Molecular dynamics study of transport mechanisms in desalination membranes

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**MOLECULAR DYNAMICS STUDY OF TRANSPORT
MECHANISMS IN DESALINATION MEMBRANES**

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**Interdisciplinary Graduate School
Nanyang Environmental and Water Research Institute**

2019

MOLECULAR DYNAMICS STUDY OF TRANSPORT MECHANISMS IN DESALINATION MEMBRANES

ZHANG HUI

**Interdisciplinary Graduate School
Nanyang Environmental and Water Research Institute**

A thesis submitted to the Nanyang Technological University in
partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

26 July 2019

Date

Zhang Hui

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

26 July 2019

Date

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Adrian W.K. Law

Authorship Attribution Statement

This thesis contains material from 3 paper(s) published in the following peer-reviewed journal(s) where I was the first and/or corresponding author.

Chapter 3 is published as Zhang, H., Liu, B., Wu, M.S., Zhou, K., & Law, A.W.K. (2017). Transport of salty water through graphene bilayer in an electric field: A molecular dynamics study. *Computational Materials Science*, 131, 100-107.

The contributions of the co-authors are as follows:

- A/Prof Law and A/Prof Zhou provided the initial project direction and edited the manuscript drafts.
- A/Prof Wu edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Liu and A/Prof Law.
- I performed the simulation work at NEWRI. I also analyzed the data.
- Dr Liu assisted in the set-up of model configurations and simulation scripts.

Chapter 4 is published as Zhang, H., Liu, B., Kieu, H.T., Wu, M.S., Zhou, K., & Law, A.W.K. (2018). Coarse-grained molecular dynamics study of membrane distillation through meso-size graphene channels. *Journal of Membrane Science*, 558, 34-44.

The contributions of the co-authors are as follows:

- A/Prof Law, A/Prof Wu, and A/Prof Zhou edited the manuscript drafts.
- I came up with the direction and prepared the manuscript drafts.
- A/Prof Law and Dr Liu revised the manuscript.
- I set up the model configuration, calibrated the force fields, and performed the simulation work at NEWRI. I also analyzed the data.

- Mr. Kieu assisted in the calibration of force fields and data analysis.

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- A/Prof Law revised the manuscript.
- I developed the methodology and performed the simulation work at NEWRI. I also analyzed the data.

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ABSTRACT

Abstract

Under the stress of water shortage and the need of reducing energy consumption, advancing the membrane technology continues to benefit the desalination applications. Research on transport mechanisms of desalination membranes drives the improvement of traditional membrane materials and development of novel membrane materials. It is challenging to use experimental approaches to probe solvent and solute transport at the nanoscale, thus making molecular dynamics (MD) simulations a necessary tool in the research of membrane transport.

The thesis is dedicated to investigating the relationships between membrane structure and membrane transport, with the objectives of improving the fundamental understanding and the tailored design of next-generation membranes. The polyamide (PA) layer in thin-film-composite membranes and graphene (GE) membranes were studied as the representatives of traditional membrane materials and novel nanomaterials, respectively. Throughout the thesis, the limitations and validations of MD as well as the implications of MD results to the classic macroscopic theories were discussed to address the utility of MD simulations.

Water and ion transport through GE bilayer in a vertical electric field was examined for pressure-driven desalination. The electric field slowed down the water transport inside the GE channels due to the increased interaction between

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water molecules and GE walls. Ions were either adsorbed on the GE wall or repelled from entering into the channel due to the electric field, both resulting in higher salt rejections.

Thermal driven membrane distillation process through meso-size GE layers was simulated using the coarse-grained MD to overcome the scale limitations of all-atom MD. The higher distillation fluxes through GE layer compared to the commercial microporous membranes were attributed to the evaporation enhancement at the GE-water interface as well as the reduced transport resistance of water vapour. Surface diffusion and activated Knudsen diffusion were identified as transport mechanisms for different channel opening. The lowest vapour transport resistance was found at the channel where only surface diffusion occurred. Besides, smaller channel opening was beneficial for water evaporation due to the elevated mobilities of the interface water molecules.

