed area to dry for ~1 h.

![Figure 4.1 CAD images describing steps of the cell assembly process. TEM grids are taped and sealed onto the a) protruding section of the cell prior to the downstream side of the cell being b) sealed between two microscope slides.](image)

4.1.2 Priming and Alignment

Once the cell has dried and the solutions have been degassed for the prescribed duration the experiments can be set up. Figure 4.2 shows how the cell connects to the pressure controller and microscope. The component labels will be referenced when explaining the priming and alignment process.
Figure 4.2 Photograph of experimental setup showing the fluidic cell in between two fluid (upstream/downstream) reservoirs that are both individually attached to a constant pressure syringe pump allowing for a pressure gradient to be applied across the porous membrane. Image shows callouts to microscope components that are referenced later in the text and identifies upstream and downstream direction for later explanations.

The upstream side containing the dye mixture is primed first by using a pipette to draw ~1 mL from the dye reservoir and inject it into the upstream side of the cell while angling the cell to force air out of the channel by buoyancy (Fig. 4.3). Once the upstream side has been filled, one of the ports is capped off and the dye reservoir is connected to the constant pressure syringe pump. Pressure is applied to flush air out of the connecting tubing before connecting to the other port in the cell using the threaded tubing connectors. For cases with larger (50, 30 μm) pores, a 15 mbar pressure difference is maintained during the priming of the downstream side of the cell to ensure there is no backward flow of air or water. The downstream side is primed via a similar method while the cell is shaken to dislodge air bubbles in the measurement window, when both sides are filled and capped any pressure gradient applied during priming is turned off.
Prior to placing the cell under the microscope, to assist in aligning the FOV, a line is drawn on the cover slip directly behind the pore location (blue line Fig. 4.4a). The microscope is set to a reflected light brightfield filter with a 5% light source intensity and 5x objective lens to focus on the marker line on the cover slip. Moving the stage so that the mark is in the center of the FOV sets the cell in place in the $Y$ direction for experiments. An attachment for the microscope used to hold the cell square to the camera and allow for the cell to be moved with the stage adjustment knobs was designed and 3D printed (Fig. 4.4b). From this position, the cell is moved in the negative $X$ direction until the protruding edge of the cell in the measurement window is roughly aligned with the left edge of the microscope FOV (Fig. 4.4a), setting the cell in the correct $X$ location for flow experiments. The last step is to move the stage upwards in the $Z$ direction so that the focal plane lies at the midway point between the two glass slides. This is done by raising the stage from the location where focus is on the cover slip to the bottom slide and then back downwards half of that distance, in some cases dye is visible at the zero-pressure gradient case and can be used to help focus on the flow plane.
4.1.3 Image Acquisition

Once the cell is primed and aligned with the flow axis within the focal plane of the microscope, the microscope settings can be switched to enable epifluorescence and to the desired objective. 5x magnification was sufficient for all pores greater than 1 μm. Time series capabilities are also enabled in the Zen Blue software with baseline settings as 1 s frame rate, 500 ms exposure and 5% light intensity. The pressure applied to the upstream side of the cell is increased (using an ElveFlow MK1 pressure controller; accuracy ± 0.5 mbar) sequentially in set denominations (smaller for larger pore sizes) while images are acquired in the time series. The images for a few pressures are observed and time series settings are adjusted to increase the visibility of the resultant concentration field (or to see it at all) These parameters are recorded for later image calibration. Once satisfied with the visibility, the series are rerun for all desired pressures or until the observation area is saturated with dye, at which point it could be reprimed for further experimentation. After the flow experiments were complete, the TEM grids were carefully cut out of the cell by removing the glass slides using a hot plate to soften the marine weld. The grids were imaged under the optical microscope and occasionally SEM (at Western nanofabrication facility or Surface Science Western) to ensure the membrane was not compromised or to analyze individual experiment failure modes which are discussed later.
Raw images for a few different diameter pores and pressure gradients are presented in Figure 4.5. A distinct difference between concentration fields of low, intermediate, and high Reynolds number are evident and have a large impact on the method of image processing and flow quantification. For the purposes of preliminary image processing, these images are distinguished as “hemispherical plumes” (Fig. 4.5a), “plumes” (Fig. 4.5b), “partial jets” (Fig. 4.5c), and “jets” (Fig. 4.5d). The influx of dye mixture occurs from the left-hand side of the image. Dye dispersion shapes stabilize once the jet has reached steady state at its pressure gradient and the advection of dye into the FOV is balanced by the diffusion of dye at the edge of the dispersion. Creating a steady concentration field and the “shapes” that are shown below. The Reynolds numbers listed in the figure are calculated via OpenFOAM computational fluid dynamics simulations for the given pore diameters and pressure gradients. The Reynolds number is \( Re = \frac{Vd}{\nu} \) where \( V \) is the average fluid velocity through the pore, \( d \) is the pore diameter, and \( \nu \) is the kinematic viscosity of the fluid. A 1° slice of the cylindrical domain is simulated while imposing a constant pressure gradient across the plate. Calculations were performed on a uniform grid extending 15 pore radii upstream, downstream, and radially outward from the pore, using a grid spacing of 0.02 radii.
4.2 Preliminary Image Processing

As previously stated, type of concentration dispersion observed played a large role in determining the preliminary image processing steps. Unique algorithms and in-house image processing code were produced for each of these cases. This section outlines said algorithms and explains the rationale behind them.

The result of the flow experiments were datasets containing sequences of images at known frame rates that represent the steady state and, in some cases, the transient evolution of concentration fields. The FOV was approximately 2 by 2.3 mm with a resolution of 2464 x 2056. The overall goal of the image processing algorithms is to extract information about the two dimensional, rotationally symmetric dye concentration
field \([C(z, r), C(R, \theta)]\) in relation to the radial distance from the pore based on pixel intensity values \([I(z, r), I(R, \theta)]\) in the steady state. Full datasets for all successful experiments are available in the Appendix (A1 – A5). The role of the preliminary image processing is to locate the pixel index of the pore in the image which will be taken as the origin for all coordinate systems, rotating the datasets so that the flow axis is parallel to the camera frame to simplify subsequent analysis. The last responsibility of the preliminary image processing algorithms was to identify the range within datasets that is at steady state.

4.2.1 Locating the Pore

To extract information about the concentration field relative to radial distance (\(R\)) from the pore, one must first locate the pore in all datasets. This was done by initially converting all RGB image files into grey scale images (16-bit depth), allowing for a single intensity value to be used at its pixel location in the analysis (rather than R G and B intensity values).

For cases where transient behaviour is captured in the dataset and for hemispherical plumes, finding the pore location in the image is quite simple. For cases where the transient flow development is recorded, the pore is located at the location of the maximum intensity \((I_{\text{max}})\) pixel in the earliest frame that a fluorescent signal is visible. For extremely low Reynolds number, hemispherical plumes, the pore is located based on the average location of the pixel with the highest intensity across a dataset. The location of the \(I_{\text{max}}\) corresponds to both the location where \(C\) is expected to be highest and where the plume is at its widest in the \(Z\) direction. Meaning that there should be no shift in the location of maximum pixel intensity based on perspective effects associated with the light emitted by out of plane dye molecules.

The perspective effects encountered when trying to approximate a 3D concentration field with a 2D image are shown in Figure 4.6, The intensity of a pixel in the image is not a perfect representation of the concentration of the fluid at the focal plane due to the pixel intensity being increased by light emitted by out of focal plane dye molecules over the effective path length (red lines in lower part of Fig. 4.6). This becomes a problem when the shape of the concentration field is elongated and the shape of the plume scales
dissimilarly to the concentration field. Figure 4.6 shows an arbitrary plume shape comparing two different pixel intensity values \( I_1 \) and \( I_2 \) at differing distances from the pore \((z_1 \text{ and } z_2)\) along the horizontal plume axis \((Y=0)\). Intensity values in the image are proportional to the integral of the concentration profile at that point along the effective path length of the plume.

\[
\text{e.g. } I_2 = I(z = z_2) \propto \int_{-A_2}^{A_2} C(r, z = 0) dZ \tag{13}
\]

Molecular diffusion causes the magnitude of the \( C \) at the focal plane to decrease with increasing distance from the pore \((C(r = 0, z = z_1) > C(r = 0, z = z_2))\). The increased effective path length at location 2 causes intensity values to be higher than at location 1 even though the concentration at location 1 is higher. This is an important consideration when finding the pore location and later when acquiring and analyzing concentration field data.
With the effects of variable effective path length in mind, a separate method of locating the pore was developed for plumes and partial jets. This process relied on generating iso-intensity contours for all images in a dataset that ranged from 10-50% of $I_{\text{max}}$. This value was decided for each individual dataset by manually increasing the percentage until the location where the plume meets the wall is clearly visible. At the average pixel location across a dataset of the farthest left point on the concentration contour was taken as the pore. Pore locations in images of jets were found using a more subjective process that
similarly produced iso-intensity contours at usually higher percentages where the pore location was manually identified (Fig. 4.7). This was necessary because the jets often had much lower contrast with the surrounding fluid due to their slender profile. This low contrast increased the impact of noise caused both by scattered light and reflections from the cell wall (left of Fig. 4.7). The uncertainty for these locations are approximately ±25 pixels (~22 μm) for the location of the pore in hemispheres and ±40 pixels (~36 μm) for the plumes. These uncertainty values vary for each individual dataset; the methods in which they were estimated are discussed in Appendix B.

4.2.2 Rotating Datasets

The cell and attachments are designed to keep flows as square as possible to the camera, but there are factors such as the seating of the TEM grid and loose fits in the attachments that can cause the flows to be slightly off axis. To correct for this, all images are rotated
around the pore location based on dataset average angles acquired from iso-intensity contours. For all plume images, the rotation angles are obtained by taking the points on the contours the greatest distance away from the pore in the $\pm Y$ direction. Plumes are expected to propagate symmetrically about the horizontal axis, therefore the bisection of the angle the points make with each other about the pore location can be taken as the horizontal flow axis (Fig 4.8a, b). Jet images are much simpler to square, where the rotation angle is the angle needed to horizontally align the pore location with the midpoint between the two pixels on the contour in the last column of pixels (Fig 4.8c). The rotation slightly enlarges the image and pixel scaling from the raw images is adjusted accordingly. After the rotation, contour plots containing multiple relative intensity ranges were produced to help visualize the flow behaviour. They are presented in the Appendix (A.1 - A.5) and an example is provided in Figure 4.9.

![Figure 4.8](image)

**Figure 4.8** Calculating the image rotation value a, b) using the bisecting angle between the two furthest pixels in the $Y$ direction as the jet axis assuming that plumes will propagate symmetrically about the jet axis. c) Taking the bisecting angle between the furthest ($X$) direction pixels on an iso-intensity contour.
4.2.3 Identifying Steady State Data

The images exhibiting transient behaviour are disregarded from subsequent analysis so that data may be compared to previously discussed solutions that address steady flows in this geometry. The behaviour of these flows prior to steady state assuredly could be used for interesting studies based on plume propagation but are not discussed in this thesis.

Jet images become stable quickly compared to plume. Selecting the last image in the time series for analysis is sufficient in this case. All plumes, on the other hand, require a more involved procedure to select an appropriate range as steady state. The plume front location at various iso-intensity percentages are plotted versus time (Fig. 4.10a) to determine when the size of the plume stabilizes. This was paired with the intensity range over the time series (Fig. 4.10b) to determine when the flow reached steady state. The idea is that both the plume front and intensity range will increase as the plume grows and stabilize when it stops. The plume fronts of iso-intensity contours 10% and 20% less than the maximum is shown to continue to grow throughout the experiments. This is attributed
to the growth of the average $I$ of an image over time due to the continual influx of fluorescein dye (Fig. 4.10b). If these experiments were run for long durations, eventually the entire downstream reservoir would be filled with dye and pixels would all be at an identical intensity. This continual growth does not occur for the 50% iso-intensity profile as it stabilizes in this and other cases. This inspires confidence that steady state of the velocity field driving the dye dispersion can be identified by pairing the stability of the intensity range and 50% plume front. The uncertainty in the distance to an iso-intensity profile is $\pm 1$ pixel. The uncertainty is inconsequential for determining when steady state is reached as it is the trend of the reading that is used. The same estimate for steady state would be reached regardless of uncertainty.

