Analysis and simulation of desalination processes via advanced low-dimensional material systems

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**ANALYSIS AND SIMULATION OF DESALINATION
PROCESSES VIA ADVANCED LOW-DIMENSIONAL
MATERIAL SYSTEMS**

ANG YUN MEI ELISA

SCHOOL OF MECHANICAL & AEROSPACE ENGINEERING

2019

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PROCESSES VIA ADVANCED LOW-DIMENSIONAL
MATERIAL SYSTEMS**

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School of Mechanical & Aerospace Engineering

A thesis submitted to the Nanyang Technological University in partial
fulfilment of the requirements for the degree of
Doctor of Philosophy in Mechanical Engineering

2019

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7
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9 The contributions of the co-authors are as follows:

- 10 • A/Prof Ng provided the project direction, guide the project progress and
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- 12 • I prepared the manuscript drafts. The manuscript was revised by Dr
13 Geethalakshmi, Dr Yeo, A/Prof Liu and A/Prof Lin.
- 14 • All MD simulations study, analysis and literature review were conducted
15 by me. MD simulations study was ran using the high performance
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25 Han, S. Gray, G. Millar, A. Du, H.K. Shon, T.Y. Ng, K. Ostrikov, Anti-fouling
26 graphene-based membranes for effective water desalination, Nature
27 Communications, 9, 683 (2018), DOI: 10.1038/s41467-018-02871-3

28
29 The contributions of the co-authors are as follows:
30

- 1 • Dr Seo and Dr Pineda performed and optimized the ambient-air graphene
2 synthesis technique, and respective characterizations using SEM and
3 Raman spectroscopy.
- 4 • Dr Woo conducted the water desalination experiments of salt rejection,
5 SDS/water separation, and real seawater purification.
- 6 • Dr Xie conducted the water desalination experiments of oil/water
7 experiment.
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9 developed the understandings of the water transport mechanisms.
- 10 • Dr Murdock conducted the TEM characterizations of the graphene film.
- 11 • Mr Lawn conducted the AFM measurements.
- 12 • Using the graphene microstructure, interpretation was co-developed by
13 Dr Seo, Dr Murdock, Dr Han, and A/Prof Ostrikov.
- 14 • Dr Jiao and A/Prof Du conducted the simulation of water passage in
15 permeable CVD grapheme film and performed calculation of adsorption
16 energy.
- 17 • I performed the molecular dynamics simulations with guidance from
18 A/Prof Ng.
- 19 • Dr Seo, Dr Pineda, Dr Borghi, Dr Woo, Dr Xie, Dr Jiao, A/Prof Du, Dr
20 Murdock., Dr Han, and A/Prof Ostrikov wrote the paper with input from
21 all of the authors.

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24 26 May 2020
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Date

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1

2

Abstract

Desalination is seen as a possible sustainable solution for global water crisis due to the large amount of salt-water available on Earth. However, for desalination to be used for the large-scale production of potable water, its cost must reduce. Low-dimensional material membranes have the potential to significantly reduce desalination cost. This is due to their ultra-low thickness, which results in orders of magnitude increase in permeability when compared to conventional polymeric desalination membrane. This significant increase in permeability can lead to a huge reduction in desalination cost, operating close to the thermodynamic minimum energy required for desalination. Due to the difficulty in fabrication and manipulation of low-dimensional material systems currently, computational simulation is the method of choice to further advance this field at this point in time. This project deploys molecular dynamics (MD) simulation to explore design ideas for low-dimensional material membrane systems and investigate the feasibility of using such systems to overcome the high cost of desalination. Two low-dimensional material membrane designs are proposed and tested extensively, namely the graphene slit membrane, and the transverse flow carbon nanotube membrane (TFCM). The TFCM is found to have the best desalination performance and its design parameters were optimized. The current project also performed comparison studies against experimental data on the anti-fouling properties of graphene films with overlapping grain boundaries. Different two-dimensional materials other than carbon were also considered, including borophene, MXene and molybdenum disulfide. Finally, the thesis report ends off with some recommended future directions that can be taken to further advance the field of low-dimensional material membrane.

List of Publications

1. **Ang, E.Y. M.**; Ng, T.Y.; Yeo, J.; Liu, Z.; Geethalakshmi, K. R. Free-standing graphene slit membrane for enhanced desalination. *Carbon* 2016, 110, 350-355.
2. **Ang, E. Y. M.**; Ng, T. Y.; Yeo, J.; Lin, R.; Geethalakshmi, K. R. Nanoscale Fluid Mechanics Working Principles of Transverse Flow Carbon Nanotube Membrane for Enhanced Desalination. *International Journal of Applied Mechanics* 2017, 09 (03), 1750034.
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6. **Ang, E. Y. M.**; Ng, T. Y.; Yeo, J.; Lin, R.; Liu, Z.; Geethalakshmi, K. R. Carbon

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9 Review on Low dimensional Carbon Desalination and Gas Separation
10 Membrane Designs. *Journal of Membrane Science* 2019, 117785.
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1 **Common Abbreviations**

- 2 MD: Molecular Dynamics
- 3 RO: Reverse Osmosis
- 4 2D: Two-dimensional
- 5 1D: One-dimensional
- 6 TFC: Thin film composite
- 7 CNT: Carbon Nanotubes
- 8 VA: Vertically aligned
- 9 AQP: Aquaporin
- 10 LAMMPS: Large-scale atomic/molecular massively parallel simulator
- 11 VMD: Visual Molecular Dynamics
- 12 LJ: Lennard-Jones
- 13 TFCM: Transverse flow CNT membrane
- 14 CP: Concentration Polarization
- 15 K: Permeability
- 16 R: Salt rejection
- 17 L_c : critical slit size
- 18 J: Water flux
- 19
- 20

Chapter 1 Introduction

This thesis aims to investigate in detail low-dimensional advanced material systems to be used for membrane desalination. As the physical manufacturing of low-dimensional advanced material membranes is still extremely challenging technically, the method of choice in this thesis project is computer simulations. In particular, molecular dynamics (MD) simulation is used to study and analyze the performance and underlying physics of low-dimensional material desalination membrane. This chapter introduces the thesis project topic by discussing the background and significance of the project and presenting the project's objectives.

1.1 Background

The rapid growth in water use has led to a very real pressing problem of water scarcity globally. In 2014, the United Nations (UN) estimated that about one-fifth of the world's population are already living under water stress conditions (highlighted in yellow and pink in Figure 1), and projected that by 2025, two-thirds of the world population will have to deal with problems of water scarcity in their daily life [1-3]. Locally in Singapore, water shortage has always been an imminent threat due to our lack of natural resources. By recognizing this limitation and proactively addressing the water scarcity challenge, Singapore has been able to significantly reduce her reliance on foreign sources and is already close to the goal of self-sustenance [4-6]. However, the demands for clean water will continue to rise in order to support our growing population and economy [7, 8]. Hence, the need to confront the problem of water scarcity is as imperative as it was in 1965, when the city-state just gained independence.

Figure 1 Water stress regions. This map colors regions with respect to their ratio of water withdrawal to water supply. Yellow indicates severe water stress and pink indicates water stressed regions. These water stress regions are expected to increase as demands for water continue to rise [9].

Water resources on earth can basically be classified into fresh or saline water. While 70% of earth's surface is water, less than 3% is freshwater [3, 10, 11]. This is illustrated in Figure 2. The sheer limitation in volume of freshwater means that freshwater resources are unlikely to support growing water demands. Recent breakthrough in technologies, such as NEWater, seeks to reuse as much wastewater as possible, but it is limited by the amount of usable water producible from raw water resources [12]. Owing to the large volume of saline water available, desalination is increasingly seen as the ultimate sustainable solution. The high energy consumption of current desalination technology is currently limiting the output of usable water via desalination [13]. The most energy efficient method available for water desalination today is membrane-based reverse osmosis (RO), which accounts for 65% of the total desalination plants globally [11, 14]. Nevertheless, the energy cost for RO is still too high to meet the demands for clean water.

1 It is believed that this cost can be driven down substantially with a next generation
 2 membrane material that can allow significantly higher water permeability over present
 3 conventional membrane materials [13, 15-18]. This project therefore seeks to investigate
 4 the feasibility of a membrane made of low-dimensional material. Numerical testing
 5 would be conducted to gain fundamental understanding in the performance and
 6 limitations of such membrane, and these would be used to drive new design ideas.

7
 8 Figure 2 Diagram to illustrate distribution of water on earth.[19]

9
 10 As this technology is still at its infancy, the successful completion of this project can
 11 provide valuable insights to drive the development of low-dimensional membrane
 12 materials to enhance desalination operation. These insights include identification of
 13 effective design, method of fabrication and the important parameters that can be tuned
 14 for optimization. It is hopeful that the knowledge gained upon the completion of the
 15 project can bring the notion of using advanced low-dimensional material systems for
 16 desalination closer to physical realization.

1.2 Project objectives

The project objectives are:

- To investigate the feasibility of using advanced low-dimensional material systems as the next generation membrane material, replacing conventional RO membrane materials. Possible advanced low-dimensional material systems include graphene-like two-dimensional (2D) materials and one-dimensional (1D) carbon nanotube (CNT) membranes. As experimental studies involving such low-dimensional membrane materials are still technically challenging, MD simulations will be the main tool used for the analysis of these low-dimensional material systems.
- Using MD simulations, gain fundamental insights into the behavior, potential performance and limitations of low-dimensional material membrane system.
- With insights gained from MD study, propose innovative low-dimensional material membrane designs and perform numerical testing to assess the desalination performance of the proposed design.
- Optimize the low-dimensional material membrane design.
- Identify and propose alternatives to overcome the current limitations impeding the physical implementation of advanced 2D materials for desalination. In this regard, limitations relating to physical fabrication of the membrane, as well as the estimated cost savings when such membranes are employed for desalination will be considered.

1.3 Significance and innovation

The successful development of an ultra-permeable low-dimensional materials system

1 for desalination can potentially resolve the global water scarcity issue. However, there
2 are still many challenges that need to be overcome such system to become a reality. One
3 of the major hurdles today is the difficulty to physically fabricate such membranes with
4 pores of angstrom level precision, and to minimize defects that could weaken their
5 structure [20]. Hence although the technology has been verified numerically since 2012
6 [21] and experimentally since 2015 [22], it has not been proven in practical application
7 scenario yet. This thesis aims to explore innovative alternative designs and suggest
8 possible solutions for current bottlenecks limiting further development of this
9 technology. As Mi (2019) accurately suggest, to successfully scale up graphene
10 membranes for practical applications, new design ideas and morphologies need to be
11 explored [23]. This is the spirit of this thesis.

12 **1.4 Scope of thesis**

13 This thesis first covers a summary of the literature review conducted in Chapter 2. Next,
14 the research hypothesis, methodology and plan are detailed in Chapter 3. The project
15 achievements and results are presented in Chapters 4 through 6. In Chapter 4, our two
16 low-dimensional material membrane design, the graphene slit membrane and the
17 transverse flow CNT membrane (TFCM) are introduced. The thought process and
18 design philosophy are elaborated in detail. Chapter 5 then discusses further numerical
19 experimental work done on the TFCM, which is the more efficient membrane of the two
20 designs proposed. This include the performance of the membrane with differing CNT
21 size and layers, as well as under oscillating operating conditions. Chapter 6 focuses on
22 the use of materials other than carbon as low-dimensional material membrane. The
23 thesis then ends off with a conclusion and recommendations for future work in Chapter
24 7.

Chapter 2 Literature Review

This chapter summarizes the literature review conducted for this project. The literature review begins by looking at current desalination membrane performance and technology. Next, the current candidates that could potentially outperform current membranes for desalination are reviewed. These candidates helped to set the research direction and form the starting point of this research work. Finally, the key performance indicators in the field of desalination are introduced to guide the performance evaluation of low-dimensional material membrane in the later parts of the project.

2.1 Current desalination membrane

Current desalination membranes employ a thin film composite (TFC) design under RO based operations [24]. The TFC membrane has steadily gained popularity since its introduction in 1970s, and currently dominates the RO membrane market [25]. TFC membranes consist of a thin polyamide active layer supported by a porous sublayer. Some of the TFC membranes in use today are listed in Table 1, together with their permeability and salt rejection performance.

Company	Product	Permeability ($\frac{L}{m^2 \cdot h \cdot bar}$)	Salt rejection (%)	Comments
Toray[26]	TM820C-400	0.50	99.75	Toray supplies RO membrane modules for our Singspring and Tuaspring desalination plant [27]. Other countries using Toray membranes include UAE [28] and China (Shandong and Hebei) [29].
	TM840V-1760	0.69	99.8	
DOW[30]	Filmtec SW30HRLE-400	0.57	99.8	DOW supplies RO membrane modules for Australia [31] and Israel [32]
	Filmtec SW30XLE-440i	0.69	99.8	
Hydranautics[33]	SWC4 MAX	0.51	99.8	Hydranautics supplies RO membrane modules for Mexico [34], China (Yuhuan power plant in Zhejiang) [35], Spain and Algeria [36].
	SWX6 MAX	0.94	99.8	

1 Table 1 Summary of some commercial RO membranes in use today

2 2.2 Current candidates for next generation membrane

3 materials

4 Although the concept is still relatively new, three potential candidates have been
5 identified to become the next generation membrane material to replace the current
6 polymeric TFC membrane. These are graphene-like two dimensional (2D) materials,
7 CNT-like one dimensional (1D) materials, and biomimetic aquaporin (AQP). The water
8 permeability and salt rejection performance of these candidate materials are summarized
9 in Figure 3. As compared to conventional RO membrane, which has permeability on the
10 order of $1 \frac{L}{m^2 \cdot H \cdot bar}$ (LMBH), these candidate materials boost permeability orders of

magnitude higher with comparable salt rejection. The following subsections discuss the current research activities for each of these candidate materials.