A new MD approach was developed to build and hydrate the PA thin films with varied monomer ratios. The digital membranes reproduced the realistic atomic compositions, structure, and properties such as density, membrane swelling, pore size distributions, and so on. Membrane swelling was linearly dependent on the degree of cross-linking (DC), and higher water flux was obtained in the more swelling-prone PA films due to the transition in water transport mechanisms. Continuum-like and jumping transport both occurred in PA films with smaller DC, where visible and more persistent channels existed. In the denser films, water molecules relied only on the on-and-off channels to

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jump from one cavity to another. The flux changes with respect to the driving pressure were non-linear for all the examined PA structures. The commonly used linear solution-diffusion (S-D) model was no longer valid at high pressure regime, and the nonlinearity resulted from the nonlinear density variations with pressure and the convective flow inside the membrane. The S-D model was improved to directly use the MD results and to account for the two non-linear factors.

In conclusion, membrane structures can be optimized in MD to enhance water transport and salt rejection. New molecular insights into the composition-structure-property relationships of desalination membranes were obtained, and the transport mechanisms were identified. Furthermore, molecular level interpretations of the classic macroscopic transport theories were highlighted.

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Chapter 1. Introduction

1.1. Background

Desalination is a process to remove salts and other minerals from saline water. It is an attractive potential solution to provide an alternative source of portable water from the seawater in the coastal environment. The history of desalination can be traced long before human beings are confronted with water shortage. Recorded in a Chinese story book *Gui Xin Za Zhi* by Zhou Mi from the Song dynasty, the legend of “sea well” describes a precious bucket that can turn seawater to drinking water for people going on a voyage.¹ A poet named Fan Chengda, also from the Song dynasty, suspected that the “sea well” functioned as a filter consisting of fish bones (reference).² Records in the west can also be found in Aristotle’s *Meteorologica*, in which a distillation process is described.³

Among the desalination processes recorded in the ancient literature, distillation was first adopted in a large scale in the Middle East region in 1930s.⁴ Distillation is a thermal driven process, in which water is vaporized by heat and then condensed to recover the desalinated water. Distillation remained the major desalination technique globally, until the emergence of membranes for pressure driven reverse osmosis (RO) desalination in 1960s.⁵ RO is currently the dominant technique for desalination due to the development of membrane technology. Particularly, thin-film-composite (TFC) membranes have largely advanced the large-scale industrial application and become the gold standard in RO

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desalination. Under the stress of water shortage and the need of reducing energy consumption, various other desalination techniques are also emerging such as capacitive deionization, membrane distillation, and forward osmosis. Meanwhile, advancing the membrane technology continues to benefit the desalination applications, in which the fundamental understanding of membrane transport plays an essential role.

Over the last few decades, debate has been focused on the transport mechanisms inside polymeric RO membranes. There are two major distinct mechanisms, the pore flow model over solution-diffusion (S-D), and currently the S-D model is more widely accepted.⁶⁻⁸ In the S-D model, solvents and solutes dissolved into the dense membrane, and then diffuse through the membrane matrix down a chemical potential gradient by “jumping” through the transiently connected gaps.^{6,9,10} However, researchers also revealed that convective flow may also occur in RO membranes, and the convective effect has been included as a correction term in the S-D model for highly swollen membranes.^{8,11} To enhance the transport efficiency and selectivity, researchers have also turned to channel-based biological membranes. A major focus is now on aquaporins protein channels where water can transport straight through and salts are rejected by amino acid gates.¹² Inorganic nanomaterials such as carbon nanotube (CNT) and graphene (GE) can also form channels with controllable diameter,^{13,14} which can provide rapid pathways for water and meanwhile reject solutes via size exclusion, electrostatic repulsion, and so on.^{15,16}