A drop in the intensity range is also useful for identifying blockages that may not be portrayed by the plume front location. For the case below, the experiment commenced with the first image in the time series showing the plume front and $I_{\text{max}}$ as approximately zero. From here the fronts quickly propagate away from the pore location where the 50% iso-intensity contour stabilizes at $\sim 30$ s. The intensity range stabilizes much quicker than this ($\sim 12$ s) but is shown to drop at around 40 s. From these two plots it is determined that the flow was stable between 30 and 40 s. The images outside of this time frame are disregarded in the development of flow quantification methods and measurements of flow rates. The stable range for each dataset is provided in the appendix.
Figure 4.10 a) Plume front location of various intensity percentages versus time for pore diameter 3 μm and applied pressure difference 400 mbar. b) The intensity range across a data set and the increasing value of average intensity with time. The results of these two plots are combined to determine when the flow field is steady.
Chapter 5

Results

This thesis set out to develop a method for quantifying flows through individual micropores that avoids limitations imposed by commercially available flow sensors. The method is developed with nanoscales in mind and is intended for taking permeance measurements of membranes for separation processes. This study proposes that the rate of decay of concentration with distance from the pore can be extracted from pixel intensity values of solute dispersions and can further use them to measure the flow rate through a pore itself. There is little theory that discusses the expected fluid behaviour through nanoscale geometries. For that reason, the quantification method was developed using a series of microscale flows where $Re = 2 - 40$. The flow in this regime is well documented and simulation data\textsuperscript{64–70} can be used to validate the measurement method.

Flow experiments were set up and run at various pressures for TEM grids of pore diameters of 50, 6, 3 and 1 μm and a square orifice with 30 μm sides. Figure 5.1 illustrates the solute dispersion at various applied pressure differences for a 6 μm pore. Reynolds numbers listed are estimated by OpenFOAM simulation for flows with the same $d$ and pressure difference. Visually, there is a distinct change in solute dispersion with increasing $Re$ progressing from a hemispherical plume at low $Re$ to a jet at higher $Re$. Summarizing the perceived flow fields throughout experiments over all diameters: Flows with Reynolds number $< 7.2$ were hemispherical shaped dispersions and became elongated in shape between this limit and $Re \approx 18$. These elongated plumes saw $I_{max}$ shift away from the pore location. At the end of the previous range, the dye dispersion entered what appeared to be a transitional region. In this region, the dye appeared to enter the reservoir at a visibly high velocity, where it then slowed down sufficiently so that molecular diffusion again appeared to be causing the transport of the dye. Beyond this limit ($Re \approx 21$) the flows appeared purely as jets (Fig. 5.1d). It is entirely possible that the behaviour exhibited in Figure 5.1c continued but the slowing of the jet occurred outside of the microscope FOV.
Figure 5.1 Transitions of solute dispersion as a function of Reynolds number a) example of a hemispherical plume shape that was observed from the lowest Re to ~ 7.2 where plumes became b) slightly elongated until c) ~18 where dispersions no longer resembled plumes and appear to be a transitionary stage between plume and d) jets that have highly elongated shapes that protrude past the camera FOV. All images are 2.3 x 2 mm.

Nanoscale flows are expected to have $Re << 1$ and be hemispherical in shape consistent with the shapes presented above (Fig. 5.1a). The low Reynolds number limit of the experimental data will be used to develop a quantification method that will apply at $Re$ less than the ones experimentally replicated in the calibration studies. For this $Re$ limit the dispersions grow until they reach a steady state size and shape where the dye flux into the reservoir is equal to the flux out of the plume shape via diffusion at the shapes edges.

5.1 Low Reynolds Number Micro Scale Flows

The following sections discuss analytical solutions and plots that are in various coordinate systems. To eliminate confusion, Figure 5.2 summarizes all relevant coordinate systems in relation to the camera plane. The pore location is the origin for all cases and the oblate spheroidal coordinate system is the same as previously defined in the literature review (Fig. 2.10). Note that cartesian coordinates are not used in the subsequent analysis but were defined earlier for purposes of describing microscope stage movements and discussing the concept of effective path length. For all analytical solutions and subsequent analysis, the velocity fields are assumed to be rotationally symmetric about the $z$ axis and both analytical solutions and intensity value transformations are defined in two dimensional cylindrical or spherical coordinates with no variation in $\phi$, $\omega$ directions.
5.1.1 Analytical Velocity and Concentration Field

Atwal et al.\textsuperscript{42} present an approximate solution (Eqn. 5) for an advection diffusion problem where a solute tracer is dispersed by Sampson’s\textsuperscript{41} velocity field solution (Eqn. 3) for Stokes flow through an orifice in a plane wall. The group’s approximation defines a dimensionless concentration field in oblate spheroidal coordinates that shows the dispersion of dye in a reservoir is solely dependent on Peclet number. This thesis proposes to use the rate of decay of concentration with distance from the pore along the pore axis ($z, X$) as a way to measure the flow rate through the pore.

With the hemispherical plume images in mind, the concentration field expression is normalized by the maximum concentration ($c_{\text{max}}$) that occurs at the pore location.

\[ c(q, 0) = \frac{\left[ 1 - \exp\left(\frac{\pi Pe}{8}\right) \right]}{\exp\left(\frac{\pi Pe}{8}\right) - \exp\left(\frac{\pi Pe}{8}\right)} \]

\[ 1 - \frac{c(q, s)}{c_{\text{max}}} = \frac{1 - \exp\left(\frac{\pi Pe}{8}\right) \arctan(s)}{1 - \exp\left(\frac{\pi Pe}{8}\right)} \tag{14} \]

Where,

\[ Pe = \frac{V d}{D}. \tag{15} \]

For distances far from the pore along the $z$ axis: $s \gg 1$, $s \approx 2z/d$ and $\arctan(s) \approx \pi/2 - d/2z$, reducing Eqn. 14 to

\[ 1 - \frac{c}{c_{\text{max}}} = \frac{\exp\left(\frac{\pi Pe}{8}\right) - \exp\left(-\frac{d Pe}{8z}\right)}{\exp\left(-\frac{\pi Pe}{8z}\right) - 1} \tag{16} \]
The distant decay rate of the concentration field is defined as the slope of the natural logarithm of the normalized concentration field versus the inverse of the distance from the pore. Evaluating this slope for Eqn. 16 gives a decay rate of:

\[ a = \frac{d}{d \left( \frac{1}{x} \right)} \left[ \ln \left( 1 - \left( \frac{c}{c_{\text{max}}} \right) \right) \right] = \frac{-Pe d}{8} \frac{\ln \left( 1 - \exp \left( \frac{-\pi Pe}{8} \right) \right)}{1 - \exp \left( \frac{-\pi Pe}{8} \right)} \quad (17) \]

where \( V \) is the fluid velocity; \( d \) is the diameter of the pore and \( D \) is the diffusion coefficient of the solute tracer. For \( Pe << 1 \), \( a \) becomes \(-d/\pi\), whereas for high \( Pe \), it becomes \( a = -Pe \frac{d}{8} \). Eqn. 17 along with the low and high \( Pe \) limits are compared to the full numerical solution for the low Reynolds number concentration field. Eqn. 17 approximated to one term is accurate to within 5% for the points shown. For \( Pe > 10 \), the high \( Pe \) limit is accurate to within 2%. The diffusivity of 1.5 mM fluorescein dye is taken as \( 4E-10 \, \text{m}^2/\text{s} \) and simulated data for the lowest Reynolds number cases shows \( Re > 1 \). Therefore, \( a \) is evaluated for the high Peclet limit and substituting the definition of \( Pe \) gives:

\[ a = -\frac{V a^2}{8 D} = -\frac{Q}{2 \pi D} \quad (18) \]

Where \( Q = V \pi d^2 / 4 \) is the volume flow rate through the pore. This means that measurements of normalized concentration field decay rates can be used to predict the volume flow rate through a pore without knowledge of its diameter.

This slope expression is derived based on Stokes equations valid for flows where \( Re << 1 \) such that inertial effects are negligible. This makes it a suitable option for nanoscale flows where such low \( Re \) are expected. Gusarov\textsuperscript{48} derives a similarity solution for the same geometry that scales proportionally to the one presented by Sampson\textsuperscript{41} at large distances from the pore.

Gusarov’s spherical coordinate velocity (Eqn. 10) field scales as follows:

\[ v_R \propto \frac{\cos^2(\theta)}{R^2} \quad \text{and} \quad v_\theta = 0 \quad (19) \]
At distances far from the pore \((R >> d)\), \(s >> 1\) and \(0 \leq q \leq 1\) and \(R \approx 1/2sd\). Furthermore, 
\[
tan \theta = \frac{r}{z} \approx \frac{\sqrt{1-q^2}}{q}
\]
meaning that \(\sin \theta \approx \sqrt{1-q^2}\) and \(\cos \theta \approx q\). Transforming from spherical to cylindrical coordinates yields the proportionality 
\[
\nu_r \propto \frac{q^2}{s^2} \sqrt{1-q^2} \quad \& \quad \nu_z \propto \frac{q^3}{s^2} \tag{20}
\]
Similarly, Sampson’s solution (Eqn. 3) scales as follows for large distances from the pore:
\[
\nu_z = \frac{3}{2} V \frac{q^3}{s^2 + q^2} \rightarrow \nu_z \propto \frac{q^3}{s^2} \tag{21}
\]
This means that the similarity solution for the concentration field using Gusarov’s velocity field\(^{48}\) would lead to the same prediction for the rate of decay of concentration as the one presented in Eqn. 18 for distances far from the pore. Gusarov compared this velocity field to simulation data and found that it was in good agreement at Reynolds numbers up to 10. This implies that the method of extracting volume flow rate using the slope of \(\ln(1-c/c_{max})\) vs. \(1/z\) at large \(z\) may not be bounded by the Stokes approximation limit. The hemispherical experimental data falls well within this range and are processed using the discussed method.

5.1.2 Pixel Intensity and Scaling

The previous section discussed a method for extracting volume flow rates independent of pore diameter from the radial decay rate of concentration at distances far from a pore. Experimental data was collected for various micron scale flows that fall within the permissible \(Re\) regime to apply this relationship.

To extract the slopes from the dataset, the pixel \(I\) values in the images must be correlated to the concentration field of the plumes that created them. The peculiarities of this were touched on earlier when discussing image processing methods for acquiring pore locations (section 4.2.1). \(I\) in the raw images is not proportional to concentration because of the three-dimensional volume being imaged through. The impact of the out of image plane dye molecules is explained by imagining two separate reservoirs of fluorescent dye at the same constant concentration where one reservoir is twice as deep as the other. If a camera (with florescence engaged) imaged both from above with the same camera settings and incident light intensity \((LI)\), the image of the deeper reservoir would appear
twice as bright as the other due to there being twice the amount of light emitting dye molecules in the focal path of the camera. The distance through a volume being imaged is called the effective path length and must be corrected for to correlate intensity to concentration.