Figure 3 Performance matrix of current TFC membrane and the three candidates for next generation membranes (Note that the results for graphene-like 2D materials membrane and vertically aligned CNT membrane are based on MD simulation, and that for biomimetic AQP membrane is based on theoretical prediction (which is higher than experimental measurements). On the other hand, the data for commercial RO membrane is based on commercial product data sheet) [18, 33, 37, 38].

2.2.1 Graphene-like 2D materials

Graphene-like 2D material has the potential to increase water permeability by orders of magnitude due to its atom-thick property. While the thin polyamide active layer in TFC membranes have thicknesses in the order of 100nm, the single atom thick property of 2D materials means that membranes made of 2D materials have thicknesses that are two orders of magnitude lower than conventional TFC membranes. Since the Hagen-

1 Poiseuille equation predicts that flux is inversely proportional to the membrane thickness,
2 the water flux through such atom thick 2D membrane is expected to be orders of
3 magnitude higher than the current RO membrane [39]. Indeed, in 2012, Cohen-Tanugi
4 & Grossman showed that a graphene-based membrane (illustrated in Figure 4a) can
5 achieve a flux two to three orders of magnitude higher than conventional RO membranes
6 using molecular dynamics (MD) simulations [21]. Following this, Heiranian, Farimani
7 & Aluru showed in 2015, also through MD simulations, that a membrane based on
8 molybdenum disulfide (MoS_2) (illustrated in Figure 4b) can theoretically boost flux 2
9 to 5 orders of magnitude higher than conventional RO membranes [18]. Apart from MD
10 simulations, Surwade *et al.* in 2015 conducted an experimental study on nanoporous
11 graphene membranes [22]. They reported that graphene membranes with nanopores
12 introduced using oxygen plasma can effectively separate salt while maintaining water
13 flux. Their fabricated graphene membrane is illustrated in Figure 4c.

1

2

3

4 Figure 4 Illustration of currently studied 2D materials membrane. (a) Nanoporous graphene
 5 membrane by Cohen-Tanugi & Grossman [21]. (b) Nanoporous MoS₂ membrane by Heiranian ,
 6 Farimani & Aluru [18]. (c) Surwade graphene nanoporous membrane [22].

1 While the studies above prove the potential of such atom thick membranes for
2 desalination purposes, there are several challenges that need to be overcome for such
3 membranes to be practically realized. One of the most prominent obstacle of the
4 development of such membranes is the difficulty in introducing controlled pores into
5 pristine sheets of graphene-like 2D materials [40]. A handful of experimental studies
6 have been published in this regard. Techniques used for the introduction of controlled
7 pores include electron irradiation [41], atomic ions irradiation [42] or oxygen plasma
8 etching [22], producing nanopores of size ranging from about 0.5 to 20 nm in the three
9 works quoted. However, such methods are difficult to scale up, and the control of pore
10 size distribution remains a substantial challenge. This is exemplified by the graphene
11 nanoporous membrane created by Qin *et al.* in 2017 [43]. Whilst the size of the graphene
12 membrane created through bombardment by gallium ions followed by acidic etching is
13 large (63cm^2), the resultant membrane has a poor salt rejection, indicating that the pore
14 size was too large for desalination operation.

15

16 In addition, the thinness of such membrane necessitates the use of either a porous
17 substrate or multiple layers of graphene for practical implementation. This may curtail
18 the promised orders of magnitude increase in permeability shown in simulation studies
19 [11].

20

21 Thus, to bring the use of membrane made of such graphene-like 2D materials closer to
22 reality, the above challenges need to be overcome. For instance, strategies to side-step
23 the need to introduce controlled pores, or methods that can further increase the
24 permeability of such membrane can be explored. These will be discussed further in the
25 next chapter.

2.2.2 Carbon nanotube or its derivatives

The second candidate material is carbon nanotube (CNT), which is seen as a viable alternative due to the observed fast frictionless transport of water molecules through the tubes [44, 45]. There are two main designs proposed for membranes made of CNT: vertically aligned (VA) or mixed [46]. Of the two designs, VA CNT displays higher permeability since the CNTs are specially aligned to face the flow such that maximum conductance of water can occur. In 2006, Holt et al. successfully fabricated a membrane made of VA 2nm wide CNT in a silicon nitride matrix [44]. The group showed that such membranes boost permeability far exceeding that of a reference polycarbonate membrane.

Figure 5 Illustration of (a) VA CNT membrane and mixed CNT membrane [46].

While this is encouraging, current methods to fabricate VA CNT membranes are complicated and cost intensive. This is because the CNT must be of a size that is small

1 enough to reject salt, but large enough to permeate water. Such nanoscale precision and
 2 uniformity requirements are a strong impedance for eventual large-scale production [13].
 3 Taking the work of Trivedi and Alameh as an example, the group used commercial CNTs
 4 of average inner diameter of 5nm [47]. However, it was only able to reject 97.26% of
 5 the iron oxide salt ions with an average diameter of 10nm. This implies that a tighter
 6 CNT size distribution is required to achieve the same rejection as the commercial TFC
 7 membrane in use today. Even in a laboratory environment, the control of CNT size is
 8 challenging. Hence, the large-scale fabrication of such membranes still remains a
 9 significant challenge today.

10 **2.2.3 Biomimetic aquaporin membrane**

11 The third candidate is biomimetic aquaporin (AQP) membranes, which are engineered
 12 to resemble the naturally occurring AQP protein. Such membranes have also been
 13 proven to perform much better than conventional membranes for desalination purposes.
 14 In one of the early works on biomimetic AQP membranes, Kumar *et al.* incorporated an
 15 AQP from the bacteria *Escherichia Coli*, known as AQPZ, into block copolymer
 16 vesicles [45]. From stopped flow experiments performed on such vesicles, the authors
 17 estimated then that the resulting membrane can theoretically have a permeability two
 18 orders of magnitude higher than conventional RO membranes [17]. The results for the
 19 theoretical estimate made by the group is plotted in Figure 3.

20
 21 Since then, many designs based on the addition of AQP have been proposed and studied
 22 [16, 17]. The design approaches can be divided into two main categories. First, AQP-
 23 laden bilayer sitting on a polymeric support, and second, AQP immobilized in a dense
 24 polymeric membrane [16, 17, 48]. An example of the first design is given by the work

from Zhong *et al.* in 2012, who used vesicle rupturing to form an active layer of AQP polymeric layer on NF membrane [49]. The work by Qi *et al.* in 2016 exemplifies the second design approach, where the AQP is incorporated into a dense selective layer and then fixed on a polymeric substrate using interfacial polymerization (IP) [16]. It is notable that while Kumar *et al.* [38] predicted orders of magnitude increase in water permeability, the actual water permeability of such AQP membranes is much lower at a two fold increase when compared to conventional RO membrane [16, 50]. Whether the theoretical potential of biomimetic AQP membrane as predicted by Kumar *et al.* [38] can be achieved still remains a question.

Figure 6 Illustration of biomimetic AQP membrane design. Left: AQP laden bilayer on polymeric surface. Right: AQP immobilized in polymeric support [17].

The advantage of this class of membranes is that it is much closer to practical implementation as compared to the first two types discussed. In contrast to the graphene-like membrane or CNT membrane, there is already a significant amount of experimental work reported in the area of biomimetic AQP membranes [16, 38, 49, 51, 52]. In recent years, there are even already products related to biomimetic AQP membranes patented, for example, that by the founder of Aquaporin A/S Peter Jensen and his team [53]. That being said, the previous two classes of materials have the potential to achieve a permeability much higher than biomimetic AQP membranes. In addition, such

membranes are often affected by problems associated with mechanical strength and stability. The inherent weak mechanical strength of proteins and lipids necessitates a dense polymer layer as a matrix, which can limit the actual effective permeability of the membrane. This is also mostly the reason why experimental results depict a much lower increase in permeability. Stability problems stem from the compatibility between protein and host, as well as the challenge in controlling the protein reaction to external conditions like temperature, pressure and presence of chemicals [16, 48].

2.3 Important parameters for desalination

The most important parameters for desalination performance are the water permeability and salt rejection characteristics of the membrane. The importance of the permeability of a membrane can be explained by considering the flux-force relationship as shown in Eq. 1. In Eq. 1, J = water flux $< \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} >$, A = permeability $< \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1} >$, ΔP_{net} = net pressure across membrane $< \text{bar} >$.

$$J = A\Delta P_{\text{net}} \quad \text{Eq. 1}$$

From the flux-force relationship, increased permeability A means that a lower net pressure ΔP_{net} is required to achieve the same flux J . Reducing the pressure differential required across the membrane means that lower energy is required to achieve the same permeate output. Since the bottleneck of today's membrane-based desalination is precisely the high-energy input required, increase in permeability is well desired. The relationship between energy, cost and permeability is further deliberated in Section 7.5.

1
 2 Together with high permeability, high salt rejection is of equal importance to a RO
 3 membrane. The average salt rejection performance of current desalination membranes
 4 is about 99.8%, and the new membrane materials should achieve equal or higher salt
 5 rejection to be considered for practical use. With regards to the mechanism of salt
 6 rejection in RO membrane, there are two known separation mechanisms identified so
 7 far: the sieving effect, and the electrostatic effect. These are described in Refs [15, 54-
 8 56]. The sieving effect refers to the retention of solutes due to size exclusion. For
 9 charged solutes, one needs to additionally consider the hydrated radius since the charge
 10 on the ion will cause a hydrated shell of water molecules to be bounded around it. The
 11 bond between the surrounding water molecules and the ion can be sufficiently strong
 12 such that the ion behaves like a rigid sphere [55]. According to Wu & Zhao [55], the
 13 hydrated radii of sodium (Na^+) and chlorine (Cl^-) ions have been experimentally
 14 determined to be $3.72\text{\AA}$ and $4.54\text{\AA}$, respectively (the crystal ionic radius of Na^+ and Cl^-
 15 are $1.02\text{\AA}$ and $1.81\text{\AA}$ respectively [57]). The radii of a water molecule on the other hand
 16 is $1.25\text{\AA}$ [58]. This sieving effect is the main mechanism for the water-ion separation by
 17 nanopores when the membrane is uncharged.

18
 19 One of the earliest works which showed that nanopores in graphene can effectively sieve
 20 out ions from water is that by Sint, Wang & Kral in 2008 [59]. They showed using MD
 21 simulations, that by functionalizing the nanopores, selective passage of ions can be
 22 facilitated. The MD simulations performed by Cohen-Tanugi & Grossman [21] and
 23 Heiranian, Farimani & Aluru [18] also confirmed the salt rejection behavior of
 24 nanopores. Depending on the size of the pore and the driving pressure force, the salt
 25 rejection ranges from 100% (all salt ions are rejected), to 33% at applied pressure of

about 200MPa [18, 21].

Hence, to design a membrane system that effectively desalinates saltwater, a balance between the water permeability and salt rejection is required. The size of the pores become very important due to the size exclusion salt rejection mechanism. A bigger pore size is advantageous for increase permeability, but detrimental to salt rejection. This is the reason why tight control of pore sizes becomes vital in such nanoporous membranes. These two parameters will be constantly referred to throughout the project.

2.4 Identification of research gaps

This section aims to summarize the relevant literature reviewed in this chapter and point out the research gaps this thesis project aims to address. Three major material classes were introduced as potential next generation membrane material: graphene-like 2D materials, CNT-like 1D materials, and AQP inspired materials. Each of these materials have the potential to increase the permeability of current desalination membrane, hence reducing energy cost of desalination. It was assessed through the literature survey that graphene-like 2D materials or CNT-like 1D materials have higher potential of significantly increasing permeability performance of desalination membrane. However, the physical realization of such 2D and 1D membranes are further from reality as compared to AQP inspired membrane designs. One of the aims of this thesis project is therefore to understand fundamentally the bottle necks in preventing the physical realization of such membranes, thereby suggesting suggestions or alternatives to overcome or sidestep such challenges. Another goal of this thesis is to attempt to push the performance boundaries of such membranes by exploring different designs.

Chapter 3 Research hypothesis, methodology and plan

From the literature review conducted, the choice is made to focus on desalination membranes made from graphene-like 2D materials or 1D nanotubes like CNTs. The main reason is because significant work has already been done on biomimetic AQP membranes to the point where commercialization is already underway. On the other hand, the technology involving low-dimensional material desalination membranes is still at its very early stage and offers many opportunities for exploration. Through systematic analysis, the findings of this work can be used to guide and propel the technology towards experimental verification. This chapter highlights the research hypothesis and methodology to achieve the project's aim.