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Recent microscopic characterization methods and atomic scale simulations have advanced the understanding of S-D model and the discovery of new transport mechanisms. For example, Kłosowski, et al.¹⁷ observed the dynamic pore structure of polyamide (PA) layer in TFC membranes by scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM), and they found that the permeation of solutes relies on water solvation inside the membrane. Molecular dynamics (MD) simulations also revealed that the solutes can be trapped inside the pores of PA layer and hop into the next pore due to the dynamic nature of polymer, while the transport of ions rely on the water solvation.¹⁰ Graphene oxide (GO) membranes, with interlayer distance around 1 nm, can permeate water several-order-of-magnitude faster than commercial RO membranes.^{18,19} MD simulations attribute the fast water transport to the ultralow friction by the pristine GE walls and large boundary slip length of water molecules.^{20,21}

Meanwhile, the investigation into the influence of membrane structure and properties on transport leads to the tailored design of next-generation membranes for desalination. Studies show that PA TFC membranes with higher degree of cross-linking provide lower water permeability but higher salt rejection, and larger swelling volume of PA layer corresponds to higher water permeability and lower salt rejection.^{22,23} The interlayer distance of GE multilayer and CNT diameter play an essential part in water permeability by regulating the water structure inside the nanochannel.^{21,24,25} The functional group of GO also affect

the residence time of water molecules by hydrogen bonding, Vdw force, and electrostatic interactions.^{26,27} Systematic research of the structure-property-transport relationships can provide valuable guidance for membrane design at the molecular level so as to improve membrane efficiencies and reduce energy consumption in desalination.^{15,28}

1.2. Motivation

Experimental studies of membrane transport at the nanoscale rely on the microscopic characterizations of membrane structure using SEM, STEM, AFM, positron annihilation lifetime spectroscopy (PALS), and X-ray.^{17,29-31} However, the resolution of microscopic techniques cannot reach sub-nanometre for the moment, making the molecular-level analysis of transport mechanisms with relation to membrane structure and property very difficult using experimental approaches.^{7,15} Meanwhile, tracing the propagation of water and solutes through membranes in experiments is also very challenging, not only due to the imaging resolution, but also because the tracer with larger diameters may not reach smaller cavities and they also influence the pathways of other molecules.^{17,32} The fundamental understanding of membrane structure and transport at the molecular level is still in great need.¹⁵

MD simulation has thus become a necessary tool to investigate membrane structures and transport mechanisms, as well as to explore and design novel membrane materials.³³⁻³⁶ MD simulation is accelerated by the supercomputing

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hardware as well as efficient open-source software, yielding lower computational costs as well as extended time and spatial scales.^{37,38} However, to reduce computational cost and obtain broadly varied results, unpractical conditions are commonly applied.³⁹⁻⁴¹ Meanwhile, the force fields in MD simulations are empirical, and there are intrinsic limitations in spatial and time scales in MD. As such, it is of vital importance to conduct model validation and demonstrate statistical significance in MD simulations.⁴²⁻⁴⁴

One typical remaining problem is the molecular understanding of the structure-property-performance relationship of PA layer of TFC membranes. Although experimental studies have identified relationships of oxygen contents, degree of cross-linking, membrane swelling, average pore size et al. with water permeability and salt rejections,^{22,23,45-47} the underlying explanations remain unclear at the molecular level. Quite a few studies have managed to simulate the transport of water and solutes through PA thin films using MD, but unfortunately the membrane structures generated were either unvalidated or of single composition.^{9,10,48,49} Another relative topic is the molecular explanation and evidence of the prevailing S-D model, which will in return improve the macroscopic theory examined by experiments.