The effective path length, $2l$, is shown in Figure 5.3, using the slope calculated in section 5.1.1, the concentration in terms of radial distance from the pore is approximated as:

$$C = \frac{Q}{2\pi D} \times \frac{1}{R} \quad (22)$$

Where $R = \sqrt{z_0^2 + r^2}$ is the spherical radial distance and $z_0$ is the axial distance into the dye plume. The intensity of the pixel corresponding to the $z_0$ location is proportional to the integral of the concentration field through the path length. For cases where $l/z_0 >> 1$ that integral can be approximated as,

$$I(z_0) \propto \int_{-l}^{+l} C \, dr = \int_{-l}^{l} \frac{Q}{2\pi D} \times \frac{1}{\sqrt{z_0^2 + r^2}} = \frac{Q}{\pi D} \ln\left(\frac{2l}{z_0}\right) \quad (23)$$

To correlate intensity values to concentration field the slope of the intensity decay is calculated and compared. The result shows that an identical slope is acquired by dividing the intensity values by their respective $z_0$ values. Therefore, by dividing all dataset intensity fields by the distance to a common iso-intensity contour the slopes in the range of interest can be fixed to where $C \propto l$.

$$\frac{dl}{d\left(\frac{1}{z_0}\right)} = \frac{Q}{\pi D} z_0 \quad (24)$$

All datasets are scaled by the distance to their 10\% iso-intensity contour, scaling by the distance to the same intensity percentage allows for results across various datasets to be comparable. This scaling needs to use the distance to a common iso-intensity value, but the precise choice of this iso-intensity value is not critical. The value needs to be relatively small, corresponding to large distances from the pore where the slope is calculated and the concentration field decays approximately as $1/R$, but not so small that background noise interferes with accurately determining the location. A value of 10\% was selected to satisfy these criteria, this distance is henceforth denoted as $z_{10}$. 
In order for datasets to be comparable to one another, variance of camera settings across datasets must also be corrected for. When running experiments, LI percentage and exposure time ($t_{exp}$) were varied from starting settings to increase the visibility of dye dispersions in the images captured. Variations of these parameters directly impact the $I$ of pixels in an image. Doubling how bright the incident light is will double the number of photons reaching the camera per second. Similarly, by exposing a frame for double the duration will allow twice the amount of light at the same brightness to reach the camera sensor, again doubling the image pixel intensity. To compare datasets to one another they must be at the same $t_{exp}$ and $LI$. This can be corrected for by dividing $I$ values by the $LI$ and $t_{exp}$. The transformations applied to raw image pixel intensity gives the following proportionality:

$$\frac{C}{C_{max}} \propto \frac{I}{C_{ms} z_{10}}$$

(25)

Where $C_{ms}$ is the microscope calibration factor that is equal to the product of $t_{exp}$ and LI ($C_{ms} = t_{exp} \times LI$). It is important to note that $C_{max}$ is a constant for all experiments and is
equal to the upstream fluid concentration and can be accounted for in the calibration factor. The concentration field is only proportional to the transformed intensity values because $z_{10}$ is only proportional to the effective path length $l$. Multiplying by a calibration factor ($CF$) that can be later approximated using experimental data from the micron scale flow datasets. The calibration factor is a single value that is calculated once for the system using a flow of known pore diameter and pressure gradient. Whereafter the method can take flow measurements from images of other flows.

$$\frac{C}{C_{max}} = \frac{l \ast CF}{C_{ms} \ast z_{10}}$$  \hspace{1cm} (26)

By substituting Eqn. 26 into Equation 17, $a$ can be evaluated in terms of $I$, allowing decay rates of concentration to be determined based on the rate of intensity decay in the raw images where scaling factors are only implemented in the final calculation rather than altering entire datasets.

$$a = \frac{d}{d (\frac{1}{z})} \left[ \ln \left( 1 - \left( \frac{l(z) \ast CF}{C_{ms} \ast z_{10}} \right) \right) \right] = \frac{d}{d (\frac{1}{z})} \left[ \ln \left( 1 - \left( \frac{l_{max} \ast CF}{C_{ms} \ast z_{10}} \right) \frac{l(z)}{l_{max}} \right) \right]$$  \hspace{1cm} (27)

where, far from the pore where $I/I_{max} << 1$ the expression above can be approximated as:

$$a = \frac{l_{max} \ast CF}{C_{ms} \ast z_{10}} \frac{d}{d (\frac{1}{z})} \left[ \ln \left( 1 - \frac{l(z)}{l_{max}} \right) \right]$$  \hspace{1cm} (28)

and setting $m = \frac{d}{d (\frac{1}{z})} \left[ \ln \left( 1 - \frac{l(z)}{l_{max}} \right) \right]$ as the rate of decay of normalized intensity far from the pore location gives,

$$Q = \frac{2 \pi D l_{max} \ast CF \ast m}{C_{ms} \ast z_{10}}$$  \hspace{1cm} (29)

5.1.3 Slope Acquisition and Flow Rate Measurements

The relationship defined in the previous section provides a basis for relating pixel intensity values to volume flow rates through a pore in a plane wall for $Re$ up to 10. For hemispherical plumes, radial decay of intensity and concentration should be a function solely of $R$ and have no angular variation. The decay of intensity at various angles from the pore axis are shown in Figure 5.4a. As expected, for the most part, intensity is shown to decay symmetrically except for in areas where noise caused by proximity to the wall is
present. The impact of wall interference can be seen in the inconsistency of the vertical direction decay contour. The rate of decay of intensity far from the pore is acquired by taking the slope of curves of the natural logarithm of the normalized intensity field versus $1/R$. The slopes were approximated between $1/R$ values between the end of the frame and 0.0015 corresponding to distances 650 μm and more from the pore. The $m$ values for all micron scale flows that fell within the $Re$ limit (and a few outside of it) are tabulated in Table 5.1. The extraction of an $m$ value for a $Re \approx 2.88$ flow is shown in Figure 5.4b. In the figure the decay rates are shown to be comparable for all $\theta$ (except for ones with wall noise) and the slopes are taken over the prescribed distances along the jet axis ($z$).

After the intensity decay rates were found from the images, Equation 29 could be solved for values that were proportional to volume flow rate ($Q/CF$). These proportional values were fit to simulation data across all micron scale flows in the permissible $Re$ range via numerical least squares optimization to determine $CF$ (Table 5.1).

### Table 5.1
Summary of experimental data for low Reynolds number micron scale orifice flows. Volume flow rates are calculated based on Eqn. 29 where $CF$ was fit to match flow rates calculated from simulation data for the same pore diameters and applied pressure differences. $LI$ and $t_{exp}$ are recorded from the experiment procedure and $I_{max}/z_{10}$ are solved for based on pixel intensities.

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Residual 8.11E-22

CF [μm s] 4.66E+00
Figure 5.4 a) Radial decay of intensity at various angles from the cell wall. The coinciding contours are expected for a hemispherical plume. Wall proximity is shown to skew intensity data as there is excess light reflected. Inset shows the locations of the plotted intensity contours. b) Radial decay rates of intensity are approximated over distances greater than 650 μm from the pore. The decay rates at various angles agree with one another for hemispherical plumes where this c) ceases to be the case once plumes become elongated.
The measured volume flow rates for micron scale flows are shown to be in good agreement with OpenFOAM simulation data\textsuperscript{64–70} (Fig. 5.5). This agreement suggests that volume flow rates of submerged, low Reynolds number flows emerging from pores in plane walls can be estimated based on the behaviour of a solute dispersed downstream of the pore. The process established in this thesis that uses pixel intensity of an imaged concentration field to estimate the minute volume flow rates through small geometries is developed with large nanoscale flows in mind where $Re \ll 1$ are expected. Although this method was developed based on experimental data with relatively large $Re$, the similar proportionality of analytical velocity fields discussed earlier suggests that the method could be a useful tool for probing flows at nanoscales that are seldom explored experimentally provided that the pore geometry is within the continuum limit ($d \geq 10\text{nm}$).

Uncertainty analysis is provided in the appendix (A.7). The main considerations when calculating uncertainty and error bars were the pore location, location at which the slope was acquired and non-zero thickness of the plate.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure_5.5.png}
\caption{Measured volume flow rates of low Reynolds number flows through micron scale pores. The measurements agree well with simulated data and suggest the potential of the measurement system for probing nano scale flows. This plot also outlines the validity of the method beyond the range originally expected. Dashed lines are the simulated data while solid lines denote the limits of the simulation when incorporating non-zero thickness and uncertainty in the pore diameter.}
\end{figure}
At approximately $Re = 7.5$ the hemispherical plumes become elongated, and the intensity decay rate is not rotationally symmetric and varies with $\theta$ (Fig. 5.4c). Despite their elongated shape, the flow rate measurements had good agreement with simulation data. Not only was the method effective for shapes other than hemispheres, measured values agreed with simulation data passed the expected Reynolds number limit where the velocity fields were applicable.

5.1.4 Validity Outside of Expected Range

The method developed in the previous section applies multiple assumptions that the concentration field is of hemispherical shape. The images captured of micron scale flows show a distinct change in shape at $Re \approx 7.2$ from a hemisphere to a plume. At $Re \approx 10$ it is also true that the velocity field will no longer match the velocity field used to derive the relationship between concentration decay rate and volume flow rate. Based on these two facts, one would intuitively assume that the validity of Eqn. 29 would diminish once either one of these limits was reached. Surprisingly, this appears not to be the case: volume flow rates based on $m$ are extracted up to $Re \approx 17$ that agree well with simulation data. This unexpected validity range is rationalized because during the analysis only the decay rate far from the pore is taken. At elevated $Re$, the solute dispersion in the range close to the pore is expected to be dominated by advection and inertial effects (e.g., vortices shown by Guasrov at $Re > 10$). Conversely, at large $R$, fluid momentum has dissipated, and solute dispersion is expected to depend heavily on diffusion. The ensuing analysis explores a one-dimensional control volume problem in regions far from the pore where diffusion dominates the solute dispersion. The analysis shows that the decay of concentration in these areas is identical to the lower Reynolds number cases described above.

In regions where diffusion dominates the solute dispersion, an isoconcentration contour can be approximated as hemispherical. Taking a control volume (Fig 5.6) at this contour and assuming radial symmetry of the concentration field gives the one-dimensional solute mass flux relation:
\[ \dot{m} = Q \Delta C \approx -\mathcal{D} 2\pi R^2 \frac{\partial C}{\partial R} \]  \hspace{1cm} (30)

Where \( \dot{m} \) is the solute mass flux through the control volume, \( C \) is the concentration as a function of \( R \), and \( \Delta C \) is the total difference between the concentration upstream and far from the pore in the downstream direction.

Figure 5.6 A control volume analysis of mass flux for regions far from the pore

Solving Eqn. 30 for \( C \) subject to the boundary condition \( C(R \to \infty) = 0 \) gives:

\[ \frac{C}{\Delta C} = \frac{Q}{2\pi DR} \]  \hspace{1cm} (31)
Taking the slope in the same manner as before yields the exact same relation as the one derived for Stokes flow above.

\[ a = \frac{d}{d\left(\frac{1}{R}\right)} \left[ \ln \left(1 - \frac{c}{\Delta c}\right) \right] = \frac{-\frac{Q}{2\pi D}}{1 - \frac{Q}{2\pi D R}} \approx \frac{-\frac{Q}{2\pi D}}{1} \] 

(32)

This similarity in concentration decay rates at far distances from the pore explains why the method exhibited an effective \( Re \) range larger than originally expected. The similarities in fluid behaviour over such a wide range of \( Re \) at distances far from the pore is an interesting discovery that experimentally validates discussions by Schneider\textsuperscript{44,45} and Sthern\textsuperscript{46} that posturized that at high distances from the source, flow can be approximated by mass flux and that, in this area, the Stokes approximation is applicable.