3.1 Research hypothesis

This project hypothesized that membranes made of low-dimensional material can revolutionize desalination due to its high permeability and comparable salt rejection as current polymeric membrane used in RO. Existing literatures have confirmed, experimentally and computationally, that low-dimensional membranes have the capability to reject salt effectively with significant increase in permeability. It has also been shown using numerical MD experiments that such membranes have the potential to attain orders of magnitude higher permeability. However, the practical fabrication and testing of such systems remains fraught with technical challenges. This project therefore seeks to verify the potential of such systems and show that effective design of low-

dimensional material membranes can practically achieve ultra-high permeability and high salt rejection for desalination.

3.2 Research methodology

3.2.1 Molecular Dynamics as the main tool

Because of the difficulty in fabricating membranes made of graphene-like 2D materials or CNT, computational simulation is currently the main tool used to study such membrane systems. Simulation techniques range from the smallest length scale at quantum levels, to large scale continuum-based methods [15]. A summary of these simulation techniques is presented nicely in a review by Cohen-Tanugi and Grossman, as shown in Figure 7. With a decrease in length scale, an increase in computational cost is expected. Molecular dynamics (MD) is a technique based on computation of the forces on atoms or molecules at every time step, and subsequently solving for the positions of the atoms/molecules using Newton's equations of motion. Because it is at the length scale of atoms/molecules, it is particularly suited for studying membrane systems for desalination. At such length scales, MD simulations can provide insights into the behavior of salt ions, water molecules and their interactions with the porous membrane. As compared to quantum level techniques like Density Functional Theory (DFT), it is much less computationally expensive, therefore enabling us to study the desalination system at a system size that is physically meaningful. Continuum-based methods are not suitable for the study of such systems since it is well known that classical mechanics based on continuum assumptions breaks down at the nanoscale [60]. Therefore, MD is the chosen computational technique to be employed in this project.

Figure 7 Summary of computational simulation methods adapted from [15]

The large-scale atomic/molecular massively parallel simulator (LAMMPS) is used for the MD simulations in this study [61]. The results are visualized using Visual Molecular Dynamics (VMD) [62].

3.2.2 Theory and formulation of the MD Approach

The beauty of MD lies in its straightforward concept. Atoms or molecules are represented as spherical particles with associated size and force potential models. The particles in the simulations then interact with each other according to Newton's equation of motion, given for a particle i in Eq. 2.

$$F_i = m_i a_i \quad \text{Eq. 2}$$

Where F_i is the net force acting on the particle i at that instant in time t , m_i is the mass of particle i and a_i is the acceleration of the particle i . The velocity v_i and position x_i at the next time instant $t + dt$ is then obtained by numerical integration of a_i . The

1 simulation then repeats itself by calculating the net force on all particles in the
 2 simulation at this time instant $t + dt$. This computational process is illustrated in Figure
 3 8. For more details on MD implementation, the reader is referred to the many textbooks
 4 and references available, for e.g. [63].

Figure 8 Principles of MD

7 For our problem, we employ an atomic MD model, where each individual atom is
 8 simulated as a particle. For instance, each water molecule is modelled by 3 particles (1
 9 oxygen and 2 hydrogen), bonded together as shown in Figure 9. Sodium and chloride
 10 ions are modelled as individual particles. The typical simulation domain is depicted in
 11 Figure 10.

1

2 Figure 9 MD model of water (red and white), sodium ion (yellow) and chlorine ion (green)

3 The force models that we adapt for each particle determine its behavior and they are an
4 extremely important part of the simulation protocol. The force models employed in this
5 simulation are elaborated in Section 3.2.3.2.

6 **3.2.3 Simulation setup**

7 **3.2.3.1 Simulation domain**

8 After the initial literature review, the simulation domain is set up in LAMMPS for
9 further studies. A typical simulation domain designed for this project is shown below,
10 and is similar to that adopted by Cohen-Tanugi & Grossman and Heiranian, and
11 Farimani & Aluru [18, 21].

12

Figure 10 Typical simulation domain in this project

The feed and permeate water are bounded by two pistons made of graphene (labelled left and right piston in Figure 10). Feed water zone is the region between left piston and membrane, while permeate zone is the region between the membrane and the right piston. Within the feed region, water molecules, sodium (Na^+) and chlorine (Cl^-) ions are initially placed such that the salinity amounts to about 1.0mol/L, about twice the salinity of seawater. This high value of salinity allows for a more efficient MD simulation since there is a higher chance that salt ions will encounter the membrane. Furthermore, it represents the worst-case scenario, since it is more difficult to maintain a high salt rejection for a feed solution of higher salinity. For the same reasons, the differential pressure applied across the system (ΔP) is usually high, on the order of 200MPa. This is higher than the conventional operating pressure of RO membrane (typically about 5MPa), but it allows for a more efficient MD simulation as the high pressure difference allows water to be permeated in a shorter time. Moreover, it represents the worst case scenario in many ways, especially since salt rejection

decreases with increasing pressure [37]. In the permeate zone, pure water molecules are positioned.

The simulation domain is set up to ensure the density of water is close to its standard value of 1g/cm^3 at standard conditions and that there will be sufficient space for the piston to move through the simulation. Periodic boundary conditions are employed throughout the simulation. In this case, it indicates periodicity in the y and z directions, since the elongated x direction ensures each periodic box is independent of the neighboring cells. By implementing the boundary conditions in this way, effects of concentration polarization (CP) is modelled in our simulation, similar to the work done by Thomas and Corry in 2015 [37].

3.2.3.2 Force potential

The force potentials that decide how the atoms, molecules and ions interact within the MD simulation is critical to realistically model the system. In the initial stage of the project, only carbon materials are considered. Hence, force potentials for water, ions and carbon atoms need to be established. The force models employed in this thesis are explained when they are utilized.

The structure and interactions of water molecules are modeled using the TIP4P water model [64] with a long-range coulombic solver. The TIP4P water is a four-site water model, a Lennard-Jones site for the oxygen atom and 3 charge sites, one each for the two hydrogen atoms and one for the oxygen atoms. The model is succinctly described in this Wikipedia page [65], with its parameters summarized in , and elaborated in [64].

1

2

3

Figure 11 TIP4P water model parameters summarized in SklogWiki [65]

4 The particle-particle particle-mesh (PPPM) solver [66] long-range coulombic solver
 5 was employed for this study. The PPPM is used to calculate interaction forces in an
 6 efficient manner by separating the total interaction into short range and long-range
 7 interactions. At each step of the simulation, the bond lengths and angles within each
 8 water molecule is held rigid. The carbon atoms that made up the pistons and membrane
 9 are bonded together with the AIREBO potential [67]. The AIREBO potential consists
 10 of an intramolecular term that allow for the formation and dissociation of covalent bonds,
 11 and at the same time a non-bonded interactions component that account for
 12 intermolecular interactions. Such potential is especially relevant in our system where
 13 the covalent bonds exist within the membrane structure and drives the movement of the
 14 membrane, while intermolecular forces drives the interactions of the membrane with the
 15 system of water and salt ions. The rest of the interactions are implemented via the
 16 Lennard-Jones (LJ) and Coulombic interactions. The standard LJ potential and
 17 coulombic interaction potentials are given by Eq. 3 and Eq. 4 respectively (σ and ϵ are

LJ parameters that differs for different atom types, C = energy conversion constant, q_i and q_j are the charges on particle i and j). The well depth and radius of Na^+ and Cl^- ions that define the LJ interactions are obtained from the work by Joung and Cheatham [68]. The intermolecular interactions are then modelled using a mixing rule for the LJ potential [69, 70]. The actual parameters used are detailed in Table 2.

$$E = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad \text{Eq. 3}$$

$$E = \frac{Cq_iq_j}{r} \quad \text{Eq. 4}$$

Atoms/Ions	Well depth of potential ϵ_{ij} (kcal/mol)	Radius at the minimum potential energy σ_{ij} (Å)
O [64]	0.1628	3.164
H [64]	0	0
Na^+ [68]	0.1684	2.452
Cl^- [68]	0.01166	5.520
C [64]	0.08600	3.400

Table 2 Parameters for the definition of LJ potential used in the MD simulations

The global cutoff distance for LJ and Coulombic forces are both specified to be $8.5\text{\AA}$ for the implementation.

3.2.3.3 Typical simulation run

A typical simulation run progresses this way: Before each production run, the water molecules and salt ions are given a random initial velocity at 300K and the entire system is subjected to energy minimization using conjugate gradient algorithm. Time integration on Nose-Hoover style non-Hamiltonian equation of motions is used to compute positions and velocities at each time step. The time step is kept constant at 1fs. The pistons and membrane are first kept rigid, while the system undergoes a further energy minimization in isothermal and isobaric conditions (NPT ensemble) for 250ps, and then in canonical NVT ensemble for a further 250ps. The pistons are then allowed to move at a differential pressure (ΔP) of 0 Pa and the entire system undergoes an additional energy minimization of 500ps. Finally, a differential pressure is applied across the pistons at NVT conditions for a period varying from 1 to 20 ns depending on the system configuration. For each system configuration considered, the process could be repeated for 3 to 10 different sets of initial velocity and the results may be averaged for statistical reasons.

As mentioned above, quantities of interest for membrane desalination are the water permeability (K) and salt rejection (R). In this work, water flow rate across the membrane is measured until 80 to 90% of the feed water has permeated through in units of water molecules per ns. Water permeability is then computed by normalizing the water flow rate with membrane area and applied pressure. K is typically presented in units of $\frac{L}{m^2 \cdot bar \cdot hr}$ (LMBH) to be consistent with current industrial standards. Salt rejection R is measured as a percentage of salt that is rejected by the membrane with respect to the original salt ions count. This measurement is taken at the point where a

certain percentage, usually 80 to 90%, of the feed water has permeated through.

3.2.3.4 Feasibility and validation study

An initial feasibility and validation study is conducted to ensure the integrity of the simulation domain set up in LAMMPS. Graphene membrane with one circular pore of varying sizes is performed with the membrane fixed in space. The graphene membrane is constructed by removing atoms from a pristine sheet of graphene. Conditions were set to mimic as closely as possible those used to obtain published results for comparison [18, 21]. The results we obtained are shown below in Figure 12 and are close to the results obtained in published literature, which are also plotted in the same graph for reference [18, 21].

1

2 Figure 12 (a) Water permeability and (b) salt rejection of graphene membrane with circular pores
 3 at an applied pressure of 264 MPa.

4 3.2.3.5 Convergence and reproducibility of the simulations

5 Although there are currently no widely accepted convergence test in molecular
 6 dynamics, the notion of convergence can still be read relative to the application [71]. In
 7 our case, convergence is judge based on several levels. First and foremost, for each
 8 simulation, critical physical phenomena are monitored to ensure stable values are

1 obtained. Apart from permeability and salt rejection, temperature, pressure and total
2 energy are also monitored to ensure the simulation is stable and results are coherent.
3 Figure 13 illustrates this. A coherent and stable simulation will depict a controlled
4 increase in number of water molecules filtered and a controlled decrease in number of
5 salt ions rejected, as can be observed in Figure 13a. Temperature, pressure and total
6 energy of the simulation should typically stabilize early in the simulation in the
7 equilibration phase, as can be seen in Figure 13b-d.

8

9 Efforts were also made to ensure that the simulation is reproducible and consistent. In
10 the early works for the thesis, each MD was repeated several times with different initial
11 conditions. As illustrated in Figure 14, the results from these independent MD runs
12 converges to the same result. The standard deviation is very low as can be seen from the
13 error bars for each data point in Figure 14. Therefore, later simulations no longer repeat
14 the MD simulations for different initial conditions to save computational cost. In
15 addition, a domain sensitivity study is carried out and it was found that the MD
16 simulations are not sensitive to the size in y or z direction, nor the size of the initial
17 permeate section, but is sensitive to the size of the initial feed. Therefore, later
18 simulation studies assumed a bigger feed size to ensure convergence and reproducibility
19 of results. This is further elaborated in Section 5.1.

Figure 13 Monitoring of vital data to ensure coherence and stability of the MD simulation. Data is obtained from the simulation of CNT_(5,5)_10 from the multilayer TFCM study (Section 5.3). (a) Water permeability and salt rejection history. Depending on the membrane configuration, there should be a controlled increase in number of water molecules filtered and a controlled drop in salt rejection. (b) Temperature variance with simulation time. (c) Pressure variation with simulation time. (d) Total energy variation with simulation time. Temperature, pressure and total energy typically stabilizes early in the simulation during the equilibration phase.

Figure 14 Each data point in the water flow rate graph (left) and salt rejection graph (right) is obtained by taking the average of 5 independent MD runs. The data variance is represented by the black error bars for each data point. Data are obtained from CNT size study (Section 5.2).