There also emerged new problems in membrane transport for membranes incorporated with nanomaterials, and simulations have largely contributed to the discovery of novel transport phenomena.^{24,25,39,50-52} However, when phase transition is involved, especially for evaporation, MD is less attractive for its

increased computational cost, since it requires longer sampling duration to obtain statistically significant results.^{36,53,54} Nanomaterials have been incorporated into desalination membranes for processes involving evaporation, including solar distillation, membrane distillation, pervaporation and so on,⁵⁵⁻⁵⁷ while little is known in terms of their function to enhance selectivity and permeability. It is thus of great importance to develop an approach to simulate evaporation related transport with moderate computational costs in MD.

1.3. Objectives

This thesis is targeted for the molecular investigation into the remaining and emerging problems of membrane transport for desalination. Specifically, membrane transport in pressure-driven nanofiltration and thermal-driven membrane distillation through graphene nanochannels, as well as RO desalination through cross-linked PA thin films will be examined.

In terms of methodology, the research is to develop an approach to build PA thin films in MD to reproduce realistic properties and to use coarse-grained MD to facilitate simulations of membrane distillation. Model validation and the influence of unrealistic modelling setup in MD will be highlighted.

The ultimate objective is first to improve the fundamental understanding of membrane transport and provide molecular implications to macroscopic theories. Secondly, the MD study of the composition-structure-property relationships will benefit the tailored design of next-generation membranes at the molecular level.

1.4. Dissertation outline

This thesis is organized into the following seven chapters.

Chapter 1 briefly introduces the research background of membrane transport for desalination from cross-linked polymeric membranes to channel-based nanomaterial membranes. It discusses the significance of the molecular-level investigations of membrane transport with respect to fundamental theoretical study and optimized design of membranes. Research objectives and thesis outline are presented. Chapter 2 summarizes in detail the research background and current progress of the thesis topic. It provides a review on microscopic structure and membrane properties of PA thin films and nanomaterials incorporated membranes. Transport studies of water and salts by experiments and simulations are also reviewed. It describes and summarizes MD approaches in building membrane structure, modelling desalination processes, and computing transport properties.

Chapter 3 presents the MD study of water and salt transport through GE nanochannels within electric field for nanofiltration. The influence of vertically imposed electric field is investigated. This chapter also highlights the effects of abnormally large pressure and electric field intensity on simulation results. Chapter 4 uses a validated coarse-grained MD approach to simulate membrane distillation through meso-size GE channels. Influence of channel opening, temperature, and hydrostatic pressure is investigated. It reveals transitions in

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water transport mechanisms for different channel opening and analyses the implications to macroscopic transport theories.

Chapter 5 describes the methodology of building and hydrating the PA layer in TFC membrane in MD simulation. The generated digital PA thin films can reproduce realistic membrane properties. It presents the composition-structure-property relationship of PA thin films and provides molecular explanations of experimental observations in terms of pore structure, membrane density, swelling, and permeability. Chapter 6 investigates the water transport mechanisms of PA thin films with different cross-linking degree. It also links the MD results to macroscopic S-D model.

Chapter 7 summarizes the major finding of the research and draws key conclusions. It emphasizes the significance of membrane transport study and proposes future work on solute transport mechanisms of salts and emerging pollutants.

Chapter 2. Literature Review

This chapter reviews the transport mechanisms through polyamide (PA) thin film composite (TFC) membranes and nanomaterial-based membranes. The former is the gold standard for RO desalination, and the latter demonstrate new transport phenomena for advanced membrane technology. Although the debut time of nanomaterial-based membranes is later than TFC membranes, their molecular-level research is more abundant due to the simpler molecular composition and structure of nanomaterials compared to polymer. As such, literatures on membrane transport in nanomaterials (with emphasize on graphene-based membranes) are reviewed before TFC membranes in this chapter. MD simulations provide the fundamental understanding of the experimental observations and macroscopic theories, which can also be used to validate the simulation results in return.