The one-dimensional control volume analysis considers only mass fluxes in and out of the system regardless of pore geometry. Its validity suggests that the described method is applicable for taking flow rate measurements through orifice plates containing any amount or shape of pores that have \( Re \leq 17 \). This makes it an interesting tool that could potentially be used for permeance measurements of nanoporous membranes of any chemical or physical characteristics.

5.2 High Reynolds Number Micron Scale Flows

As discussed previously, some cases were encountered at \( Re \gtrsim 21 \) that did not resemble plumes at all but instead had elongated shapes that protruded past the camera FOV (jets). It is important to note in this section that the intermediate cases identified earlier (18 < \( Re < 21 \)) will not be discussed in this thesis and may be the subject of a future work.

Visually, the shape of these dispersions become slenderer with higher Reynolds number and gradually flatten out to where they appear linear within the camera FOV. The behaviour of jets with increasing \( Re \) is shown in Figure 5.7. As the jets become thinner so does their effective path length. Imaging through a smaller volume of dye leads to lower intensities and less contrast with the background. This is depicted well in Figure 5.7c where a large portion of the image is at least 20\% of \( I_{max} \).
Squire’s\textsuperscript{43} and Gusarov’s\textsuperscript{48} velocity field similarity solutions for high Reynolds number flows emerging from pores in plane walls are discussed in the above literature review (Section 2.3). Both solutions present streamlines of laminar jets as streamlines of constant $f R \sin \theta$. Solutions were compared previously in Figure 2.11 where streamlines were shown to coincide close to the jet axis. Unfortunately, neither of the solutions correspond to a jet with a non-zero mass flow rate but Gusarov\textsuperscript{47} did find sufficient agreement with numerically produced streamlines starting at $Re \approx 30$. Similar to the low $Re$ case, prior to any analysis, the images must be scaled to correct for the effective path length. Contour plots of all jet images are available in the Appendix (A.3.6 - A.5).

5.2.1 Scaling Jet Images

Again, a non-uniform effective path length being imaged at all pixel locations means that concentration is not directly proportional to pixel intensity. For the proposed method, the jet images must be scaled prior to comparison. This is done by scaling each column of pixels so that the intensity at the jet’s axis is constant for the entire image. In jet cases it is expected that $Pe >> 1$ because for the dye mixture Schmidt number ($Sc = \nu/D \approx 2500$) and $Pe = Re*Sc$ where $Re > 1$. At high $Pe$, advection dominates and dye molecules follow streamlines closely with negligible diffusion. This implies that the concentration at every point in the jet is approximately equal to the concentration of the upstream reservoir fluid and that the pixel intensity in the images are only proportional to the effective path length at a given location. Placing each column of pixels on the same scale where the intensity at the jet axis is constant provides clarity for defining jet limits and acquiring streamline data. The magnitude of the scaling is independent of the result as measurements are taken to intensity contours represented by percentages of the maximum. The images are scaled
by the intensity at the jet axis 1 mm away from the pore. The image transformation is described by the following formula where $I_{\text{max1}}$ is the intensity value at 1 mm on the jet axis.

$$I_{\text{scaled}}(r, z) = I_{\text{raw}}(r, z) \frac{I_{\text{max1}}}{I(0,z)}$$ (33)

5.2.2 Streamline Overlay

For jet cases, because $Pe >> 1$, diffusion of the solute is negligible compared to advection within the microscope FOV. The high jet velocity is sufficiently large to the point where dye molecules follow streamlines within the camera frame. This thesis proposes that high Reynolds number flows can be analyzed by comparing the edges of an iso-intensity contour to symmetric streamlines about the jet axis because a solute dispersed downstream of the pore follows said streamlines.

Streamlines of Gusarov$^{47}$ and Squire’s$^{43}$ analytical solutions for laminar jets were overlayed on the acquired jet images for each dataset simulated (Fig. 5.8) (Table 5.2). The edges of the solute dispersions appear to align well with the overlayed streamlines. The exception is shown in Figure 5.8a ($Re = 21.9$) where the shape of the dispersed dye deviates at the edge of the frame far from the pore. This is attributed to the loss of validity of the high $Re$ solution at this lower Reynolds number. This solute dispersion behaviour assuredly occurs for flows at all $Re$ but for the other cases occurs outside of the FOV of the microscope. The agreement in the subsequent images suggests that one can estimate aspects of laminar jet flow of $Re \gtrsim 22$ through a submerged pore by approximating the edges of a solute dispersion downstream of the pore as symmetrical streamlines about the jet axis. Applying this method to get quantitative data about imaged flows would be cumbersome as without prior information one would have to iteratively overlay streamlines until a case coincided with intensity contours. Extrapolating to the later intent of this quantification method, it is important to note that $Re$ at this scale are not expected for nanoscale flows so it is unlikely that this method would have to be applied.
This estimation method is limited beyond $Re \approx 45$ due to both the reduction in contrast at higher Reynolds number and jets becoming approximately horizontal as $Re$ increases. The contrast issue previously mentioned makes locating the edges of solute dispersion using epifluorescence images increasingly difficult. Furthermore, as Reynolds number increases, the slope of the solute dispersion becomes closer to zero within the camera frame; at a certain point, dispersions will be indistinguishable from one another. It is possible that the applicability of the overlay method could be extended by increasing magnification but issues with focusing on the flow plane could arise.

5.3 Summary
Analytical solutions predict that for a solute dispersed by the flow from an orifice in a plane wall, at distances far from the pore, the concentration field scales proportionally to $1/R$. From this proportionality, a relationship was derived that estimates the flow rate
through the wall based on the rate of decay of pixel intensity with radial distance from the pore. This relationship was used to estimate volume flow rates of $Re \lesssim 17$ flows from micron scale pores and showed reasonable agreement with simulation data. A 1D control volume analysis was used to rationalize the validity of the method outside of the expected $Re$ limit. This analysis suggests that the method would be applicable for any orifice geometry including parallel pores in membrane materials. For flows where $Re \gtrsim 25$ advection dominates the solute dispersion and plume shapes follow streamlines from analytical solutions for laminar jets. Resolving small differences in $Re$ would be difficult using the streamline overlay but $Re$ of this magnitude are not expected for flows through individual nanoscale geometries.
Chapter 6

Permeance of NATM

Having devised and validated a method for measuring permeance through small areas in plane walls, this thesis next explored the possibility of applying the technique to measure the permeance of small areas of NATMs. This chapter focuses on the fabrication of NATM devices intended for flow experiments. Future work will apply the flow rate measurement method developed to explore the permeance of various porous two-dimensional materials in search for membranes with properties favourable for membrane separation processes.

6.1 Relevant Literature on NATM

The constraining trade-off limiting efficiency of membrane separation processes is a driving factor for investigations into novel membrane materials and geometries. Candidate materials include polymers, ceramics, zeolites, metal organic frameworks (MOF) and two-dimensional nanomaterials. Many studies focus on creating ultra thin membrane structures which increase permeance based on the understanding that flow rates scale inversely with membrane thickness. Recent advancements reveal semi-permeable two-dimensional materials that have the potential to push flow rates of membrane separation processes orders of magnitude higher than is currently possible.

In their pristine state, materials such as graphene and hexagonal boron nitride (hBN) are impermeable to gasses. This impermeability is due to their tightly packed atomic structures that have single atom thick hexagonal lattices with interstitial diameters at scales an entire order of magnitude smaller than the van der Waals radii of the smallest gas molecules (H\(_2\) 3.14 Å and He 2.8 Å). Multiple research groups use density functional theory calculations to investigate the permeability of pristine graphene by calculating the potential barrier for various gas molecules to pass through the membrane. The results showed that H\(_2\) and He had potential barriers of 4.2 eV and 11.7 eV, respectively. This impermeability has led to graphene and hBN being used as protective coatings against oxidation on substrates in both low and high temperature applications.
Both graphene and hBN are able to sustain defects in their crystal lattice that do not compromise chemical stability and mechanical strength.\textsuperscript{14,49} Simultaneously, many 2DP contain inherent pores with size dependent on monomer and polymerization chemistry selection.\textsuperscript{52,53} Unlike the pristine case, membranes that contain defects have an exponentially lower barrier to transport.\textsuperscript{50} With no thickness dimension, transport through NATM with no functionalized pore terminations is dependent only on the probability that a molecule will come in contact with the pore and the potential barrier it must overcome to pass through\textsuperscript{2}. This relationship between pore size and potential barrier and the ability of atomically thin membranes to contain pores of tunable sizes/densities, presents an exciting opportunity for fast, size selective mass transport trough well defined channels.\textsuperscript{3,11,14,15} Methods for nanoscale patterning of two-dimensional materials are emerging and provide a basis for realizing this potential.

6.1.1 Fabrication of Graphene NATM

Graphene is the name given to a singular layer of interlinked carbon atoms arranged in a hexagonal lattice. This two-dimensional layer of atoms is the basis of carbon materials of other dimensionalities, some examples being: zero-dimensional fullerene, one-dimensional carbon nanotubes, and three-dimensional graphite.\textsuperscript{49}

Graphene sheets can be fabricated via three notable methods: mechanical exfoliation, chemical exfoliation, and chemical vapour deposition. Exfoliation processes are methods that extract individual graphene sheets from bulk graphite. Graphene was isolated for the first time by mechanical exfoliation which uses tape to remove the top layer of a graphite block.\textsuperscript{54,55} Mechanical exfoliation produces pristine sheets but encounters difficulties controlling size, number of layers, and location of graphene flakes.\textsuperscript{55} Single layer graphene sheets can be made by CVD synthesis where material is deposited on a solid surface by chemical reaction with a catalyst. Although the process can control thickness and location of the graphene, the membranes often contain defects and require complex transfer processes to remove the catalyst which has been the topic of a great deal of literature.

As previously mentioned, graphene is impermeable to the smallest of gasses in its pristine state and must contain pores or defects to facilitate selective mass transport. Introduction
of these pores comes with some difficulties because graphene is chemically inert in ambient conditions. Of course, nanoporous graphene can be produced by CVD but the density and size of the defects are inconsistent and uncontrollable. In the production of separation devices, nanopores would have to be statistically isolated.\textsuperscript{56} It is possible to create nanoscale geometries in graphene membranes by etching methods using strong acid, plasma,\textsuperscript{23} or ultraviolet (UV) exposure.\textsuperscript{17,19,57} Two groups, Yang et al.\textsuperscript{57} and Koenig et al.\textsuperscript{30} use repeated exposure to UV etching to create nonuniform, randomly oriented defects in graphene surfaces for their experiments. In Koenig’s case,\textsuperscript{30} this process took fifteen one-minute exposures to produce pores in bi-layer graphene sheets. Figure 6.1 shows an AFM image of a graphene sheet after prolonged UV etching. Etching processes are effective in producing membranes with a large number of pores with no uniformity in size nor distribution.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{graphene_membrane_AFM.png}
\caption{AFM image of a graphene membrane after prolonged ultraviolet etching.\textsuperscript{30} From [30]. Reproduced with permission from Springer Nature.}
\end{figure}
For applications where pore location and size are relevant, other researchers present “physical bombardment” methods that provide precise control of size, density and location based on the ability to control exposure duration and area. These methods also present the ability of producing individual defects which are advantageous for transport mechanism explorations of individual pores. Fischbein et al. utilize a transmission electron microscope (TEM) to “sputter” carbon atoms from a graphene lattice by condensing the imaging electron beam to its minimum diameter (approx. 1 nm, corresponding to an 800 000x magnification and 0.3 pA/nm²) and exposing a graphene sheet. This process removes atoms from the graphene and grows pores at a rate of approximately 1 nm²/s producing pores as small as 3.5 nm for a 5 s exposure. It is also capable of creating channels or partial pores in multilayer graphene under lower exposure times by removing top layers in the exposure region while leaving the lower ones intact. TEM images of the geometries created via this method are shown in Figure 6.2.