3.3 Research plan

With the simulation set up verified, the system can be configured with different low-dimensional material membrane design or system parameters for investigation. The following studies were performed throughout the span of the project to achieve the project's objectives as laid out in Chapter 1.

1. Free-standing versus frozen membrane study: to understand the impact of interactions of membrane with water molecules and salt ion on the desalination performance
2. Graphene slit membrane and transverse flow CNT membrane (TFCM) design and numerical validation: to come up with innovative 2D and 1D membrane design that has not yet been proposed in existing literature and perform numerical testing to determine its performance.
3. Oscillatory pressure study: to understand the impact of oscillatory pressure on low-dimensional membranes' performance

- 1 4. Multilayer TFCM study: to investigate effects of multilayering on the
2 performance of TFCM
- 3 5. Different 2D materials study: To consider other 2D materials that can be
4 employed for desalination membrane and characterize the performance
- 5 6. To quantify the energy and cost savings to be expected during practical
6 desalination operation, identify limitations and propose changes that can be
7 made to current desalination operation in order to fully exploit the 2D and 1D
8 membrane.

9

10 The results of these studies are presented in the next few Chapters.

11

Chapter 4 Graphene Slit Membrane and Transverse Flow CNT Membrane

In this chapter, we will present two of our proposed low-dimensional material membrane design – namely the Graphene Slit Membrane, and the Transverse Flow CNT Membrane (TFCM). These two designs are conceived after gaining fundamental insights by doing numerical experiments on current available low-dimensional material membrane designs. In this chapter, we will first look at the results of one such experiment, that is the free-standing versus frozen membrane study, which was done using the graphene nanoporous membrane design introduced by Cohen-Tanugi and Grossman in 2012 [21]. Then, the graphene slit membrane will be introduced based on our observations from these fundamental studies. This idea was published in *Carbon* in 2016 [72]. We were further inspired by the results of the graphene slit membrane, and came up with the TFCM design, published in 2017 in the *International Journal of Applied Mechanics (IJAM)* [73]. In 2017/2018, we also collaborated with a research team in Australia to build a computational model for the experimentally fabricated overlapping graphene membrane. Although this is not our proposed design, this design is also elaborated in this chapter for completeness [74].

4.1 Free-standing versus frozen membrane study

From the literature review, all MD simulations performed to study nanoporous low-dimensional membranes are performed with the membrane held rigid during the

simulation run [18, 21, 75, 76]. This is usually done to save computational cost. Based on current reported fabrication strategies [22, 42, 77], these 2D materials are typically fixed on microporous supports. Within a micro-pore, the graphene membrane sheet is only held rigid at the edges where the graphene sheet is in contact with the micro-porous support, while the other areas of the graphene sheet can deform according to the forces acted on by the water molecules and salt ions. As such, it is believed that a free-standing membrane, that is one with only the edges fixed, can more accurately model the behavior of such 2D membranes since the dynamic deformation of the membrane is accounted for.

Thus, in this work, we carried out MD simulation of nanoporous graphene as a free-standing membrane. The difference between free-standing and frozen configurations are examined. The results obtained are summarized in Figure 15 and Figure 16.

Figure 15 Comparison between freestanding and frozen membrane at $P=264\text{MPa}$ for water permeability for different circular pores size. A64 refers to the pore with pore area $64\text{\AA}^2$, A40 the

1 pore with pore area 40Å², and A20 the pore with pore area 20Å².

2

3

Figure 16 Comparison between freestanding and frozen membrane at P=264MPa for salt rejection (a) A64 pores, (b) A40 pores and (c) A20 pores [72]

It can be observed from Figure 15 and Figure 16 that free-standing graphene nanoporous membrane provides a lower water flux, but higher salt rejection. This is observed for all three pore sizes. Water flow rate is a measure of the rate of number of water molecules filtered and is given by the gradient of the plotted lines in Figure 15. For the A64 pore (pore with area $64\text{\AA}^2$), the water flow rate reduced from 355 to 300 water molecules per nanosecond when the membrane changes from frozen to free standing configuration. For the A40 (pore with area $40\text{\AA}^2$) pore, the reduction is from 202 to 140, while for the A20 (pore with area $20\text{\AA}^2$) pore, the reduction is from 65 to 52. On the other hand, the salt rejection behavior appears to be better for the free-standing membrane, since the salt rejection graph of the free-standing configuration is generally above that of the frozen configuration (see Figure 16). If we take the salt rejection at the point where the water permeability approaches zero, the salt retention increases from 29% to 43% for the A64 pore, and from 58% to 62% for the A40 pore. The A20 pore has basically perfect salt rejection, and therefore has a value of 100% for both configurations.

1 The reason why lower water flow rate but higher salt rejection is observed in free-
 2 standing membrane is due to a frozen membrane, being a rigid membrane, is a stiffer
 3 barrier. Hence, when water and salt molecules are pushed against an essentially rigid
 4 membrane, they get through the membrane in a shorter time. Conversely, a free-standing
 5 membrane deforms with the pressure acting on it, oscillating irregularly according to
 6 the interactions between the pressure gradient and the restoring forces due to the fixed
 7 edge of the membrane. This provides a flexible, instead of a rigid barrier. The
 8 interactions between the water molecules and salt ions with the graphene sheet results
 9 in a shimmering type of deformation on the graphene sheet, where parts of the graphene
 10 membrane move back towards the permeate side as water molecules and salt ions
 11 bombard it from the feed side due to the applied pressure gradient, and then forward
 12 again due to the restoring force of the graphene membrane's fixed edges.

13

14 This study provided us with insights to the interactions of the membrane with water and
 15 salt molecules, and the impact of these interactions on the membrane performance.
 16 Subsequent simulations are performed in the free-standing configuration.

17 **4.2 Graphene slit membrane**

18 Next, we studied the viability of replacing circular pores with slits. Most earlier studies
 19 have considered circular pores [18, 21, 59, 60, 78]. However, it is conceived here that
 20 membrane with slits can be more efficient compared to a membrane with circular pores.
 21 In this configuration, slits, instead of circular pores, are made in the graphene sheet
 22 perpendicular to the transport direction. If the water-ion separation mechanism is mainly
 23 based on the sieving effect, a slit with a critical size can fully block out all salt ions,
 24 while achieving the maximum area for water molecules to permeate through. MD

simulations were performed to test out this hypothesis. The graphene slit membrane model is illustrated in Figure 17.

Figure 17 Illustration of the graphene slit membrane. Green indicates Cl^- , yellow Na^+ , red O, white H and cyan C.

Simulations were first carried out to determine the size of slit that ensures perfect salt rejection. This critical size is named here the critical slit length L_C , which is determined by systematically reducing the size of the slit until no salt is lost throughout the simulation duration of 3ns. The simulation is then repeated 10 times with different initial velocity to ensure no salt is lost in all 10 cases for statistical reasons. The critical size L_C is found to be $2.28\text{\AA}$. The size of the slit is measured using Solidworks²⁵ as described in the previous section. Any slit of length larger than $2.28\text{\AA}$ is found to allow some salt ions to pass through.

The permeability results of the graphene slit membrane at its critical slit size is presented in Figure 18. The A20 pore, which represents the critical pore area for the nanoporous

configuration, is used to compare against the slit membrane at its critical slit. For simplicity, this study was conducted with the membrane held rigid.

Figure 18 Comparison of water permeability of slit and A20 circular pore at pressure of 264MPa [72]

It is evident that the permeability of the slit membrane is significantly larger than that with a circular pore. By computing the gradient, the permeability is about 3.5 times higher while still maintaining perfect salt rejection. Analysis of the simulation results reveal two main reasons for this increase in permeability. First, slit supports a larger critical area as compared to the circular pore, as pictorially illustrated in Figure 19a. Critical area is the largest area in which water can permeate through but not salt ions. In the case of graphene slit membrane, the critical area is determined to be $56\text{\AA}^2$, whilst that of nanoporous graphene membrane is $20\text{\AA}^2$. The larger critical area already promises an increase in permeability of 2.8 times as this larger area allowed for water to permeate through. The rest of the increase in permeability is due to the higher density

of water allowed in a 2D slit as compared to a 1D circular pore. This is represented in Figure 19b, where the density of water in a 2D slit is estimated to be 25% higher than that in a 1D circular pore. Together, slits exhibit about the 3.5 times better permeability performance as compared to pores.

Figure 19 Comparison of (a) critical area and (b) water density within the pores between graphene slit membrane and nanoporous graphene membrane.

4.3 Transverse flow CNT membrane

Apart from creating slits using graphene, slits can also be created using CNT. Hence, we proposed a new membrane design based on transverse flow across CNT horizontally stacked one on top of another, separated by a critical slit size that is to be determined.

This is named the transverse flow CNT membrane (TFCM), as illustrated in Figure 20.

Figure 20 Illustration of the Transverse flow CNT membrane

A study is first performed to determine the critical slit size of the TFCM. This is termed as the slit size study. The slit size study considers three slit sizes (L_s): 2.28, 3.28 and 4.28 Å (see Figure 21a). The reason why these 3 slit sizes are chosen is because they mark the transition from perfect salt rejection to salt loss. In this study, the CNT diameter is kept constant at 6.8 Å (rolled up vector of (5,5)). For ease of reference, the new membrane is named in the following way CNT_(n,m)_(slitsize). Hence, CNT_(5,5)_2.28 refers to the transverse flow CNT membrane made from (5,5) CNT, at a separation distance of 2.28 Å.

The results of the slit size study are summarized in Figure 21b and c. From the salt rejection graph in Figure 21c, it is evident that perfect salt rejection is maintained for

1 CNT_(5,5) membrane up till a slit size of 3.28 Å. Thus, the critical slit size for the
 2 CNT_(5,5)_membrane is 3.28 Å. It is interesting to note that this critical slit size is larger
 3 than that found for the Graphene Slit Membrane, which was 2.28 Å.

4

5

6

7 Figure 21 Slit size study results. (a) The different slit size considered. (b) water permeability at
 8 different slit size. (c) salt rejection of the transverse flow CNT membrane at different slit size [73].

1

2 A series of analysis and numerical experiments were conducted to understand why
 3 TFCM can support a larger critical slit size as compared to graphene slit membrane. The
 4 potential of mean force (PMF) was calculated using equilibrium molecular dynamics
 5 with adaptive biasing force (ABF). The results are presented in Figure 22. It can be seen
 6 clearly that the TFCM impose a broader free energy peak profile on the salt ions. Thus,
 7 although the free energy barrier has the same magnitude when comparing the graphene
 8 slit membrane and TFCM of the same slit size, the broader peak profile exhibited by the
 9 TFCM explains the larger critical slit size of the TFCM.

10

11

12 Figure 22 PMF of water molecule and salt ion for CNT_(5,5) and graphene slit membrane
 13 computed using TI with ABF bias sampling [73].

14

15 The water permeability of graphene at its critical slit size is plotted in Figure 21a,
 16 together with the water permeability results for CNT_(5,5) membrane. Even at the same
 17 slit size of 2.28 Å, the CNT_(5,5)_2.28 membrane displays a higher permeability of
 18 3650 LMBH water molecules per ns than the graphene slit membrane, which has a
 19 permeability of 1627 LMBH. The main reason to this is the density of slits allowed in

the membrane. Graphene membrane can support only 1 slit in a membrane area of about $62.9 \text{ \AA}^2$, while (5,5) CNT naturally makes 2 slits in this same area. However, we also note that even if graphene membrane can support 2 slits in $62.9 \text{ \AA}^2$ of membrane area, the resulting permeability of 3254 LMBH is still slightly lower than that recorded for CNT_(5,5)_2.28. This is attributed to the hourglass channel shape that the curve outer walls of the CNTs provide in TFCM, as compared to the straight slits in graphene slit membrane. This hourglass shape resembles the shape of the channel formed in Aquaporin, and has been proven to exhibit better permeability performance as compared to straight pores [79]. This is also reflected by the lower PMF calculated for the TFCM for water molecules, as compared to graphene slit membrane, as can be seen in Figure 22.

Figure 23 Schematic diagram illustrating the channel shape of the slits formed by TFCM, as compared to the hourglass shape channel found in AQP [73]. (b) Diagram illustrating hourglass shape pore of AQP [80].

Taking into account that the CNT_(5,5) membrane can support a larger critical slit size of $3.28 \text{ \AA}$, we conclude that the CNT_(5,5) membrane has a permeability of 4279 LMBH, or about 2.6 times that of the graphene slit membrane, while still maintaining perfect salt rejection. The TFCM design and this set of simulation results have been published in *IJAM* in Apr 2017 [73].

4.4 Simulation studies on anti-fouling permeable graphene-based membranes using overlapping graphene films

In 2017, a research team from Australia reported that they successfully synthesized graphene films that forms overlapping grain boundaries from the renewable precursor of soybean oil in ambient-air condition [81]. They later went on and discovered that these graphene films can desalinate water through thermal distillation processes with excellent anti-fouling capabilities superior to commercial distillation membranes. We were approached to performed MD simulation studies to understand the fundamental molecular processes and the resulting paper was published by Nature Communications in 2018 [74]. A molecular picture of the overlapping graphene-films membrane was constructed based on experimental observations and measurements using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy and atomic force microscopy (AFM), and is modelled in LAMMPS as shown in Figure 24. A thermal distillation setup was simulated with the use of Langevin thermostat to model temperature driven flow.