2.1. Membrane transport in nanomaterials

2.1.1. Nanomaterials in desalination membranes

Nanomaterials-based desalination membranes have been developed to overcome the limitations of polymeric membrane in wide pore distributions and unwanted pore flexibility,¹⁵ because narrowed pore distributions can increase the selectivity of solutes and rigid pore structures can provide more efficient pathways for water transport. Nanomaterials used in desalination membranes

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include carbon nanotube (CNT), graphene (GE) and graphene oxide (GO), metal-organic frameworks (MOFs), zeolites, aquaporins, and so on, the first three of which are reviewed in this section as the representatives of 1D, 2D, and 3D frameworks for desalination membranes, respectively, with the emphasize on GE-based membranes. Figure 2.1 gives the molecular structure of and the microscopic images of CNT, GE and GO, and MOFs based membranes.

Figure 2.1. Molecular structure of (a) CNT,⁵⁸ (c) porous GE single layer,⁵⁹ (e) stacked GO layers,⁶⁰ and (g) UiO-66 unit cell with octahedral cavity (pore size ~ 11 Å)⁶¹ (colour codes: H, white; C, grey; O, red; Zr, blue); (b) Cross-section SEM image of packed pristine ultralong CNTs;⁶² (d) STEM image of pores created on a pristine GE membrane using ion bombardment followed by chemical oxidation;⁵⁹ (f) Cross-section SEM image of a GO membrane;⁶³ (h) Top-view SEM image of an alumina hollow fibre supported UiO-66 membrane.

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CNTs and GE are 1D and 2D carbon nanomaterials with one-atom thickness, high mechanical strength, and high hydrophobicity. Individual CNTs and GE align themselves into a bundle or thin film by π -stacking. Different from CNTs which possess intrinsic pores with diameters of several nanometres⁶⁴ as shown in Figure 2.1a, a defect-free GE monolayer is impermeable. Various methods have been developed to create pores on pristine GE, including oxygen plasma etching,⁶⁵⁻⁶⁷ focused ion beam drilling,⁶⁸ ion irradiation and electron beaming,⁶⁹ as well as ion bombardment followed by chemical oxidation (Figures 2.1c-d)⁵⁹. Pore size can be tuned by the etching time, plasma exposure, and electron dose.^{59,66,67,69}

Despite the ideal thickness and tunable pores, the fabrication of porous monolayer GE is expensive and challenging at the industrial scale. The fabrication of multilayer GO membranes is relatively easier with lower cost and higher scalability. Multilayer GO membranes, as shown in Figures 2.1e-f, are typically produced by the filtration of GO dispersions on a filter support where GO nanosheets can be held together by the interlayer hydrogen bonds and form more stable clusters in water.^{60,70-72} GO nanosheets are obtained by chemical oxidation and ultrasonic exfoliation of graphite, known as the Hummers' method.⁷³ Improvements have been made to the Hummers' method by eliminating the use of NaNO_3 to make the process more environmental friendly.⁷⁴ Considerable progress has also been made in the repacking methods of GO nanosheets to enhance stability^{18,75,76} and for scaled-up production^{75,77}.

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Unlike the artificial pores generated on GE monolayers, GO films rely on the interconnected nanochannels to permeate water.^{20,78,79} The interlayer spacing of GO multilayers in Figure 2.1e is 6–7 Å, and the spacing can be expanded to 12–13 Å when immersed in water.^{60,80,81} GO membranes can achieve high water fluxes (at least one-order-of-magnitude higher than commercial nanofiltration membranes) owing to the capillary effect at the hydrophobic pristine GE region.^{27,63} Solutes are rejected via size exclusions as well as electrostatic interactions with functional groups.^{19,81,82} Water transport and solute rejection in pristine GE regions and functional group enriched regions are reviewed in details in Sections 2.1.2 and 2.1.3, respectively. The reduction of GO is achieved by thermal annealing, photoreduction, or microwave-assisted reduction.^{71,83–85} More than 90% of the oxygen content can be removed to enlarge the pristine GE region, but with a compromise of decreased stability in water.⁸²