*Figure 6.2* TEM images of a graphene sheet (a) before bombardment, (b) after electron beam bombardment, (c) a zoomed in version of (b), (d) multiple nanopores in close proximity to one another created by electron beam bombardment (Scale bars are 50, 50, 2, 10 nm). Reprinted from [Fischbein MD, Drndić M. Electron beam nanosculpting of suspended graphene sheets. Appl Phys Lett. 2008;93(11). Doi:10.1063/1.2980518] with permission of AIP Publishing.
A similar process is carried out by Russo et al.\textsuperscript{60} that utilize incident Ar\textsuperscript{+} (3 keV) atoms to create “nucleation sites” in graphene sheets where one or two carbon atoms are sputtered from the lattice. This site is subsequently exposed to a parallel electron beam of approximately 100 nm diameter above the knockoff potential (80 keV) which removes carbon atoms from the edges of the nucleation site slowly growing pores. This process is shown to have much higher resolution, being able to produce pores ranging from 2.9 Å to 20 Å after a two-hour exposure to the electron beam.

There are also hybrid pore growth methods such as the one used by Jang et al.\textsuperscript{61} that bombard the surface with Ga\textsuperscript{+} (1 kV 6.7 nA to a 1.56 x 1.35 mm\textsuperscript{2} area) to create nucleation sites which were subsequently etched using O\textsubscript{2} plasma for 10-90 second durations. This process produced randomly distributed pores of diameters less than 1.2 nm.

6.1.2 Porphyrin Based Two Dimensional Polymers

Typical polymers such as Polyethylene and Polypropylene have a chain of covalently linked monomers packed into a three-dimensional structure via chain entanglement.\textsuperscript{62} Conversely, 2DPs are two-dimensional sheets of periodically linked monomers arranged in a singular layer. These sheets are held together by either covalent or coordination bonds and have properties tunable by varying the monomer and polymerization agent. This tunability makes them an intriguing option for many applications including membrane separation processes and optical devices.\textsuperscript{52,53,62}

Theoretical properties of 2DPs have been explored for a few decades but only recently have experiments creating and characterizing these materials arisen. Major considerations have gone into the design of functionalized monomers that have more than two bonding sites and facilitate reactions in more than one direction. Two-dimensional polymerization methods are also of interest and multiple have developed that fit in two distinct categories. The first of which is coined as a “single crystal approach.” The general process creates a crystallized substrate containing at least tri-functional monomers that align monomer bonding sites into close proximity. Photoirradiation converts these locations into covalent bonds altering the crystalized substrate into a stack of 2DP sheets.
held together by weak intermolecular forces. Like graphene, in this state individual sheets can be exfoliated into single or multilayer 2DPs.\textsuperscript{52}

The second category of polymerization of 2DPs uses an air/water interface approach. This technique preorganizes monomers on an air/water interface in a singular layer before compressing it into a crystalized state. From there either a photoinduced or chemically induced polymerization occurs to create the 2DP (Fig. 6.3).\textsuperscript{52}

![Figure 6.3 Schematic of the air/water interface polymerization.\textsuperscript{52} Used with permission from Annual Reviews, from Synthetic Two-Dimensional Polymers, Servalli M, Schi AD, 2017; permission conveyed through Copyright Clearance Center, Inc.](image)

The structure of 2DPs vary greatly based on the monomer and polymerization chemistry selections. A subclass of polymers synthesized using porphyrin monomers has begun to show potential of becoming prevalent in separation processes. Unlike graphene membranes that need to have defects introduced to allow transport, porphyrin based 2D polymers have the advantage of possessing inherent highly ordered, uniform sized nanoscale pores. The crystalline structure of such membranes is shown in Figure 6.4 and have \~1.2 nm holes in their structure, making them very attractive for size-based separation methods.\textsuperscript{31, 53}
Continual improvements of fabrication capabilities of nanoscale geometries present the opportunity for ultrathin membranes for separation processes. Classical molecular dynamics studies of water and ion transport through NATM are common and explore transport mechanisms across pores with varying size and pore termination. The studies reveal both size-based selection capabilities and separation based on charge and affinity. These simulations reinforce the potential of functionalized graphene and polymer membranes in separation applications and experimental studies are beginning to appear. This thesis attempts to measure liquid transport through graphene and a porphyrin based 2DP to contribute to the exploration of emerging NATM.

6.2 Polymer Polymerization

6.2.1 Process Imitation
The polymerization method used to create porphyrin based 2DPs was an adapted version of the procedure developed by Zhong et al. In the study the group uses various porphyrin monomers distributed in a singular molecular layer at a pentane/water interface to induce a polymerization reaction to join monomers by either coordination or covalent bonds.

Zhong et al. present the polymerization of four separate 2DPs based on porphyrin building blocks which had two variation sites shown in Figure 6.5 as locations $M$ and $R$. Note that $M$ and $R$ are used elsewhere in this paper and in this section are only used to describe permutations of porphyrin based 2DP based on the replicated image. The center
of the porphyrin ring was altered \([M = 2H, \text{Fe, or Pt}]\) to tune optical spectra of the resultant porphyrin material, while different phenyl groups (site \(R\)) were used to control the monomer-to-monomer bonds. In the case where \(R = \text{COOH}\) and \(\text{Cu}^{2+}\) is used as the polymerization agent, the monomers are linked via coordination bonds in a “copper paddle wheel” structure. Conversely, when \(R = \text{NH}_2\) the monomers are linked by covalent bonds formed using a Schiff base reaction in terephthalaldehyde. In this thesis, a coordination porphyrin based 2DP is made using monomers shown in Figure 6.6a where \(M=2\text{H}\) and \(R=\text{COOH}\). The resulting material has a periodic structure roughly depicted in Figure 6.6b.

*Figure 6.5* Schematic of the types of 2DPs synthesized by Zhong et al. and their corresponding molecular precursors. Used with permission of AAAS from Wafer-Scale Synthesis of Monolayer Two-Dimensional Porphyrin Polymers for Hybrid Superlattices, Zhong Y., Cheng B., Park C., et al., Science volume 366, 2019; permission conveyed through Copyright Clearance Center, Inc.
Figure 6.6 Building blocks of the 2DPs polymerized in this study that where a) porphyrin monomers (R = COOH and M=2H) are synthesized with Cu\(^{2+}\) as the polymerizing agent. Linking the monomers by copper paddle wheel linkages to create a b) coordination 2DP as depicted by [28] where C: gray; O: red; H: white; N: blue; Cu: purple and the atom at the center of the porphyrin ring represents 2H. b) Used with permission of AAAS from Wafer-Scale Synthesis of Monolayer Two-Dimensional Porphyrin Polymers for Hybrid Superlattices, Zhong Y, Cheng B, Park C, et al., Science volume 366, 2019; permission conveyed through Copyright Clearance Center, Inc.

The process coined by Zhong et al.\(^{53}\) as laminar assembly polymerization (LAP) was imitated to produce nanoporous porphyrin polymer membranes for construction of NATM devices intended for flow experiments. It is important to note that the listed devices and chemical suppliers in the following explanation are ones used in this thesis and may or may not be the same ones used in the reference paper.

The process begins by creating an interface of pentane (Sigma Aldrich 236705 CAS: 109-66-0) on top of a subphase of 1 mM aqueous Cu(NO\(_3\))\(_2\) solution (Sigma Aldrich 229636 CAS:13778-31-9) in a 25 x 50 mm reactor (Fig. 6.7a, b). 5,10,15,20-tetrakis(4-carboxyphenyl)-porphyrin (Sigma Aldrich 309077 CAS: 14609-54-2) monomers are then dissolved in a 3:1 volume ratio mixture of chloroform (Fisher Chemical C607-1 CAS: 67-66-3)/methanol (Sigma Aldrich 34860 CAS: 67-56-1) to form a 0.1 mM solution. Prior to growth, the target substrate is submerged in the subphase at 5~10\(^\circ\) inclination allowing for gradual transfer at the process conclusion. The monomer precursor solution is then injected into the pentane phase by a constant volume flow rate syringe pump (KD Scientific KDS Letago 200; Fig. 6.7c) at a rate of 10 \(\mu\)L/min for a total volume of 4
μL/in², 8 μl total for this reactor. The LAP process is shown in Figure 6.8a, b where upon injection, the monomers settle to the pentane/water interface and assemble in a singular monomer layer due to density differences of the interfacial fluids. Once assembled, Cu²⁺ ions in the subphase act as polymerizing agents in the formation of copper paddle wheel linkages. After approximately 30 minutes, the polymerization is complete, and the liquid is then slowly drained from the cell depositing the polymer gradually on the tilted target substrate (Fig. 6.8c).

Figure 6.7 a) CAD and b, c) photographs of the porphyrin polymer reactor and the c) setup used to synthesize 2DP membranes.
6.2.2 Polymer Characterization

Early attempts to recreate this process transferring onto various substrates were accompanied by struggles with controlling exact amounts of dispensed precursor because of resolution issues with the syringe pump. Figure 6.9a shows the results of a transfer.
process onto a 50 \( \mu \text{m} \) diameter aperture copper TEM grid. Visible inconsistencies in material thickness are shown by colour variations in material covered areas on the substrate. There were also distinct membrane defects in the form of wrinkles and cracks (Fig. 6.9b). Membrane defect sites present the opportunity to measure a step height from substrate to membrane surface via AFM (Oxford Instruments, Asylum MFP Origin; NanoAndMore AC160 probe; tapping mode). Thickness of monolayer porphyrin material is measured to be \( \sim 1 \) nm. By quantifying this step height, the number of porphyrin layers in each sample can be estimated. Samples which have such varying thickness and defects are not ideal for flow experiments but establishing such a characterization method is important.

![Image](image.jpg)

**Figure 6.9** Initial polymer transfer process a) outlines areas of varying material thickness and b) shows large tears and wrinkles in the polymer membrane. Scale bars are 200 \( \mu \text{m} \) and 20 \( \mu \text{m} \), respectively.

The same sample was imaged under AFM at both a defect site and area of varying material thickness. The defect site height retrace (Fig. 6.10b) across the profile illustrated on the corresponding AFM image shows a distinct 1.51 \( \mu \text{m} \) step height from substrate to membrane surface, corresponding to \( \sim 1500 \) layers of porphyrin polymer material. On the same sample, there is an area with no material that shows a gradual increase in surface height over an 11 \( \mu \text{m} \) range indicating a varying material thickness (Fig 6.11). This variation indicates a flaw in the imitated synthesis and transfer process because, in the case of excess monomers, entire layers would be polymerized one by one covering the entire interface as confined by the reactor walls. Unless material was bunched up, it
should not be possible to have 1500 layers in one location and 0 layers in other areas on the same sample.

Figure 6.10 a) AFM image of the defect site on the 50 μm copper TEM grid. The red line shows the section of the b) height trace profile that depicts ~1500-layer porphyrin polymer material. Inset is an image of the AFM probe in the measurement location.

Figure 6.11 a) AFM image of an area of variable thickness on the 50 μm copper TEM grid. The red line shows the section of the b) height trace profile that depicts a gradual increase in material thickness over an 11 μm range. Inset is an image of the AFM probe at the measurement location.