1

2

Figure 24 Molecular dynamics simulation of water permeation through overlapping grain boundaries in the permeable graphene based membrane [74]

Three feed solutions were considered in the study. The first feed solution is made of water with 2M of NaCl, the second has water with 2M of NaCl and 5mM of sodium dodecyl sulfate (SDS), and the third has water with 2M of NaCl and 10mM of SDS. SDS is added to the feed solution to simulate foulant, as the membrane is observed to have anti-fouling properties in the experiments. The MD simulations provided a molecular picture of the transport of water molecules and rejection of salt ions through the graphene layers. The results, as shown in Figure 25 verified the proposed mechanism

of water transport and salt rejection through the overlapping grains of graphene, and confirmed the anti-fouling property observed in experiments [74]. As can be seen in Figure 25a, the water permeability is not significantly affected by the presence of SDS. This can also be inferred from Figure 25b, which shows the water permeance and salt rejection history versus time of MD simulation. The permeance and rejection histories with or without SDS are very similar.

Figure 25 The results of the MD test. (a) The variation of water permeability and salt rejection with increasing concentration of SDS. Water permeability is obtained from the scaling

methodology detailed in Figure 26. (b) The water permeance and salt rejection time history recorded during the MD simulations. Water permeance is measured in terms of water molecules entering the permeate region, and salt rejection as a percentage of the number of salt ions entering the permeate region.

Note that the calculation of permeability as represented in Figure 25a requires conversion from the raw MD results collected from Figure 25b. The scaling methodology is explained in Figure 26.

Figure 26 Scaling methodology to scale permeability results from molecular dynamics simulations to micron-meter sized permeable graphene-based membrane. (a) Simplified schematic diagram representing the deduced structure of a micron-meter sized permeable graphene-based membrane from experimental characterizations. Darker areas indicate overlapping regions. (b) Schematic diagram illustrating the membrane constructed in the molecular dynamics simulations. (c) Process chart depicting the scaling methodology employed from the water flow rate Q measured during molecular dynamics simulation, to the estimated permeability K of a micron-meter sized permeable graphene-based membrane. This scaling methodology is used to construct the graph shown in Figure 25a.

4.5 Chapter Summary

From observations made using conventional low-dimensional material membrane design, namely nanoporous graphene membrane, we came up with two new designs, the graphene slit membrane and the TFCM. The design philosophy and performance are elaborated in this chapter. Their performance as compared to other membranes introduced during the literature review in Chapter 2 is depicted in Figure 27. The performance of overlapping graphene membrane is not included as the testing environment is different. Its performance is tested for thermal distillation, where water is transported via thermal gradient, as oppose to pressure difference in a RO environment.

Figure 27 Desalination performance comparison matrix extended from Figure 3 to include the newly proposed graphene slit membrane and TFCM.

Chapter 5 Optimizing the TFCM membrane design

From the previous chapter, we found that the TFCM outperforms the current available low-dimensional material membrane design, and our proposed graphene slit membrane. Hence, in this chapter, we will focus on optimizing the TFCM design even further. Apart from performance, focus will also be placed on the possibility of physical fabrication. In this aspect, we performed studies by varying the CNT size, the number of layers, as well as the operating environment. Before diving into the details, the numerical effects of the small simulation domain considered in the previous chapter, and most published literature work to date would be elaborated on.

5.1 Domain sensitivity study

When we started this thesis project, we sought to verify our simulation results and hence built a domain similar to published results. However, as we ran more tests, we found that the domain size does affect the results. Hence, we proceeded with a domain sensitivity study, where we measured the water flow rate at different domain sizes. Four parameters were considered, `size_feed_x`, `size_permeate_x`, `size_y` and `size_z`. These are illustrated in Figure 28 below.

1

2 Figure 28 Illustration of parameters considered in domain sensitivity study - size_feed_x,
 3 size_permeate_x, size_y and size_z

4

5 The results of the domain sensitivity study are shown in Figure 29. Previous MD
 6 simulation studies done by our group [72, 73], as well as many published work by others,
 7 used a simulation domain size of about 50 to 100 Å in the longitudinal direction (x
 8 direction in our case), and 30 Å by 30 Å in the lateral dimension [21, 37, 82]. A few MD
 9 studies have considered a longitudinal size larger than 100 Å with similar lateral
 10 dimensions [18, 83]. To decide on the longitudinal size, 1ns simulation runs are
 11 conducted with varying longitudinal sizes using CNT_(5,5)_3.28 membrane to
 12 determine the sensitivity of the results with longitudinal size. The longitudinal x
 13 direction is generally made of up 2 components: the size of the feed solution
 14 (size_feed_x) and the size of the permeate (size_permeate_x). The two components are
 15 investigated independently in this work. Size_feed_x is varied from 57 to 170 Å and the
 16 water permeance behaviour for different size_feed_x considered is shown in Figure 29a.

1 Results indicate that the size of the feed solution affects the simulation results
 2 significantly. Increasing size_feed_x from 57 to 113 Å reduces the water flow rate by
 3 37%, while further increasing size_feed_x from 113 to 170 Å reduces the water flow
 4 rate by 17%. Bearing in mind the considerable computational cost that comes with the
 5 increase in domain size, a size_feed_x of 113 Å is adopted in our study. Conversely,
 6 increasing size_permeate_x does not seem to influence the results, and hence, it is kept
 7 at 36Å (Figure 29b).

8
 9 Further analysis is done on the size of the domain in the lateral directions (size_y and
 10 size_z). Two sizes are considered, 27Å (corresponding to $2D_{CNT}+2L_s$) and 40.5Å
 11 (corresponding to $3D_{CNT}+3L_s$). The results are depicted in Figure 29c. Note that the
 12 results are normalized with respect to the number of slits in the membrane. As can be
 13 seen, increasing the size of the domain in the y direction does not significantly change
 14 the results. Hence, size_y is kept to the smallest possible. Similarly, Figure 29d indicates
 15 that increasing size_z does not significantly affect the results as well. Therefore, size_z
 16 is chosen in our study to be a nominal value of 57Å. On the side note, it can be seen
 17 from Figure 29d that increasing size_z leads to oscillatory permeance behaviour at the
 18 beginning of the simulation, when the pressure difference is applied. This is attributed
 19 to the longer CNT length, which takes a longer time to settle when a large pressure
 20 difference is applied across the domain. As a result of this domain sensitivity study, we
 21 recognize the significant influence of size_feed_x, and from here on, size_feed_x is at
 22 least 113Å. Care is also taken when comparing performance of different membranes
 23 tested in MD with different feed sizes.

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1

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Figure 29 Domain sensitivity study results (a) Water permeance behaviour for varying size_feed_x (b) Water permeance behaviour for varying size_permeate_x (c) Water permeance behaviour for varying size_y normalized with respect to number of slits (d) Water permeance behaviour for varying size_z normalized with respect to size_z.

5.2 Effects of different CNT size on TFCM membrane design

Next, a series of simulations were performed to investigate how CNT sizes can affect the performance of the membrane. MD simulations were carried out on different CNT sizes, ranging from a diameter of $6.8\text{\AA}$ for a (5,5) CNT to $21.7\text{\AA}$ for a (16,16) CNT. The slit size is kept constant at $3.28\text{\AA}$. The main results for this CNT size study are summarized in Figure 30.

As the thickness of the membrane increases from $6.8\text{\AA}$ to $21.7\text{\AA}$, Figure 30a shows a corresponding increase in water flow rate. This is perhaps counter-intuitive, since classical equations predict that membrane thickness is inversely proportional to water flow rate. However, it is well known that classical equations breakdown at the nanoscale. Detailed analysis on the oxygen mapping, potential of mean force (PMF) measurements, and friction coefficient computations revealed that this increase in water flow rate with CNT size is due to better entrance and exit effects as the CNT size increases, resulting in lower frictional forces and free energy barrier. This was further confirmed by performing a series of analysis including calculation of PMF as well as friction coefficient (λ). The results are summarized in Figure 31. Both PMF and λ reduce with CNT size, supporting the observation that water flow rate increases with CNT size due to the better entrance and exit effect from the nanochannels.

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4 Figure 30 Results for membrane's desalination performance with different CNT size. (a) Water
5 flow rate (b) Salt rejection (c) Water permeability [84].

Figure 31 Variance of (a) PMF and (b) friction coefficient of water molecules crossing the TFCM with different CNT diameter [84].

Although increasing CNT size can increase water flow rate, the size of the membrane must also be considered. The water permeability results can provide a better performance gauge by taking the membrane area into account, and this is shown in

1 Figure 30c. When membrane area or slit density is taken into consideration, the smaller
 2 diameter tubes perform better than the larger ones. This is due to the larger membrane
 3 area or smaller slit density of larger CNTs. However, when compared with the
 4 nanoporous two-dimensional (2D) membrane, TFCM still performs better for all CNT
 5 sizes considered. This is illustrated in Figure 30c, where a result for the permeability of
 6 molybdenum disulfide (MoS_2) as reported by Heiranian *et al.* in 2015, is included for
 7 easy comparison [18]. The results from Heiranian *et al.* are used due to the similar
 8 domain sizes considered (see Chapter 5.1). The reasons for this superior desalination
 9 performance as compared to 2D membrane is due to the increased density of slits in
 10 TFCM, as well as the favorable entrance/exit effects provided by the curvature of CNT
 11 [73]. Figure 30b additionally shows that the variance in salt rejection is low, remaining
 12 close to 100% for all CNT sizes considered.

13
 14 The results from this CNT size study suggest that TFCM is not adversely affected by
 15 differing CNT sizes, since the water permeability and salt rejection remains high for all
 16 CNT sizes considered in this study. Although CNT size increases by more than two times
 17 from CNT_(5,5) to CNT_(16,16), the reduction in permeability is only about 10%. The
 18 variation of salt rejection remains within 10% as CNT size changes. This is unlike
 19 conventional vertically aligned CNT membrane designs, in which the salt rejection and
 20 water permeability depends crucially on the ability to keep the CNT size small and
 21 precise. The effects of CNT size on TFCM design has been published in *Physical*
 22 *Chemistry Chemical Physics* in 2018 [84].

23

5.3 Multilayer transverse flow CNT membrane

In previous studies conducted, only single layer TFCM was considered. In this study, we seek to investigate the impact of multilayering on the desalination performance of TFCM. This is interesting, because even though single layer TFCM is expected to provide the highest permeability performance, the multilayer TFCM is postulated to be of greater practical relevance. This is because single layer TFCM has not been demonstrated experimentally to the authors' knowledge. However, prototypes that resemble the multilayer TFCM have been reported. For example, the conceptual design of the multilayer TFCM bears resemblance to the CNT-STEM device introduced by Yeh *et al.* in 2016 to separate and concentrate virus-containing samples [85]. The main difference is that the slit sizes adopted by Yeh *et al.* are between 25 to 325nm, but slit sizes need to be much smaller for desalination applications. Although typical aligned CNT arrays have slit sizes or intertube distances of 16nm and above [86, 87], it has been shown that this distance can be shortened to 1nm via densification techniques such as optimized catalyst design [88]. For a single layer TFCM, the critical slit size or intertube spacing between the CNTs have been shown to be about 0.33nm using MD simulations [73], which is significantly below this limit of 1nm. Due to the increased thickness in multilayer TFCM, the critical slit size of a multilayer TFCM is predicted to be larger, and could potentially increase to this limit of 1nm while still maintaining effective salt rejection. Thus, this work aims to investigate if the current attainable slit size of 1nm is small enough for efficient salt rejection using the multilayer TFCM. If proven to be possible, this work suggests the possibility of using currently attainable dense vertically aligned (VA) CNT forest as multilayer TFCM for desalination.

1 Figure 32 illustrates the multilayer TFCM and the various parameters that govern its
 2 design. The number of layers of CNT used to form the multilayer TFCM is given by n ,
 3 and in Figure 32, $n = 4$. n is varied from 1 to 16 in this study. As with the construction
 4 of a single layer TFCM, the distance between each horizontally stacked CNT is termed
 5 as the slit size, and denoted by L_s , and this is varied from $3.28\text{\AA}$ to $10\text{\AA}$ [89]. The
 6 interlayer distance between each array of CNTs is denoted as d , which is also varied
 7 from $3.28\text{\AA}$ to $10\text{\AA}$ as in L_s . The offset between the CNT arrays is represented by the
 8 symbol h . In this work, two offset configurations are considered. These are the cubic
 9 packing configuration, where $h = 0$, and the hexagonal packing configuration, where h
 10 is maximum. Finally, the diameter of the CNT used to construct TFCM is given by D_{CNT} .
 11 Two values of D_{CNT} , $6.68\text{\AA}$ and $13.6\text{\AA}$, are considered here. For ease of reference, the
 12 multilayer TFCM configurations used in this study are named as follows:
 13 CNT_(n,m) _{L_s} _{n} , where (n,m) represents the rolled-up vector of CNTs used to
 14 construct the membrane. Thus, CNT_(5,5)_{3.28}₄ refers to the multilayer TFCM
 15 membrane made from (5,5) CNT, at a slit size L_s of 3.28, and made with 4 layers of
 16 horizontally aligned CNT.
 17

Figure 32(a) Multilayer TFCM illustration (in this illustration, $n = 4$), L_s is the slit size, d is the interlayer distance, h is the offset between CNT layers and D_{cnt} is the diameter of the CNTs used for the construction of TFCM. Two offsets h are considered, illustrated here with the case $n = 2$: (b) Offset h is 0, known as the cubic packing configuration (c) Offset h is maximum, known as the hexagonal packing configuration [89].