GO and rGO can be fabricated into freestanding membranes, employed for membrane surface modification, or incorporated into polymer matrixes to form mixed matrix membranes (MMMs).^{78,86,87} These membranes are applied in various desalination processes. Due to the high water flux and good separation performance for large organic molecules and hydrated ions, GO and rGO membranes are used for nanofiltration (NF) and ultrafiltration (UF).^{76,77,86,88,89} GE and rGO doped PVDF membranes have been proven suitable for pervaporation and membrane distillation due to the enhancement in water vapour transport and membrane hydrophobicity.^{56,90} Besides, GO and rGO have been

synthesized into the electrodes to form intercalated 3D structures for capacitive deionization (CDI), which can facilitate ion transport and largely increase electrosorptive capacity.⁹¹⁻⁹³ Table 2.1 lists the GE-based freestanding membranes in various desalination applications in experiments.

Compared to CNTs and GE/GO, MOFs provide 3D pathways for water molecules as shown in Figure 2.1g. MOFs are often addressed as “soft porous crystals” because of the organic components.^{94,95} They possess flexible pore structures under the effects of solvent and external force.⁹⁶⁻⁹⁸ Hence, they show no clear “cut off” of the pore size and exhibit “gate opening” phenomenon similar with polymeric membranes, which could affect the separation performance of freestanding MOFs membranes.⁹⁹ However, the pore structure of MOFs is still considered rigid and can achieve molecular-sieving separation.^{100,101}

2.1.2. Liquid water transport in GE-based membranes

Table 2.1 lists the reported water fluxes in various desalination applications through GE-based membranes in experiments, and the mixed matrix membranes (MMMs) are not listed. Compared to commercial RO membranes,¹⁰² GE-based membranes can achieve up to two-order-of-magnitude enhancement in water permeability. Similar with other desalination membranes, water transport through GE-based membrane is under the combined influence of pore size, pore density, membrane thickness, functionalization, and so on, which can be tuned by varying the fabrication conditions.^{59,67,78,79,103}

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Table 2.1. Experimental investigations of GE-based desalination membranes

Membrane materials	Fabrication	Application	Pore size (nm)	Thickness (nm)	Functionalization	Water flux (m s^{-1})	Salt rejection (%)	Reference
Porous GE monolayer	Chemical etching	FO	0.162–0.5	One-atom thick		5×10^{-6} ($\Delta\pi=10$ atm)	-120	O'Hern et al. ⁸⁸
Porous GE monolayer	Ion bombardment + oxygen plasma etching	FO	0.25–1.5	One-atom thick		1.6×10^{-4} ($\Delta\pi=22.6$ atm)		Jang et al. ⁶⁷
Porous GE monolayer	Oxygen plasma etching	UF	0.5–1	One-atom thick		~ 1 ($\Delta P=0.17$ atm)	Nearly 100	Surwade et al. ⁶⁶
rGO	Filtration-assisted assembly	NF	<1	20-53	Oxidized groups	$0.45\text{--}3.0 \times 10^{-5}$ ($\Delta P=5$ atm)	20–60	Han et al. ⁷¹
GO	Layer-by-layer deposition	NF	~ 1	~ 28 (15 layers)	1,3,5-benzenetricarbonyl trichloride (TMC)	2.6×10^{-5} ($\Delta P=3.4$ atm)	6–46	Hu and Mi ¹⁸
GO	Vacuum filtration	UF	3–5	~ 1850	Copper hydroxide nanostrands	5.6×10^{-3} ($\Delta P=15$ atm)	~ 91	Huang et al. ²⁰
GO	Slow deposition by self-assembly	UF	0.69	> 4.7	Oxidized groups	2.8×10^{-5} ($\Delta P=5$ atm)	30	Xu, et al. ¹⁰⁴
GO	Vacuum filtration	FO	0.64–0.98	5×10^3	Oxidized groups	1.38×10^{-7} ($\Delta\pi=75$ atm)	97	Abraham, et al. ¹⁰⁵
GO	Vacuum filtration	Pervaporation	0.85	> 412	Diamines	$2.4\text{--}5.5 \times 10^{-6}$ ($T=90$ °C)	99.5–99.9	Qian et al. ¹⁰³
GE multilayer	Chemical vapour deposition	Membrane distillation	0.7	0.7-3.7		1.39×10^{-5} ($\Delta T=40$ °C)	100	Seo, et al. ¹⁰⁶