6.2.3 Process Modification Study

The first modification to the process was implemented in the injection phase. To avoid the issues associated with uncertainty in the volume of injected precursor, the prescribed precursor volume (8 μL at 0.1 mM, or 800 nmols) was diluted in 0.5 mL pentane to a concentration of 1.6 μM prior to injection into the pentane phase. The resolution of the syringe pump could have no impact on the result of the synthesis if a larger fluid quantity containing the same number of monomer molecules is used. This process gave more consistent presence of polymer on a case-to-case basis and saw lower variations in thickness on individual samples. Optical microscope and AFM images of one of these
samples is shown in Figure 6.12. The optical image again shows areas of varying thickness (Fig 6.12a) and AFM shows one of the thicker sections of the membrane as being ~350 layer (Fig 6.12b,c). For the samples void of defects, the AFM image measurements were made possible by scraping areas of the polymer off of the substrate using a razor blade. This also explains the lip at the edge of the height step profile. Height difference measurements are taken sufficiently far from this lip.

![Figure 6.12](image)

*Figure 6.12* a) Optical microscope image (scale bar 200 μm) of a pentane precursor mix porphyrin 2DP showing visibly fewer defects but still variable thickness areas. b) AFM image of the scraped region of the polymer membrane. The red line shows the section of the c

This is an improvement to the previous iteration, but the 350-layer thickness is still too high. Fortunately, for flow device fabrication, the 2DP must be suspended over apertures
in TEM grids. These apertures can be fabricated to diameters as low as 1 μm, meaning only a small area of single layer porphyrin polymer must be isolated. For this reason, porphyrin was then synthesized using 1/10th and 1/20th of the prescribed precursor mass used in all previous iterations, corresponding to 80 and 40 nmol of porphyrin monomer compared to the original 800 nmol. This reduces the thickness of the thickest areas on samples and lowers the range of thickness variation, thus increasing the likelihood of isolating a membrane of the desired thickness. An AFM image and height profile of a sample made with 80 nmol of monomer (Fig 6.13) shows a step height of ~10 nm, a 97% decrease from the previous sample. Optical images of membranes produced by the 80 and 40 nmol of monomer syntheses are shown in (Fig 6.14a, b) and exhibit more uniformity in terms of thickness, but also have a new form of defect (Fig 6.15). This defect is suspected to be caused by bubbles that presented themselves during the transfer stage that contained volumes of the subphase getting trapped between the polymer and substrate. It is believed that this caused bunching and folding of the excess membrane material after the subphase evaporated through the membrane. The bubbles are believed to play a role in the formation of this type of defect because of the distinct change in membrane structure in areas of the membrane that had bubbles present during transfer (Fig 6.15).

![AFM image of the scraped region of the polymer membrane synthesized with 80 nmols of monomers. The red line shows the section of the height trace profile that depicts ~10-layer porphyrin polymer material. Inset is an image of the AFM probe at the measurement location.](image-url)
Figure 6.14 Optical microscope image of a) 80 nmol and b) 40 nmol monomer synthesized that show less areas of thickness variation but the introduction of a new type of defect. a) Also shows what scraped regions for AFM imaging look like under an optical microscope. Scale bars are both 200 μm.

Figure 6.15 Zoomed in look at the new form of defect that is attributed to fluid getting caught between substrates and porphyrin membranes during the transfer process. Scale bar of the inset is 50 μm

Interestingly, analysis of these defects under AFM (Fig. 6.16) showed approximately zero thickness in comparison to the substrate areas. The size and prevalence of these defects
decreased when synthesized with 1/20\textsuperscript{th} precursor concentration (Fig. 6.14b). Due to the unknown structure of these defects, the synthesis process for finalized nanoporous devices designed and fabricated to interface with the flow cells for flow experiments and quantification with the developed method was completed with 1/20\textsuperscript{th} precursor concentration and the process was completed with multiple submerged TEM substrates to increase the chance of getting a nondefective suspended area of porphyrin based 2DP. These 1/20\textsuperscript{th} precursor concentration membranes still had greater than 10-layer porphyrin 2DP membranes so there is still room for improvement of these devices. A 100x magnified image of one of the NATM devices for flow experiments is shown in Figure 6.17 where an approximately 10 layer porphyrin membrane is suspended on a 1 μm pore SiNx TEM grid surface.

\textbf{Figure 6.16} a) AFM image of one of the defect areas on a membrane made with 40 nmol of monomer. The red line shows the section of the b) height trace profile that depicts ~zero thickness on the dark patches of defect areas. Inset is an image of the AFM probe in the measurement location.
Figure 6.17 100x optical microscope image of a finalized NATM device intended for flow experiments consisting of 1/20th precursor concentration porphyrin polymer suspended over a 1 μm hole in a SINx TEM grid.

6.3 Graphene

Unlike porphyrin polymers, there are current commercial processes for synthesis of graphene. The graphene used in this experiment was made via CVD (PMMA free: ACS Material SKU-CVCU1042 & PMMA coated: Graphenea F25596) and arrived on the copper foil catalyst used in the synthesis process. Graphene nanoporous devices designed to interface with the flow cell for later application of the developed quantification method were fabricated by transferring graphene onto TEM grids and subsequently creating pores via ion bombardment techniques described in the literature review.

6.3.1 Transfer

The transfer process used is one developed by Zhang et al. in 2016. This process is outlined in Figure 6.18 and was completed for both pristine and polymethyl methacrylate (PMMA) coated graphene. The transfer begins by creating a 0.263 M ammonium persulfate (APS) (Sigma Aldrich 248614 CAS: 7727-54-0) solution in a petri dish. The
CVD graphene is floated on the APS for ~5 minutes to etch the backside graphene from the copper. The membrane is then scooped using a piece of silicon wafer and transferred to a DI water bath for another 5 minutes to rinse away the back etched graphene. The membrane is then placed back on the APS mixture to etch away the copper substrate; a 1-1.5 hour process. Hexane (Fisher Chemical H303-1 CAS: 92112-69-1) is poured on top of the APS layer; the interface between the two is used to protect and stabilize the freestanding graphene ensuring that it is not torn apart by the surface tension of the etchant. This step is not necessary for the transfer of PMMA coated graphene as the polymer serves the same purpose. Once the copper had been etched, the graphene was scooped from the interface onto the target TEM grid substrate. The concentration of APS used was higher than the reference process to reduce the etching duration while not being high enough to cause disturbance of the membrane. This process produces PMMA coated graphene membranes suspended over 3 μm pores in silicon nitride membranes, shown in the microscope image in Figure 6.19. Membranes not coated in PMMA were not able to be suspended over similar apertures and would have partial suspension or large defects. The AFM height retrace of a PMMA free graphene sheet on a 50 μm copper TEM grid shows a large ~20 μm tear in the graphene material (Fig. 6.20).
Figure 6.18 Graphene transfer process mostly inspired by Zhang et al.\textsuperscript{63} but with some personal adaptations.
Figure 6.19 100x microscope image of PMMA coated graphene suspended over a 3μm pore SiNx TEM grid.

Figure 6.20 Height retrace of the path shown in the inset AFM image for a noncoated graphene membrane partially suspended over a 50 μm pore in a copper TEM grid. Both images show a large tear in the graphene membrane.
6.3.2 Pore Drilling

As previously mentioned, the suspended graphene to be used for flow experiments is impermeable to water until it contains pores or defects. These holes are introduced using a Ga\(^+\) focused ion beam (FIB) to drill through both PMMA coated and pristine suspended membranes by Todd Simpson in the Western Nanofabrication Facility. The FIB uses a series of magnets to focus a beam of melted gallium metal to a beam of Ga\(^+\) ions which, on impact with the surface, nucleate atoms from the graphene lattice. A schematic of the process is shown in Figure 6.21a where the membrane is exposed to a FIB operating at 30 kV and 10 nA; this initial exposure creates a vacancy in the membrane. This vacancy is enlarged by moving the beam in concentric circles (Fig. 6.21b) around the edge of the hole to sputter the pore terminating atoms. This process is monitored at an angle by a scanning electron microscope (SEM) until the desired size is obtained. This process uses lengthened exposure for PMMA coatings which creates a non-zero thickness. SEM images of a 500 nm pore in PMMA coated graphene is shown in Figure 6.22. Devices of variable pore sizes can be fabricated for flow experiments and later quantification using this transfer and bombardment technique. These devices are also subject to improvements. The first and most important is to adapt the transfer process or substrate to allow for graphene sheets to be suspended free of PMMA coating. This coating introduces unwanted thickness to what is supposed to be a two-dimensional flow device. The coating could also provide artificial impermeability to CVD grown graphene sheets that are prone to having defects.
Figure 6.21 Basic schematics of the FIB drilling process that uses a) focused Ga\(^+\) ions to open a defect in the PMMA coated Graphene sheet and then moves in b) concentric circles to widen the pore.

Figure 6.22 SEM image of finalized device for nanoscale flow experiments where a 500 nm pore is FIB drilled into a PMMA coated graphene sheet suspended over a 3 μm pore in a SiNx TEM grid.
6.4 Nanomaterial Permeance Experiments

Nanomaterial permeance experiments were set up and run for multiple 500 nm diameter (Fig. 6.22) PMMA coated graphene membranes and ~10-layer porphyrin membranes suspended on various pore sized SiNx TEM grids. Unfortunately, observable flows were never achieved for any of the fabricated devices up to pressures of 3 bar. This result is understandable for porphyrin membranes which were ~10 layers thick; the lack of flow can be attributed to the overlapping of porous polymer film layers creating an impermeable membrane. For the graphene devices, pores were only half the diameter of those of which flows were successfully measured by this method. To understand why flows were not achieved at these scales, SEM images and energy dispersive X-ray spectroscopy (EDS) data (Figures 6.23, 6.24 and Appendix A.6) were acquired of the upstream side of the TEM grid to locate and identify any blockages.

Figure 6.23 shows the upstream side of a graphene device with a 500 nm diameter pore suspended over a 3 μm pore size TEM grid. Figure 6.23b is a 10000x image of what appears to be a blockage over the pore. The EDS data in this area shows high amounts of both carbon and oxygen. Fluorescein dye with the chemical formula $C_{20}H_{12}O_5$ has a near identical proportion of carbon and oxygen, suggesting that the blockage is an agglomeration of dye particles. This information provides a basis for future iterations of this experiment. The process must be altered to facilitate the flow of a solute tracer through smaller scale pores. This can potentially be achieved by one of the following suggested methods: The first course of action would be to use a finer filter for solutions prior to the flow experiments. The one used in the current experiment was a 450 nm filter. Switching to a smaller filter (200 nm Cole Parmer or filtering through polycarbonate track etch membranes) could potentially grant a few more datasets for high nanoscale diameter flows. Either way, to achieve flows at the lower nanoscale diameters desired, the process will have to be modified more than this. It is suggested to lower dye concentrations to avoid issues with solubility limits or to change the fluid from water to ethanol in which fluorescein is more soluble or to change the fluorescent dye altogether. It is important to note that with lower concentrations there may be less contrast in the images. It is suggested to maintain as high a concentration as possible without plugging the pores.
Figure 6.23 a) SEM image of the upstream side of a TEM grid with a suspended graphene membrane containing a 500 nm pore. b) EDS data of the pore blockage that shows carbon and oxygen presence proportional to the chemical composition of fluorescein dye.
Not only were blockages caused by dye particles, but they were also occasionally caused by dust or debris somehow making its way into the flow cell or fluids. Figure 6.24 is an SEM image of a 3 μm pore, without a suspended membrane, blocked by an unknown substance. This TEM grid was used in the flow experiment mentioned in section 4.2.3 (3 μm, 400 mbar) where a blockage was encountered after ~ 40 s. When working with such small geometries, dust can have a large impact on overall experimental results. It is likely that the presence of dust or debris also played a role in the failure of earlier iteration flow cells before an acceptable filtering, cell preparation, and reservoir priming process was developed. In order to achieve flow rates through these nanoscale geometries, along with changes to the solute tracer mixture, it is likely that experiments will have to be carried out in a cleanroom.
Figure 6.24 a) SEM image and b) EDS data of the upstream side of a bare 3 μm TEM showing an unknown blockage over the pore aperture.
Chapter 7

Conclusions and Recommendations

Motivated by interests rooted in membrane separation process optimization, this thesis set out to develop a method to measure volume flow rates through individual microscale pores in thin membranes. There are few studies that explore such flows due to constraints imposed by limitations in the ability to quantify such minute flow rates. This study attempted to avoid said constraints by developing a novel method of quantifying said flows through analysis of the dispersion of a solute tracer downstream of the pore.