Three key conclusions can be drawn from the results of our MD simulations. First, the increase in number of layers n reduces the water permeability, as would be expected. This is shown in Figure 33a, where the water permeability can be seen to decrease with increase in n . The trend is almost similar for both aligned and zigzag configuration. This reduction in K can be modelled using a resistance-in-series model, similar to that used in filtration theory to describe flux-pressure relation (shown in grey in Figure 33a) [90]. Second, the salt rejection increases linearly with increase in n . As can be seen in Figure

1 33b, at a slit size of 1nm, the salt rejection increases to about 94% when n increased to
 2 16, compared to the salt rejection of about 22% when $n = 1$. This is an important
 3 observation, as it shows that while it is crucial to maintain L_s at the critical slit size for
 4 single layer TFCM to ensure effective salt rejection, increasing n can effectively
 5 improve salt rejection, such that salt can still be rejected effectively when L_s increases
 6 above its critical value to the practically attainable limit of 1nm. Furthermore, because
 7 the slit size is allowed to increase, the 16 layer CNT_(5,5)_10_16 TFCNT membrane
 8 has a permeability value (1420 LMBH) on par with the single layer CNT_(5,5)_3.28_1
 9 TFCM (1600 LMBH). Thirdly, increasing interlayer distance d also results in negligible
 10 degradation of the desalination performance of multilayer TFCNT membrane. This can
 11 be observed in Figure 33c, where it is clear that increasing d decreases K and R by less
 12 than 15% in all cases considered, with even a positive impact recorded especially for
 13 the zigzag configuration. This means that the interlayer distance d can also be increased
 14 to the practical limit of 1nm without negative impact on desalination performance of
 15 TFCM.

16

17 Thus, computational evidence is provided from this study to support the use of current
 18 dense VA CNT arrays as multilayer TFCM for efficient desalination. This study was
 19 published in *Journal of Membrane Science* in 2019 [89].

20

21

Figure 33 (a) Water permeance history of the multilayer TFCM at critical slit size $L_s = 3.28 \text{ \AA}$, with interlayer distance d set as $3.28 \text{ \AA}$. (b) Water permeability (K) and salt rejection (R) for

multilayer TFCM with $L_s = 10\text{\AA}$ and $d = 3.28\text{\AA}$. (c) Effects of increasing interlayer distance d on K and R for different sets of values of n and L_s [89].

5.4 Effects when CNT sizes are mixed

In the CNT size study, we have shown that varying D_{CNT} does not significantly affect the permeability performance of TFCM. Although the CNT size precision is shown to be not crucial, another important aspect that determines the ease of fabrication is the CNT size uniformity. This is addressed in this study as we study whether the size uniformity of CNT affects the performance of TFCM. In this series of MD simulations, we set n to be 2, and d and L_s as $3.28\text{\AA}$. Five configurations of varying D_{CNT} are considered for this NEMD simulation study, as shown in Figure 34. The first two are made entirely of (5,5) CNT in cubic and hexagonal configurations. We have then two mixed configurations made of (5,5) and (10,10) CNTs arranged in both cubic and hexagonal arrangement. Lastly, as a benchmark, we have TFCM made of (10,10) CNT in cubic configuration for comparison. Each simulation is ran till 5ns. The water permeance history is recorded as shown in Figure 34.

Figure 34 Effects of varying and mixing different carbon nanotube sizes (D_{CNT}) on permeability performance [89].

When mixed configurations of (5,5) and (10,10) CNTs are considered, the average permeability performance for cubic and hexagonal packing is at 1340 LMBH, a difference of less than 1% when compared with a 2-layered TFCM made of purely (5,5) CNTs (1330 LMBH). When only (10,10) CNTs are used, the permeability dropped to 1200 LMBH, a drop of about 10% when compared with CNT_(5,5)_3.28_2 membrane. These nonequilibrium MD simulation results are further validated by the PMF profiles computed from equilibrium MD simulation. For EMD simulations, we consider only CNT_(5,5)_3.28_2 cubic and mixed hexagonal arrangements. The computed profiles are shown in Figure 35. The PMF values recorded are rather close with each other, indicating that different CNT diameters do not significantly alter the PMF barrier of the TFCM membrane, which is in agreement with the similar K values observed in NEMD simulations.

1

2 Figure 35 PMF profiles of water as it crosses TFCM membrane made of (5,5) CNT and TFCM
 3 membranes made of a mixed of (5,5) and (10,10) CNTs. The PMFs value are close together
 4 [89].

5

6 **5.5 Effects of oscillatory pressure on TFCM's** 7 **desalination performance**

8 In all previous simulations, constant pressure was applied to push the feed water through
 9 the membrane. This is the conventional practice in reverse osmosis operation. However,
 10 the use of a constant pressure profile inevitably leads to a buildup of salt ions near the
 11 membrane at the feed side, leading to concentration polarization (CP). CP is unwanted
 12 as it results in a lower water flow rate and salt rejection. The use of oscillating flow to
 13 reduce CP was already explored for conventional polymeric membranes in the 1970s by
 14 Kennedy *et al.* [91]. It was conceptualized that by oscillating the feed flow across the

1 membrane, solute transfer away from the membrane is promoted, thereby reducing CP.
2 In their study published in 1974, Kennedy *et al.* showed experimentally, using cellulose
3 acetate membranes, that water flow rate increased by about 70% when oscillating feed
4 flow is used [91]. Despite this, oscillating pressure operation is not use widely today for
5 reverse osmosis (RO), presumably due to the cyclic stress on mechanical components.
6 On the other hand, oscillating operation has been adopted for membrane based
7 electrodialysis for large scale operation since the 1990s [92-95].
8
9 Thus, this part of the project aims to look at how oscillating operation impact the
10 performance of low-dimensional material membrane for desalination using either RO
11 or electrodialysis. Two major factors distinguish this study from other studies in
12 literature. Firstly, earlier works on oscillatory pressure focus on conventional polymeric
13 membrane, and the effects of oscillatory pressure on low-dimensional material
14 membrane has till date not been studied yet. Because of the inherent difference between
15 low-dimensional material membrane and conventional polymeric membrane, results
16 from previous works on polymeric membrane cannot be easily adapted for low-
17 dimensional membrane. In addition, periods of pulsation on the order of sub-
18 nanoseconds are considered here, while previous analysis [91, 93, 96, 97] considers
19 periods on the order of seconds. The use of these sub-nanoseconds period of pulsation
20 stems from observations from previous studies. In these past studies, it has been
21 observed that the buildup of salt ions around the membrane during the simulation occurs
22 within nanoseconds of simulation time [73]. This short time taken for accumulation of
23 salt ions is due to the orders of magnitude increase in water permeability, the size of the
24 domain considered, as well as the higher pressure used during the simulation. In such
25 scenarios, it is believed that nanosecond pulsation is more effective in introducing

instabilities to the system. In addition, the capability to generate such nanosecond electric pulses have evolved significantly in the last decades [98-100]. Therefore, it would be interesting to study the effects of such sub-nanosecond pulses on the performance of low-dimensional material membrane.

The low-dimensional material membrane used in this study is the TFCM, due to its ultra-high permeability performance. Results for the CNT_(5,5)_4.28, CNT_(5,5)_5.28, CNT_(5,5)_6.28 membrane desalination performance with sinusoidal pressure profile of varying period (T) are shown in Figure 36, and for CNT_(5,5)_4.28 with varying amplitude (A) in Figure 37. K_0 and R_0 are the permeability and salt rejection performance of the membrane under constant applied pressure, while K and R are the permeability and salt rejection of the membrane under sinusoidal pressure. Figure 36 shows the variation of the ratio $\frac{K}{K_0}$ and $\frac{R}{R_0}$ with period T of the applied sinusoidal pressure at fix amplitude $A = 0.075\text{kcal/mol-Å}$. For all three slit sizes considered, a significant increase in water permeability ranging from 30% to 36% is observed when sinusoidal pressure profile is applied. At the lowest period of 20000fs, the water permeability is 20% lower for all three cases as compared to the base case. As the period increases to 40000fs, the water permeability is increased to about 20 to 30% above the base case. Further increase in the period to 80000fs shows slight deviations from the results obtained at $T = 40000\text{fs}$. As for salt rejection, although the trend observe for salt rejection is a slight decrease when sinusoidal pressure of increasing period T is applied, the results for salt rejection shows significant standard deviation, as illustrated by the relatively larger error bars. Thus, no conclusive remarks can be made regarding the impact of sinusoidal pressure on salt rejection. The salt rejection of the respective

1 membrane when sinusoidal pressure is applied as a ratio of the salt rejection in the base
2 case can vary from 0.6 to 1.2.

3

4 More in depth studies to understand the underlying reasons behind the increase in water
5 permeability with the right oscillating pressure profiles were carried out. This include
6 mapping of the salt density variance across the membrane to study effects due to
7 concentration polarization, looking at the water orientation such as water dipole angles,
8 hydrogen bonds and height, and the permeance behavior with respect to time. Results
9 from these detailed studies revealed that the permeability improvement is due to a
10 resistance to reverse flow that is developed due to inertia of water molecules at higher
11 periods T , which results in a net increase in permeability. With these, we conclude that
12 oscillatory operation increases the permeability of the membrane by 16 to 36% at a
13 period ranging from 0.04 to 0.08ns and amplitude of 0.075kcal/mol-Å. Increasing the
14 amplitude further leads to a linear increase in permeability, as observed in Figure 37.
15 The results have since been published in *Desalination* in Apr 2018 [101].

16

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4 Figure 36 Water permeability and salt rejection performance for sinusoidal pressure profile with
5 varying T for (a) CNT_(5,5)_4.28 (b) CNT_(5,5)_5.28 (c) CNT_(5,5)_6.28 membrane [101]

Figure 37 Water permeability and salt rejection performance for sinusoidal pressure profile with varying A for CNT_(5,5)_4.28 membrane [101]

5.6 Chapter Summary

We set out to optimize the TFCM design in this chapter. It seems however that the first configuration we tested for the TFCM, the single layer CNT_(5,5)_3.28 membrane has the best permeability and salt rejection performance. From the CNT size study, although water flow rate increases with CNT size, but the slit density reduces. Overall, CNT_(5,5) still provides the best permeability performance, although all the CNT sizes tested have good permeability performance, much higher than nanoporous graphene membrane. The multilayer TFCM study shows that multilayering simultaneously increases salt

1 rejection while reducing water permeability. The end effect is that the permeability
2 performance of multilayer TFCM is slightly lower than a single layer at close to 100%
3 salt rejection, but again, the difference is not huge. Mixing CNTs in the TFCM design
4 does not significantly affect desalination performance as well. A surprising and valuable
5 finding of these optimization studies is that the performance of TFCM seems to be
6 insensitive to CNT size, CNT uniformity or CNT layers. This means that the physical
7 fabrication of TFCM may be easier to attain than the current designs, like VA CNT
8 membranes which demands CNT size uniformity and precision to have good
9 performance. The TFCM's critical performance parameter is its slit size, and the
10 physical fabrication have to ensure that the slit size is not more than the critical slit size
11 for effective salt rejection.

12

13 Changing operating conditions can also further improve the TFCM's performance. In
14 this thesis, oscillatory pressure is applied and the TFCM performs 16% to 36% better in
15 terms of permeability. Salt rejection stays roughly constant. This can be useful for the
16 application of TFCM in oscillatory processes like electrodialysis.

17

Chapter 6 Different 2D materials other than carbon

Nanostructures formed using carbon was exclusively focused on in this thesis until now. This is due to the well-established and validated molecular and force field models available for graphene and CNTs, which increases the credibility of the simulations performed. In addition, since graphene and CNTs are the model 2D and 1D material respectively, there are comparatively more experimental and numerical data available for comparison and validation. In this study, we are going to step away from the comfort zone of carbon structures, and start exploring other 2D materials. In the last couple of years, the types of 2D materials have expanded enormously due to the intense interest in the peculiar properties of graphene-like 2D materials. Some examples of such 2D materials are depict in Figure 38 [102]. In this thesis project, we will focus on borophene, molybdenum disulfide (MoS_2) and MXene. The literature review on the 2D materials to be considered, implementation and results are discussed below.