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The diameter of a water molecule is around 2.78 Å, so that pores with diameters of at least two vacancies of carbon atoms are able to permit water passage. The fast water transport through porous GE single layer is mainly attributed to the ultrathin thickness. However, compared to CNT nanotubes, porous GE membranes without functional group show lower permeate fluxes when the pore diameter is 0.78 nm, because the hydrogen bonds among water molecules break frequently when they pass through the pores so that the dipole reorientation slows down the water transport, as shown in Figure 2.2a.⁵² For larger pores of 2.75 nm, where water molecules no longer pass through the GE pores one by one, the permeate flux is larger than CNT tubes with the same diameter, because the entrance effect is eliminated due to the atomic thickness of single-layer GE.⁵²

Functional groups show significant influence on the water transport through porous GE monolayers. Hydrophobic pores, such as hydrogenated pores, impose an entropic penalty for the water passage, because water molecules must reorient into specific angles to traverse the membrane, as shown in Figure 2.2b. In contrast, hydrogen bonds can be formed when water molecules approach the hydrophilic pores, such as hydroxylated pores shown in Figure 2.2c, offering a smoother entropic landscape for water passage and thus allowing for faster permeation.⁵⁰ However, stronger interactions and steric effects between the more hydrophilic functional groups and water molecules lead to larger adsorption effect and lower water permeation.^{107,108} Gai et al. reported a reduced water flux

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through nitrating porous graphene (GN) compared to fluorinated porous graphene (GF) due to the increased interaction energy, as depicted in Figure 2.2d. Konatham et al. also reported that the water molecules encountered large energy barrier passing through nanoporous GE monolayers functionalized by charged groups, such as COOH^- and NH_3^+ .¹⁰⁷

Figure 2.2. (a) Hydrogen bond formation among water molecules through a GE nanopore with the diameter of 0.75 nm;⁵² (b) Angular distribution function (ADF) of water molecules with respect to the plane of the graphene membrane with hydrogenated pores, where blue colour indicates hydrogen atoms facing back to the membrane;⁵⁰ (c) Oxygen density map inside a hydroxylated pore of GE monolayer with open pore areas 28 Å², where oxygen atoms in water molecules more likely distribute around hydrogen atoms in hydroxyl groups of the pore and form hydrogen bonds;⁵⁰ (d) Higher water adsorption energy for nitrating porous graphene (GN) leads to a lower water flux through GN compared to fluorinated porous graphene (GF).¹⁰⁸

Water transport in pristine GE nanochannels had been reported in MD studies, featuring significant boundary slips (slip length larger than 60 nm)¹⁰⁹ due to the low friction with hydrophobic GE sheets and resulting in remarkable flux enhancement.^{27,40} The high water flux is also attributed to the capillary force of

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2D GE channels.²¹ However, oxygen-content functional groups in GO reduced the water velocity by two orders of magnitude due to the weakened boundary slip by hydrogen bonds.^{27,110,111} As such, Wei et al.²⁷ attributed the main cause of faster transport in GO membranes to the expanded microporous structures formed by the wrinkles, holes, and interlayer spaces of the GO sheets. Meanwhile, the reduction of oxidized groups in rGO can also facilitate the faster water transport by enhancing the boundary slip.^{27,83}