The experiments performed in this paper explored micron scale flows at a multitude of pressure gradients and saw a distinct correlation between Reynolds number and the shape of a solute dispersion. Findings indicate that at low Reynolds numbers, where momentum flux into the downstream reservoir is small, solute dispersion occurs with radial symmetry centered about the pore location. With increasing $Re$, there is an increasing momentum flux into the reservoir which carries dye molecules away from the pore causing elongated concentration profiles. The magnitude of this elongation is directly related to the momentum flux into the reservoir. Some cases defined as being within a “transition” regime in the above discussion are interesting datapoints that show the dispersion of momentum over a finite length scale. For these images, the solute is carried away from the pore rapidly where, at a certain point, concentration profiles appear to diverge as the jet is slowed sufficiently that diffusion becomes important.

An expression for volume flow rate was derived based on the rate of decay of normalized intensity values of images captured of the dispersions from a cross flow perspective. This derivation related a concentration field approximation of a solute tracer downstream of a pore to intensity values via a series of calibration constants and normalizing for the variable effective path length in the captured images. This expression was solved using intensity decay values extracted from a series of low Reynolds number micron scale flows and exhibited reasonable agreement with simulated data. Although this method was developed based on experimental data with relatively large $Re$, this process was developed with nanoscale flows in mind where $Re << 1$ are expected. Gusarov’s ($Re <10$) and Sampson’s ($Re <<1$) velocity fields scale proportionally at distances far from
the pore and the 1D control volume analysis is valid independent of pore size or geometry. This suggests that the method could be a useful tool for probing flows at nanoscales with Reynolds number less than 17. This measurement technique is limited to explorations of liquid permeance of porous membranes. It could theoretically be scaled to work in other applications but would be of little use as it requires the presence of a solute and the generation of a steady state concentration field. The applicability of the method is constrained by the following limitations:

1. For the method to work the flow must contain a solute and reach a steady state concentration field
2. Optical access is needed to acquire images off the solute dispersion
3. The plume must not be impacted by the walls of the reservoir (downstream must be sufficiently large)
4. Calibration must be completed for different solutes and camera factors such as focal length and working distance
5. Another consideration is that for prolonged exposure the solute may become photobleached

Essentially, this method is designed for the very specific purpose of investigating permeance of NATM and taking flow rates through pores in plane walls.

The concentration decay rate method is applicable for any mass flux from a plane wall while \( Re \leq 17 \), but once advection begins to dominate the solute dispersion (\( Re \approx 25 \)) the area in which diffusion takes over is outside of the FOV. For this reason, without adjustment of magnification or camera placement, the method is inapplicable. To quantify flows in this regime without prior knowledge of the system, streamlines must be iteratively overlayed on experimental images until they matched with iso-intensity contours. It is expected that flow through nanoscale geometries will not reach this \( Re \) limit.

Two-dimensional materials that can sustain defects of variable size and density without compromising their mechanical strength are emerging and bring with them the potential of producing ultrathin membrane separation devices that support selective mass transport with minimal flow resistance. Methods of nanoscale patterning of these materials provide
a basis for realizing this potential in producing atomically thin membranes with well defined channels for size selective mass transport.

In order to further the development of said devices, an understanding of fluid flow behaviour must be cultivated, and transport properties of various membrane materials have to be explored. Constraints imposed by detection limits of current flow sensors hinder experiments at these scales. The quantification method developed in this thesis is a useful tool that can be applied to measure volume flow rates at these nanoscales and contribute towards future explorations into membrane separation process optimization.

This thesis attempts to begin this exploration by using the quantification method to investigate the permeance of porous graphene and 2DP membranes. The nanoporous devices were developed using nanofabrication techniques and variation of polymerization chemistries and material transfer processes. Unfortunately, attempts to generate nanoscale flows through said devices for which the quantification method could be applied and further validated were met by serious limitations.

Overall, this thesis developed a method for measuring volume flow rates through small pores in plane walls based on the dispersion of a solute. It verified said method for micron scale pores by comparison to simulation data and analytical solutions. It simultaneously explored fabrication methods of potential NATM for membrane separation processes and provided recommendations for measuring liquid permeance through them.

Previous research groups struggled to unambiguously measure flow rates of low Reynolds number flows through an orifice in a plane wall. The main contribution of this thesis is the development of a novel quantification method designed to probe the permeance of 2D materials for separation process applications that was verified for micron scale pores.

7.1 Recommendations
In attempts to adapt this process to take permeance measurements of membranes containing nanoscale geometries, there were complications associated with fluorescein solubility limits and the presence of dust/debris in the flow cell causing blockages. It is highly suggested that the process be modified to take place in a clean room to eliminate the possibility of debris blockages. To avoid solubility limits, the solute or solvent could
be switched to increase dissolution at comparable concentrations. Another option would be to experiment with imaging lower concentration aqueous fluorescein solutions with higher exposure times. It would also be valid to develop an associated μPIV method for this geometry which would avoid solubility issues and provide a higher resolution for $Re \gtrsim 25$ flows. It is anticipated that for μPIV, complications with requirements of large magnifications and long working distances will arise. Also, the solute method maintains the advantage of having a large, visible, plume downstream of the pore while visualizing the movement of tracer particles will become increasingly difficult as pore sizes approach the continuum limit.
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Ahin B, Ceyhan H, Cntr 'i ~r = ~r ~t ~ = R~u ’ P/. Numerical and Experimental Analysis of Laminar Flow through Square-Edged Orifice with Variable Thickness Kinematic Viscosity ~ Stream Function w Vorticity Superscripts k Number of Iterations * Notation for Dimensionless Quantities Subscripts I, j Coordinate Indices in the Computational Grid in the Radial and Axial Directions Terms Used in Dimensionless Equations ~* ~* ~* ~* ~* L* ~ I/R T*~: Tf~.


Appendix A: Experimental Data

A.1 $d=1\, \mu m$ Flows

A.1.1 550 mbar $Re = 2.88$

Figure A - 1 Time series microscope images of solute dispersions captured at 5 x magnification, $t_{exp} = 5\, \text{s}$ and $LI = 10\%$. All images are $2.3 \times 2\, \text{mm}$
Figure A - 2 Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index.
Figure A - 3  a) Intensity range and b) plume front plots that are used to identify when the flow field has reached steady state.  c) Plots showing the change in each radial intensity profile over the duration of the time series.

Figure A - 4  a) Radial intensity decay averaged over the steady images in the dataset at various angles from the cell wall as depicted by the inset.  b) Plot of the natural logarithm of normalized intensity with respect to $1/R$.  Radial decay rates of intensity ($m$) are approximated over distances greater than 650 $\mu$m from the pore and are plotted on the contours.  c) Binary images showing areas where pixels of the last image in the dataset are within 10, 20, 50% of the maximum intensity value.
A.1.2 750 mbar $Re = 3.87$
Figure A - 5 Time series microscope images of solute dispersions captured at 5 x magnification, texp = 5 s and LI = 10 %. All images are 2.3 x 2 mm.
Figure A - 6 Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index.

Figure A - 7 a) Intensity range and b) plume front plots that are used to identify when the flow field has reached steady state. c) Plots showing the change in each radial intensity profile over the duration of the time series.
Figure 4.8 a) Radial intensity decay averaged over the steady images in the dataset at various angles from the cell wall as depicted by the inset. b) Plot of the natural logarithm of normalized intensity with respect to 1/R. Radial decay rates of intensity (m) are approximated over distances greater than 650 μm from the pore and are plotted on the contours. c) Binary images showing areas where pixels of the last image in the dataset are within 10, 20, 50% of the maximum intensity value.

A.1.3 950 mbar Re = 4.86
Figure A - 9 Time series microscope images of solute dispersions captured at 5 x magnification, texp = 5 s and LI = 10 %.
All images are 2.3 x 2 mm.
Figure A - 10 Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index.

Figure A - 11 a) Intensity range and b) plume front plots that are used to identify when the flow field has reached steady state. c) Plots showing the change in each radial intensity profile over the duration of the time series.
Figure A - 12 a) Radial intensity decay averaged over the steady images in the dataset at various angles from the cell wall as depicted by the inset. b) Plot of the natural logarithm of normalized intensity with respect to $1/R$. Radial decay rates of intensity ($m$) are approximated over distances greater than 650 μm from the pore and are plotted on the contours. c) Binary images showing areas where pixels of the last image in the dataset are within 10, 20, 50% of the maximum intensity value.

A.2  $d = 3\ \text{um}$ Flows

A.2.1  200 mbar $Re = 8.47$
Figure A - 13 Time series microscope images of solute dispersions captured at 5 x magnification, texp = 1 s and LI = 25 %. All images are 2.3 x 2 mm.
Figure A - 14 Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index.

Figure A - 15 a) Intensity range and b) plume front plots that are used to identify when the flow field has reached steady state. c) Plots showing the change in each radial intensity profile over the duration of the time series.
Figure A - 16 a) Radial intensity decay averaged over the steady images in the dataset at various angles from the cell wall as depicted by the inset. b) Plot of the natural logarithm of normalized intensity with respect to 1/R. Radial decay rates of intensity (m) are approximated over distances greater than 650 μm from the pore and are plotted on the contours. c) Binary images showing areas where pixels of the last image in the dataset are within 10, 20, 50% of the maximum intensity value.

A.2.2 400 mbar $Re = 14.1$
Figure A - 17 Time series microscope images of solute dispersions captured at 5 x magnification, texp = 1 s and LI = 25 %. All images are 2.3 x 2 mm.
**Figure A - 18** Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index.

**Figure A - 19** a) Intensity range and b) plume front plots that are used to identify when the flow field has reached steady state. c) Plots showing the change in each radial intensity profile over the duration of the time series.
Figure A - 20 a) Radial intensity decay averaged over the steady images in the dataset at various angles from the cell wall as depicted by the inset. b) Plot of the natural logarithm of normalized intensity with respect to 1/R. Radial decay rates of intensity (m) are approximated over distances greater than 650 μm from the pore and are plotted on the contours. c) Binary images showing areas where pixels of the last image in the dataset are within 10, 20, 50% of the maximum intensity value.

A.2.3 500 mbar $Re = 16.4$
Figure A - 21 Time series microscope images of solute dispersions captured at 5 x magnification, $t_{exp} = 1 \text{ s}$ and $LI = 25 \%$. All images are 2.3 x 2 mm.
Figure A - 22 Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index.

Figure A - 23 a) Intensity range and b) plume front plots that are used to identify when the flow field has reached steady state. c) Plots showing the change in each radial intensity profile over the duration of the time series.
Figure A - 24 a) Radial intensity decay averaged over the steady images in the dataset at various angles from the cell wall as depicted by the inset. b) Plot of the natural logarithm of normalized intensity with respect to $1/R$. Radial decay rates of intensity ($m$) are approximated over distances greater than 650 μm from the pore and are plotted on the contours. c) Binary images showing areas where pixels of the last image in the dataset are within 10, 20, 50% of the maximum intensity value.

A.3 $d = 6$ um Flows

A.3.1 11.6 mbar $Re = 2.21$
Figure A - 25 Time series microscope images of solute dispersions captured at 5 x magnification, texp = 0.15 s and LI = 5 %. All images are 2.3 x 2 mm
Figure A - 26 Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index.