Figure 38 Range of 2D materials [102]

6.1 Background on the different 2D materials considered

In this study, four different 2D materials will be focused on. The first is graphene, which is use here as a baseline for comparison. The second is borophene, which like graphene, is a monoelemental 2D material, but from Group III instead of Group IV in the periodic table. The difference, or similarity, in desalination characteristics between monoelemental graphene and borophene is deliberated in this study. The third material considered in this paper is MXene. MXene is a relatively new 2D material, being discovered in 2011 by Gogotsi and Barsoum [103]. The natural lamellar structure of MXene, as well as ease of surface functionalization, has already generated interest in MXene as separation membranes [104-106]. In this work, the desalination performance of MXene membrane to effectively reject monovalent salt ions in reverse osmosis setup is studied. The last 2D material considered in this paper is MoS₂. Unlike the newer borophene and MXene, MoS₂ is one of the most commonly studied 2D materials apart from graphene [107]. MoS₂ membranes have been studied for desalination and good desalination performance has been observed for MoS₂ membranes in various configurations. This inspired us to include MoS₂ as one of the 2D materials for comparison [18, 108, 109].

6.2 Molecular Dynamics Implementation

To implement the different 2D materials into our membrane system in molecular dynamics, we need to first build the molecular membrane model, and second find the

1 force field parameters that can best describe the behavior of these materials.

2

3 Figure 39 Molecular Model for the five 2D materials slit membrane considered (For each
4 membrane, left graphic depicts front view, right graphic depicts side view)

5

6 The membrane models built for this study is depicted in Figure 39. The graphene model
7 was described in our graphene slit membrane study described in Chapter 4. In the case
8 of borophene, the molecular structure was constructed based on a triangular network
9 reported by Zhou and Jiang in 2017 [110]. Their reported structure is based on *ab initio*
10 calculations. However, it has been found that stable borophene sheets typically have
11 periodic hexagonal holes incorporated in this triangular lattice. Hence, future work can
12 consider the implementation of this newly found structure [111]. At this stage, we used
13 the theoretically obtained triangular network as a first approximation.

14

15 For MoS₂, two configurations are considered. These are slits terminated with S and Mo
16 respectively. Previous investigation conducted by Heiranian *et al.* [18] found that pores
17 terminated with Mo have higher permeability as compared to pores terminated with S.

1 It is therefore interesting to look at whether the same effects are observed in 1D slits as
 2 well. In the case of MoS₂, the structure presented by Stewart and Spearot in 2013 is
 3 reconstructed [112]. This is the same model built by Liang *et al.* in 2009 [113], or
 4 Ramana *et al.* in 2008 [114].

5

6 In the case of MXene, the molecular structure of Ti₂CF₂ was implemented based on that
 7 reported by Khazaei *et al.* in 2013 [115]. For MXene, there are many possible candidates
 8 as one can choose from a number of early transition metal as M, and any group IIIA or
 9 IVA elements to be X, mixed in different ratios [116]. Again, Ti₂CF₂ was chosen
 10 arbitrarily as a starting point.

11

12 With the molecular model set up, we must then decide if a freestanding or frozen
 13 simulation is to be performed. Whilst a freestanding simulation will be a more accurate
 14 representation of the behavior of the membrane, unlike graphene, there is a lack of well-
 15 validated potential models for these 2D materials. We have done an initial feasibility
 16 assessment of the available potential model, including SW potential for borophene [110],
 17 ReaxFF force field for MXene [117], SW potential [118] and REBO potential [113] for
 18 MoS₂. However, the membrane does not hold up and disintegrate in aqueous
 19 environment even without a pressure gradient. Due to a lack of validated force potential
 20 models and experimental results, especially for the newer 2D materials, the membranes
 21 are kept frozen throughout the simulation. Details of the LJ and Coulombic parameters
 22 used to model the interactions of the membrane with water molecules and salt ions are
 23 tabulated in Table 3.

24

Atoms/Ions	Well depth of potential ϵ_{ij} (kcal/mol)	Radius at the minimum potential energy σ_{ij} (Å)	Charge
O [64]	0.1628	3.164	-1.0484
H [64]	0	0	0.5242
Na+ [68]	0.1684	2.452	+1
Cl- [68]	0.01166	5.520	-1
C (graphene) [21]	0.08600	3.400	0
B [119]	0.09500	3.543	0
Ti [120, 121]	0.01700	2.829	0
C (MXene) [120, 121]	0.1050	3.431	0
F [120, 121]	0.05000	2.997	0
S [18]	0.4610	3.130	0
Mo [18]	0.01350	4.200	0

1 Table 3 Details of LJ and Coulombic parameters used for different 2D materials membrane study.

2 **6.3 Results**

3 The results of the MD simulations to compare the performance of different 2D materials
4 are presented here. In this study, we chose the slit membrane configuration to begin
5 studying the effects of using different 2D materials since the simplicity of the slit design
6 allows us to study the performance of the different 2D materials as a desalination

1 membrane with few differences in other configuration parameters, allowing comparison
2 under similar conditions. The membranes are named according to its respective material
3 and the slit size. For instance, a graphene membrane with a slit size of $2.6\text{\AA}$ is referred
4 to as graphene_2.6 membrane.

5

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4 Figure 40 Variation of desalination performance of the different 2D materials membrane with slit

5 size

6

7

1 The different 2D materials slit membranes' desalination performance with varying slit
2 sizes are shown in Figure 40. In general, MXene slit membrane has high permeability
3 but low salt rejection performance. This is attributed to its hydrophilic nature. However,
4 its low salt rejection implies that it has low critical slit size, and hence, may not have
5 better permeability performance as compared to the other materials. On the other end,
6 MoS₂ slit membranes with S terminated pores has the lowest permeability and good salt
7 rejection characteristics. Due to the different salt rejection characteristics, proper
8 comparison between the membrane can only be made when salt rejection requirement
9 is specified.

10

11 With regards to this, column charts in Figure 41 can be used. Should perfect salt
12 rejection be required, as with desalination for potable water, Figure 41a can be referred
13 to. In this case, the monoelemental 2D materials membrane have the best desalination
14 performance, with permeability of about 750 LMBH. Although MXene had the best
15 permeability performance when comparison is made with constant slit size, to achieve
16 100% salt rejection, the slit size must be reduced dramatically, resulting in a
17 permeability performance of only about 400 LMBH. MoS₂ membranes in the two
18 different configurations (S or Mo terminated) turn out to have similar permeability
19 performance when perfect salt rejection is required (about 600 LMBH). It is also to be
20 noted that while there is variation in desalination performance across the different 2D
21 materials slit membrane, their permeability is still 2 orders of magnitude higher than
22 current polymeric membranes used in desalination plants (about 1LMBH).

23

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2

3

4 Figure 41 Comparison of water permeability performance for different 2D materials slit
5 membrane at different salt rejection requirement

1
2 Detailed analysis is also carried out to determine the main reasons for the performance
3 deviation across different 2D materials. It is found that the hydrophobicity of the
4 materials plays a big part in determining its behavior. The more hydrophobic materials
5 are found to have larger critical slit size, but reduce permeability. The hydrophobic
6 materials, MoS₂ with S terminated slits, graphene and borophene have critical slit size
7 between 2.4 and 2.6 Å, whilst the more hydrophilic MXene membrane has critical slit
8 size of 0.8 Å. Another influencing factor is the materials' inherent interaction parameters.
9 This is in our simulations represented by the Lennard-Jones parameters, σ and ϵ .
10 Materials with larger σ and ϵ is found to exhibit lower permeability, and the higher salt
11 rejection. This relationship is summarized in Figure 42. In Figure 42, the results for
12 MoS₂ are always outliers. This is due to the shape of the channel formed in MoS₂
13 membranes.
14

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2

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4 Figure 42 Relationship between desalination performance of the 2D materials slit membrane
 5 with its LJ interactions parameters. (a) Water permeability K with LJ interaction parameter σ (b)
 6 K with LJ interaction parameter ϵ (c) Critical slit size $L_{s,crit}$ with σ (d) $L_{s,crit}$ with ϵ .

7

1 Unlike the monoelemental or MXene membrane, which have relatively straight
 2 channels, MoS₂ channels either have a diverging-converging geometry seen in S
 3 terminated slit, or converging-diverging geometry seen in Mo terminated slit. This is
 4 illustrated in Figure 43 below. The Mo terminated converging-diverging geometry
 5 resembles the hourglass shape pores of AQP, which are known to increase water flow
 6 rate [122]. The same observations on the shape of the channels forced by Mo only and
 7 S only pores are made by Heiranian *et al.* for MoS₂ nanoporous membrane. This
 8 explains the higher permeability observed in Mo terminated slits as compared to S
 9 terminated slits.

10

11

12 Figure 43 Illustration of different shape of slits. The diverging-converging geometry of S
 13 terminated slit and converging-diverging geometry of Mo terminated slit in MoS₂ slit membrane.

14 This study has been published in *Journal of Membrane Science* in 2019 [123].

15 6.4 Chapter summary

16 Among the materials considered, monoelemental graphene and borophene are found to
 17 be the most suitable 2D materials for desalination. These membranes can reject 100%

1 of the monovalent salt ions while maintaining a permeability 25% higher than both
2 MoS₂ slit membranes and 87% higher than MXene slit membrane. Even for other
3 applications that does not require such high salt rejection, monoelemental graphene and
4 borophene membranes' desalination performance is still on par with MXene, and higher
5 than MoS₂.

6

Chapter 7 Conclusion and future directions

In this thesis project, the potential of advanced low-dimensional material systems for desalination purpose has been ascertained with MD simulations. Different design approaches, specifically the graphene slit membrane and the transverse flow CNT membrane have also been proposed and tested. We also supported the experimental results of the overlapping graphene film membrane proposed by CSIRO Manufacturing and University of Sydney with our MD model. Apart from these, a significant amount of work has also been done to characterize graphene slit and transverse flow carbon nanotube membranes. In the final part of this thesis project, other 2D materials are also considered and the effects of changing 2D materials are deliberated. The conclusion showed that monoelemental 2D materials like graphene are still the best choice for desalination. Nonetheless, there are still much work that can be done. In this section, we begin by summarizing the publications and conference presentations that were completed based on the work done for this thesis project. We then provide some suggestions for future development in this area. Lastly, we make some remarks regarding the limitations of this thesis work, before concluding this thesis report.

7.1 Publications and conference presentations

Till date, eight papers have been published and four conference presentations has been made in association with the work performed under this thesis project. The details are tabulated below in chronological order:

1

S/N	Journal/conference	Title	Date	References
1	Carbon	Free-standing graphene slit membrane for enhanced desalination	Dec, 2016	[72]
2	International Conference on Membranes in Drinking and Industrial Water Projection (MDIW)	Slit membranes for efficient desalination using graphene	Feb, 2017	[124]
3	International Journal of Applied Mechanics	Nanoscale fluid mechanics working principles of transverse flow CNT membrane for enhanced desalination	Apr, 2017	[73]
4	International conference on computer modeling and simulation	Desalination performance prediction of low-dimensional material membranes using empirical molecular dynamics (Awarded the Best Presentation)	Jan 2018	[125]
5	Nature	Anti-fouling graphene-	Feb 2018	[74]

	Communications	based membranes for effective water desalination		
6	Physical Chemistry Chemical Physics	Effects of CNT size on desalination performance of outer-wall CNT slit membrane	May 2018	[84]
7	Desalination	Effects of oscillating pressure on desalination performance of transverse flow CNT membrane	Feb 2019	[101]
8	Journal of Membrane Science	Carbon nanotube arrays as multilayer transverse flow CNT membrane for efficient desalination	Jul 2019	[89]
9	International Conference on 2D materials and Technologies	Single Layer Transverse Flow Carbon Nanotube Membrane for Desalination	Dec 2018	[126]
10	International Conference on Computational Methods	Computational design of single- and multi-layer Transverse Flow Carbon Nanotube membrane using empirical molecular dynamics	Jul 2019	[127]

11	Journal of Membrane Science	Investigations on Different Two-Dimensional Materials as Slit Membranes for Enhanced Desalination	Dec 2019	[123]
12	Journal of Membrane Science	A Review on Low dimensional Carbon Desalination and Gas Separation Membrane Designs	Dec 2019	[20]

1 Table 4 Publications and conference presentations till date

2

7.2 Future direction 1: Towards further improvement of low-dimensional material membrane through numerical analysis

The use of slits instead of pores, and the design of the transverse flow CNT membrane has already increased the permeability performance significantly as compared to nanoporous 2D materials membrane or vertically aligned CNT membrane (see Figure 27). Additional studies can be continued in this direction to try to improve the permeability performance, while retaining perfect salt rejection, by utilizing new design approaches. This is built upon the understanding of the behavior and limitations of current designs.