Figure A - 27 a) Intensity range and b) plume front plots that are used to identify when the flow field has reached steady state. c) Plots showing the change in each radial intensity profile over the duration of the time series.
**Figure A - 28** a) Radial intensity decay averaged over the steady images in the dataset at various angles from the cell wall as depicted by the inset. b) Plot of the natural logarithm of normalized intensity with respect to 1/R. Radial decay rates of intensity (m) are approximated over distances greater than 650 μm from the pore and are plotted on the contours. c) Binary images showing areas where pixels of the last image in the dataset are within 10, 20, 50% of the maximum intensity value.

A.3.2 35 mbar $Re = 6.26$
Figure A - 29 Time series microscope images of solute dispersions captured at 5 x magnification, texp = 0.15 s and LI = 5 %. All images are 2.3 x 2 mm
**Figure A - 30** Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index.

**Figure A - 31** a) Intensity range and b) plume front plots that are used to identify when the flow field has reached steady state. c) Plots showing the change in each radial intensity profile over the duration of the time series.
Figure A - 32 a) Radial intensity decay averaged over the steady images in the dataset at various angles from the cell wall as depicted by the inset. b) Plot of the natural logarithm of normalized intensity with respect to 1/R. Radial decay rates of intensity (m) are approximated over distances greater than 650 μm from the pore and are plotted on the contours. c) Binary images showing areas where pixels of the last image in the dataset are within 10, 20, 50% of the maximum intensity value.

A.3.3 41 mbar Re = 7.20
Figure A - 33 Time series microscope images of solute dispersions captured at 5 x magnification, texp = 0.15 s and LI = 5 %. All images are 2.3 x 2 mm.
Figure A - 34 Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index.

Figure A - 35 a) Intensity range and b) plume front plots that are used to identify when the flow field has reached steady state. c) Plots showing the change in each radial intensity profile over the duration of the time series.
Figure A - 36 a) Radial intensity decay averaged over the steady images in the dataset at various angles from the cell wall as depicted by the inset. b) Plot of the natural logarithm of normalized intensity with respect to 1/R. Radial decay rates of intensity (m) are approximated over distances greater than 650 μm from the pore and are plotted on the contours. c) Binary images showing areas where pixels of the last image in the dataset are within 10, 20, 50% of the maximum intensity value.

A.3.4 80 mbar $Re = 12.1$
Figure A - 37 Time series microscope images of solute dispersions captured at 5 x magnification, $t_{exp} = 0.15 s$ and LI = 5 %. All images are 2.3 x 2 mm
Figure A - 38 Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index.
Figure A - 39 a) Intensity range and b) plume front plots that are used to identify when the flow field has reached steady state. c) Plots showing the change in each radial intensity profile over the duration of the time series.

Figure A - 40 a) Radial intensity decay averaged over the steady images in the dataset at various angles from the cell wall as depicted by the inset. b) Plot of the natural logarithm of normalized intensity with respect to $1/R$. Radial decay rates of intensity ($m$) are approximated over distances greater than 650 μm from the pore and are plotted on the contours. c) Binary images showing areas where pixels of the last image in the dataset are within 10, 20, 50% of the maximum intensity value.
A.3.5 130 mbar $Re = 16.79$
Figure A - 41 Time series microscope images of solute dispersions captured at 5 x magnification, $t_{exp} = 0.15$ s and LI = 5 %. All images are 2.3 x 2 mm.
Figure A - 42 Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index.
Figure A - 43 a) Intensity range and b) plume front plots that are used to identify when the flow field has reached steady state. c) Plots showing the change in each radial intensity profile over the duration of the time series.

Figure A - 44 a) Radial intensity decay averaged over the steady images in the dataset at various angles from the cell wall as depicted by the inset. b) Plot of the natural logarithm of normalized intensity with respect to 1/R. Radial decay rates of intensity (m) are approximated over distances greater than 650 μm from the pore and are plotted on the contours. c) Binary images showing areas where pixels of the last image in the dataset are within 10, 20, 50% of the maximum intensity value.
A.3.6 180 mbar $Re = 20.54$ – Transitionary state flow
Figure A - 45 Time series microscope images of solute dispersions captured at 5 x magnification, texp = 0.15 s and LI = 5 %. All images are 2.3 x 2 mm
Figure A - 46 Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index. Transitional state flow where it is not clear if advection or diffusion dominates solute dispersion.
Figure A - 47 Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index. A first glance, this flow appears to be in a jet but when compared to other jets it is shown to be a transitional state flow where it is not clear if advection or diffusion dominates solute dispersion. l) indicates locations where vertical distance between iso-intensity contours were taken for extracting the jet slope.
Figure A - 48 Streamlines of Gusarov and Squire’s solution at the simulated Re value overlayed on the last image in the dataset.

A.3.8 250 mbar Re = 24.93
Figure A - 49 Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index. h) indicates locations where vertical distance between iso-intensity contours were taken for extracting the jet slope.

Figure A - 50 Streamlines of Gusarov and Squire’s solution at the simulated Re value overlayed on the last image in the dataset.
A.4 \( d = 30 \, \mu \text{m} \) Flow

A.4.1 15.58 mbar Re = 32.07
**Figure A - 51** Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index. *p*) indicates locations where vertical distance between iso-intensity contours were taken for extracting the jet slope.

**Figure A - 52** Streamlines of Gusarov and Squire’s solution at the simulated Re value overlayed on the last image in the dataset.
A.4.2 17.7 mbar $Re = 34.44$
Figure A - 53 Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index. m) indicates locations where vertical distance between iso-intensity contours were taken for extracting the jet slope.

Figure A - 54 Streamlines of Gusarov and Squire’s solution at the simulated Re value overlayed on the last image in the dataset.
A.4.3 21.41 mbar $Re = 38.19$

**Figure A - 55** Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index. h) indicates locations where vertical distance between iso-intensity contours were taken for extracting the jet slope.
Figure A - Streamlines of Gusarov and Squire’s solution at the simulated Re value overlayed on the last image in the dataset.

A.5 $d = 50 \, \mu\text{m}$ Flows

A.5.1 6.2 mbar $Re = 33.92$
Figure A - 57 Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index. g) indicates locations where vertical distance between iso-intensity contours were taken for extracting the jet slope.

Figure A - 58 Streamlines of Gusarov and Squire’s solution at the simulated Re value overlayed on the last image in the dataset.
A.5.2 9.14 mbar $Re = 41.88$

Figure A - 59 Contour plots of normalized intensity for the current dataset. The scale bar is the proportion of the max intensity and axis values denote pixel index. h) indicates locations where vertical distance between iso-intensity contours were taken for extracting the jet slope.
Figure A - 60 Streamlines of Gusarov and Squire’s solution at the simulated Re value overlayed on the last image in the dataset.
A.6  SEM Images and EDS of Blockages

Figure A - 61  a, b) SEM images of a partial blockage of a 1 μm pore by a substance with c) EDS data showing carbon and oxygen content at a similar ratio to the chemical structure of fluorescein dye.
Figure A - 62 a) SEM images of a partial blockage of a 6 μm pore by a substance with b) EDS data showing carbon and oxygen content at a similar ratio to the chemical structure of fluorescein dye.
Figure A - 63 EDS data of a large unidentified blockage on a 3 μm TEM grid
Appendix B: Uncertainty Analysis

The uncertainty analysis begins with the initial measured values compared to the base simulation data for the flow through an infinitesimally thin orifice plate at the exact prescribed diameter.

![Figure B - 1 Data pre-uncertainty analysis.](image)

The uncertainty introduced in the simulation data compared to the actual is introduced by 3 major factors:

1. Uncertainty in the pore diameter as prescribed by Norcada.
   a. ± 50 nm for both 3 μm and 1 μm pore sizes
   b. ± 100 nm for the 6 μm pore size
2. The simulation data is completed for 0 thickness orifice plates where in reality the silicon nitride has a non zero thickness.
   a. 200 nm for both 6 μm and 3 μm pore sizes
   b. 50 nm for the 1 μm pore size
3. Uncertainty in the applied pressure difference prescribed by Elveflow as ± 0.5 mbar

The impacts of nonzero thickness were explored by Dagan\textsuperscript{72} in 1982 who provides an infinite series solution for the creeping flow emerging from a pore of a finite length. He
then approximates to a single expression that accounts for flow resistances of both Sampson and Poiseuille flow. This expression (Eqn. 34) agrees with his infinite series solution within 1%. A comparison of Sampson’s to Dagan’s velocity is shown in Figure B-2.

\[ v = \frac{\Delta p d}{\mu (6\pi - 32 \frac{L}{d})} \]  
(34)

Figure B - 2 Comparison of Sampson's (solid) to Dagan's (dashed) velocity for the silicon nitride membranes with the pore diameter and thicknesses listed above.

To account for these three factors, simulation data for an infinitesimal thickness orifice plate flow are interpolated based on the maximum possible diameter and pressure of each measurement to obtain an upper bound on flow rate. Similarly, a lower bound is found by interpolating simulation data for the minimum pore diameter and applied pressure while including the Poiseuille flow resistance for the TEM grid thickness in series for each case. The error bars of the pressure uncertainty lie within the size of the markers on the graph.
The uncertainty of an experimental measurement can be estimated using a combination of the effects of each of the individual inputs. In this case there is a measured volume flow rate that is a function of six separate variables summarized below.

$$Q = Q(D, t_{\text{exp}}, LI\%, z_{10}, I, m)$$ \hspace{1cm} (35)

To calculate the error bars and to give a region where the exact value lies, the absolute maximum and minimum possible flow rates (based on the uncertainty in each variable) are calculated.

For diffusivity, the uncertainty is dependent on the concentration of the fluorescein dye mixture and the ambient temperature. The same dye mixture was used for all flow experiments therefore the uncertainty of this parameter is accounted for in the calibration factor. Simultaneously, the resolution of the exposure time was milliseconds, while exposure times in experiments were multiple seconds. This means that its impact on the overall uncertainty will be minute and can be ignored. This leaves four major contributors to uncertainty. The incident light intensity has an uncertainty of 0.5% of its set point and...
is simple to quantify. On the other hand, there are factors such as pore location which are more complex.

The uncertainty for the pore location in hemispherical plumes is calculated by segmenting the top 2% of intensity values in the images. It can be said with confidence that for hemispherical plumes the pore location will exist within the region of segmented pixels. The uncertainty for each individual dataset is estimated by taking half of the size of the segmented area.

Unlike hemispherical plumes, the maximum pixel intensity does not provide the pore location in oblong plumes. To estimate uncertainty in this measurement the pore location was identified multiple times (using the method explained in the body of the paper) and the standard deviation of the dataset was used to estimate uncertainty.

Meanwhile, the uncertainty in the rate of decay of concentration was accounted for by calculating the maximum and minimum slope values over a range of 300 to 1000 μm from the pore.

These slope values, pore locations, and light intensities were used to calculate the limits of volume flow rate for each individual measurement and are shown by the error bars in Figure B-4.
Figure B - 4 Plot with full error bars

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2. Figure 2.1b, Stern et al. [33] – open access
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4. Figure 2.3a & b, Bunch et al. [29]
5. Figure 2.4a & b, Surwade et al. [23]
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7. Figure 2.6, Secchi et al. [24]
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8. Figure 2.7a & b, Figure 2.8 a, b & c, Figure 2.9, Secchi et al. [25]
9. Figure 2.10, Atwal et al. [42]
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10. Figure 6.1, Koenig et al. [30]
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11. Figure 6.2, Fishbein et al. [59]
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12. Figure 6.3, Servalli et al. [52]
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13. Figure 6.4, Cheng et al. [31]
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14. Figure 6.5, Figure 6.6b, Figure 6.8b, Zhong et al. [53]
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