One possible way is to further optimize the shape of the nanochannels. From this thesis project, we find that although the transverse flow CNT membrane is inherently thicker than 2D graphene slit membrane, even at the same slit size and slit density, a slightly higher permeability is observed. This is somewhat unexpected, since classical mechanics predict that flux is inversely proportional to thickness. Thus, we would expect the transverse flow CNT membrane to have a slightly lower permeability as compared to atom thick graphene. However, it also well-known that classical mechanics can breakdown at such small length scales. Studies have shown that in cases where frictional forces in the nano channels are negligible and entrance effects dominates, flux could be invariant to thickness [60]. In fact, in a MD study done by Gravelle *et al.* in 2014, an hourglass shaped pore with finite thickness is observed to have better permeability as compared to ultrathin porous graphene [79]. Thus, it is likely that the

transverse flow CNT membrane has a more favorable entrance effect for water permeability as compared to the graphene slit membrane, resulting in the slightly higher permeability observed for transverse flow CNT membrane. This is still an area which is not well understood, hence, providing opportunities for further studies. A possible research direction is then to study the optimal shape of the nanochannels that can optimize the entrance and exit effect to increase permeability.

Another possibility is to add chemical functionalization or electrical charges to the membrane to increase permeability and salt rejection. In the study by Cohen-Tanugi and Grossman in 2012, they functionalized the nanopores in graphene with hydrogen and hydroxyl groups. The nanopores functionalized with hydroxyl groups were found to increase permeability [21]. Earlier in 2011, Corry conducted a similar functionalization study, but with CNT instead [128]. In a recent study published in 2016, Feng *et al.* incorporated vibrational charges to both ends of the CNT and showed that this can effectively block out all salt ions, allowing a wider CNT to be used for desalination [129]. Similar studies can be done for both the graphene slit membrane and the transverse flow CNT membrane to see if functionalization can further increase permeability.

7.3 Future direction 2: Exploring other nanotube materials

In this thesis, we have started exploring the use of 2D materials other than graphene for 2D slit membranes, although the finding was that graphene could still be the best

material for this purpose. Moving on, more potential 2D materials can be identified to study on for the 2D slit membranes, and in addition, other 1D materials for the TFCM design can also be considered. One possible candidate is the halloysite nanotube, which is a naturally occurring nanotube found in the clay mineral, halloysite [130]. Being naturally and abundantly found in Australia, US, China, New Zealand, Mexico and Brazil, the halloysite nanotube is touted as a low cost alternative to synthetic nanotubes [130].

Figure 44 Schematic diagram of (a) the crystal structure of HAL-(10 Å) halloysite nanotube (b) representation of a halloysite nanotube particle (c) TEM image of a halloysite (d) AFM image of a halloysite [130].

7.4 Future direction 3: Towards physical fabrication and experimental testing of low-dimensional material membrane

Undoubtedly, the most challenging aspect to the practical implementation of advanced

1 2D materials as desalination membrane is the fabrication approach [13, 30, 40, 131].
2 Even laboratory scale fabrication of such membranes remains a challenge today due to
3 the need for nanoscale precision. This is reflected in a review that we did in 2019 and
4 was published in 2020 in Journal of Membrane Science [20]. It can be seen from Figure
5 45 that experimental results (represented by hollow spheres) are either low in salt
6 rejection or permeability. This is due to the difficulty in controlling the size of the
7 nanopores as well as difficulty in producing such membranes with minimal defects. To
8 overcome this challenge and push the LDM membrane technology towards physical
9 realization, there is a need to explore more innovative ideas and designs. MD and
10 simulations provide the optimal environment for such designs as can be seen by the
11 numerous works represented by solid circles in Figure 45.

12
13 Figure 45 Desalination performance comparison matrix for low dimensional carbon
14 membrane, showing differences in performance of the membrane obtained through
15 simulations and experiments. [20]

1
2 The TFCM could be a step towards this direction. In the MD study for the TFCM, we
3 observed that the TFCM is much less sensitive to CNT size as compared to conventional
4 VA CNT membranes. Thus, it does not require a very small diameter or precisely sized
5 CNT, which is a major obstacle for typical desalination membrane made of CNT. The
6 control parameter changes from precisely sized CNT to the control of the spacing
7 between the CNT. Whether it is easier to control the spacing is still a question that needs
8 to be answered. The use of slits, as opposed to circular pores could also potentially make
9 fabrication less challenging, since the problem of creating tightly distributed nanopores
10 is sidestepped. Instead, the focus shifts to separating the graphene nanosheets precisely
11 such that critical slit size is maintained. Additionally, naturally occurring pores such as
12 that in graphyne can be explored [132]. Nevertheless, each of these approaches are still
13 full of uncertainties and further research work needs to be carried out before conclusion
14 can be drawn.

15
16 Another key area that can impede the practical implementation of such membranes is
17 the stability of the membrane under RO operating conditions. For instance, whether such
18 membrane system can withstand the operating pressure of RO, which is typically on the
19 order of 5MPa. Preliminary studies in this area have already began for nanoporous
20 graphene by Cohen-Tanugi and Grossman in 2014 [133]. In the configuration studied,
21 graphene is attached to a porous substrate to provide mechanical support. Using MD,
22 they showed that graphene membranes sitting on a polysulfone substrate can withstand
23 the typical operating pressure if the substrate pore radius is more than 8 microns. Before
24 experimental verifications can be carried out, such results can substantiate the viability

of the use of these 2D material systems for desalination. Therefore, it can be useful for similar strength analysis to be carried out for the membrane designs proposed in this project.

7.5 Future direction 4: Identifying potential challenges for the integration of such membrane into desalination system

While it is true that low-dimensional membrane systems have the potential to achieve ultra-high permeability, how such membranes can be integrated into desalination systems to fully exploit the orders of magnitude increase in permeability is another crucial area of interest. Recent insights in the incorporation of such membranes into reverse osmosis (RO) system revealed that the energy reduced may not be as substantial as previously assumed [37, 134]. That is, orders of magnitude increase in permeability does not equate to orders of magnitude reduction in energy required for desalination. This is mainly due to the thermodynamic minimum energy required to overcome osmotic pressure during desalination. As such, when the permeability is tripled, the energy consumption is only reduced by about 15% in a typical RO operation [134]. However, the analysis presented in [134] considered typical operating scenario of reverse osmosis currently using polymeric thin film composite membrane. The question is whether the operating process of reverse osmosis can be altered such that the ultra-high permeability of these next generation membranes can be fully exploited to reduce the energy required by desalination considerably.

To illustrate this limitation in energy cost savings, a simplified scenario of one typical

1 RO element in a cross flow configuration is considered, as illustrated in Figure 46.

2

3 Figure 46 Simple one RO element scenario considered

4 The relationship between energy required for desalination (E) and the membrane's
5 permeability (K) is given by Eq. 5 . The symbols used in the equation is described in

6 Table 5 .

$$E = \left(\frac{Q_P}{A_m \eta Y} \right) \frac{1}{K} \times \frac{1000 \times 10^2}{3600} + \frac{f_{cp} \Delta \pi}{\eta Y} \times \frac{1000}{3600} \quad \text{Eq. 5}$$

Symbol	Description	Typical Units
J	Permeate flux	$\frac{L}{m^2 \cdot h}$
K	Permeability	$\frac{L}{m^2 \cdot h \cdot bar}$ (LMBH)
ΔP	Pressure applied	Pa
f_{cp}	Concentration polarization factor	dimensionless
E	Energy required	$\frac{kWh}{m^3}$
P	Power required	kW
Q_p	Volume flow rate of permeate (usable water)	$\frac{m^3}{h}$
Q_F	Volume flow rate of feed (sea water)	$\frac{m^3}{h}$
Q_R	Volume flow rate of retentate (brine)	$\frac{m^3}{h}$
A_m	Membrane area	m^2
η	Pump efficiency	%
$\Delta \pi$	Osmotic pressure	Pa
Y	Recovery	dimensionless

7 Table 5 Symbols used in this work, its corresponding description and units

8 When conventional RO operating parameters as shown in Table 6 are inserted into Eq.
9 5, the graph as shown in Figure 47 is obtained.

1

Parameter	Units	Values
Q_F	$\frac{m^3}{h}$	4.875
A_m	m^2	164
η	-	90%
Y	-	8%

2 Table 6 Reference parameters to represent current operating scenario (Taken from specification
3 sheet of Toray TM840 membrane)

4

5 Figure 47 Energy required in terms of membrane's permeability in current typical operating
6 scenario

7

8 The results obtained is in agreement with the conclusion drawn by Cohen-Tanugi *et al.*
9 in 2014 [134]. The reduction in the required amount of energy is less than 10 % as K
10 increases, and any improvements in K beyond about 5 LMBH has insignificant effect
11 on the required energy E . This behaviour is due to the thermodynamic limit set by the

osmotic pressure, which limits the minimum energy required to about 11.1 kWh/m³ in this operation setting.

By studying Eq. 5, it can be observed that the benefit of having increased permeability can only be fully exploited if we operate significantly above this thermodynamic limit.

Figure 48 illustrates the energy required versus permeability graph for feed flow rate varying from 4.875 to 4875 m³/h. When the feed flow rate is increased, a significant energy reduction is observed as K increases. At a feed flow rate of 4875 m³/h, the two orders of magnitude increase in K is accompanied by two orders of magnitude reduction in E .

Figure 48 Energy required in terms of membrane's permeability in different operating scenario

Looking at Eq. 5 in another way, we can plot E with respect to Q_F for different permeability K . The resulting graphs are displayed in Figure 49. The benefit of

1 increasing K by orders of magnitude is clearly shown by this chart, as we can see that
 2 the feed flow rate can be increased significantly with marginal increase in the energy
 3 required as K increases.

4
 5 Figure 49 Energy required in terms of feed flow rate at different permeability

6
 7 While theoretically, increasing the feed flow rate can fully realize the benefit of ultra-
 8 permeable membrane, one must consider whether it is practical to increase the feed flow
 9 rate by orders of magnitude. The limitation to this increase in feed flow rate can stem
 10 from firstly the mechanical strength of the membrane, secondly, the power of the high-
 11 pressure pump use to push the feed water, thirdly the mechanical strength of the
 12 supporting equipment like pipes, and lastly whether there are any undesirable
 13 hydrodynamics effects at such high flow rate. More reviews and analysis will be
 14 required before any conclusions can be drawn. Other ways in which this ultra-high
 15 permeability can be exploited is also an area that is worth investigating. It is clear at this
 16 point that advances in this area is vital for ultra-permeable membrane to truly

revolutionize desalination.

7.6 Limitations of current work

Before concluding this chapter, some remarks about the limitations of this thesis work will be made to help guide future work. This work uses MD for most analysis. Although MD is a great tool that is of a suitable length scale for this problem, there is still a gap between MD and the physical implementation. For instance, despite our efforts to model appropriately the overlapping graphene membrane presented in Section 4.4 with worst case scenarios as much as possible, there is still a difference in an order of magnitude when compared to experiment. There is a limitation to how authentic the simulation can resemble the actual physical product and environment. The domain size and simulation time is one severe limitation of MD. It is often impractical to have domain size or simulation time close in the micro range. Therefore, it is believed that MD is an excellent tool of exploratory analysis and optimization, but it has to be supplemented with physical experiments in due time.

The second limitation is the focus on membrane design. However, for the desalination system to work, one must think about the accompanying technology required. For instance, we show in Section 7.5 that to fully exploit the benefits of ultra-high permeability, the flow rate have to be increased. Current mechanical pump and pipings may not be able to support this flow rate. Thus, as the technology mature, one has to take a broader outlook and consider the system instead of just a component.

1 **7.7 Concluding remarks**

2 This thesis report summarizes the work that have been completed in the four years of
3 my PhD program. Literature review has been carried out to survey what has already
4 been done in the use of advance low-dimensional material systems for desalination. As
5 the main tool used in this project is envisaged to be MD, the system is set up in
6 LAMMPS and validated with published results. With this, we moved on to look at the
7 different parameters that affect desalination performance and tested some new design
8 approaches that can contribute towards the physical realization of such 2D materials
9 membrane. The main design approaches studied include the use of slit instead of circular
10 pores in graphene membrane, and the TFCM. The TFCM is seen as the most promising
11 design for now. Much of the characterization of this membrane has already been
12 completed, where the performance of the membrane with respect to varying slit size,
13 CNT size, number of layers, and operating conditions have been documented. We have
14 also moved on to look at the use of different 2D materials for the slit membrane
15 configuration. Further, collaboration with a team based in Australia allowed us to study
16 a recently proposed low-dimensional membrane design based on overlapping graphene
17 film. This collaboration provided me with a valuable opportunity to look at an
18 alternative low-dimensional membrane design and validate my molecular model and
19 simulation methodology with experimental results.

20

21 Possible future work that is related to the findings of this thesis is detailed in this chapter.
22 This include numerical studies to further increase desalination performance,
23 investigating the use of other low-dimensional material, as well as identifying the
24 technical barriers preventing experimental verification and physical implementation of

1 such membrane. In addition, the adaptation of the low-dimensional membrane into
2 desalination systems is identified as one of the crucial areas that needs to be investigated.
3 Changes to current desalination system may have to be made to fully exploit the ultra-
4 high permeability that low-dimensional membrane system brings.

5

6 **Appendix**

7 The LAMMPS input scripts and datafiles generated for the simulations study in this
8 thesis is available for download at:

9 https://github.com/elisaaym/LDM_membrane_for_desalination_Molecular_Dynamics
10 [Studies](#)

11

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