It has been identified in first-principle calculations and MD simulations that water molecules form monolayer, bilayer, and three-layer structures inside GE and GO channels with the interlayer distance of around 0.6, 0.9, and 1.2 nm respectively, as shown in Figure 2.3a.^{27,40,112} It was speculated by Nair et al. that water molecules form a highly ordered monolayer (Figure 2.3b) in pristine GE channels when the interlayer distance is 0.7 nm.⁶³ The speculation was overthrown by Muscatello et al. using MD simulations showing that significant mixing of water molecules occurred even for the monolayer water structure inside GE channels, as shown in Figure 2.3c.¹¹³ The mixing of water molecules indicates the hydrodynamic behaviour inside GE membranes remains continuous, which is consistent with recent studies that continuum hydrodynamic theories are still valid for the prediction of water flow in GE membranes, given that the viscosity change, entrance effect and boundary slip are accounted for.^{114,115} However, Jiao and Xu¹¹⁶ confirmed using MD simulations that water molecules formed highly ordered solid-like structures as depicted in Figure 2.3b, but only

at a specific temperature range and with certain number of water molecules.¹¹⁶ Moreover, no highly ordered water structure is observed in oxygen rich regions in GO membranes, because the hydrogen bonds formed between water molecules and the functional groups can disrupt the hydrogen bond network among water molecules (Figure 2.3d).^{27,111,116}

Figure 2.3. (a) Layered water structure inside pristine GE channels;⁴⁰ (b) Speculated water transport mechanisms with highly ordered and hydrogen bonded monolayer network inside GE nanochannels;⁶³ (c) MD results on mixing of water molecules inside the GE membranes;¹¹³ (d) Interactions of water molecules with oxidized functional groups in GO membranes.¹¹¹ In (a) and (b), white, red, and green balls represent hydrogen, oxygen, and carbon atoms respectively, while in (c) white, red, and grey sticks represent hydrogen, oxygen, and carbon atoms respectively.

2.1.3. Water vapour transport in GE-based membranes

The transport mechanisms of water vapour inside GE/GO membranes are less investigated compared to the liquid phase. The filtration-based desalination applications involving phase transfer from liquid to vapour water include membrane distillation and pervaporation. Membrane distillation is a thermal-

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driven separation process with phase transition occurring at the hydrophobic membrane surface, and only vapour can pass through the microporous membrane. Membrane wetting should be avoided to achieve stable and high salt rejection. Besides the freestanding multilayer GE fabricated by Seo et al.¹⁰⁶, GE and rGO flakes can also be doped in PVDF microporous membranes to improve hydrophobicity and facilitate fast water vapour transport.^{117,118} So far, no MD simulations have been conducted for membrane distillation process.

Pervaporation is also a thermal-driven separation process, and the membrane used is dense and hydrophilic. The phase transfer could happen both inside the membrane and at the permeate membrane surface, as shown in Figure 2.4. The water transport in pervaporation is generally described as a solution-diffusion-evaporation process. However, disagreements were raised on the phase transfer in GO layers. Chong, et al.¹¹⁹ suggested that the phase transition area should be extended to the whole membrane surface (Figure 2.4b) to match the high water fluxes obtained in experiments, otherwise water evaporation would be abnormally slow. However, Li, et al.¹²⁰ proposed a four-stage transport mechanism as shown in Figure 2.4c where the phase transition took place inside the GO nanochannels, so that it explained the unchanged flux with different number of GO layers. A more recent MD study (Figure 2.4d) showed that the phase transition occurred at the permeate surface of GE membrane for the separation of ethanol and water. The location of phase transition could be related to membrane hydrophilicity, tortuosity, and the driving force.

Figure 2.4. (a and b) Schematic illustrations of water transport mechanisms inside GO membranes for pervaporation;¹¹⁹ (c) Schematic diagram of water transport and salt rejection in GO membranes for pervaporation;¹²⁰ (d) Snapshot of MD simulations for ethanol/water mixture separation using pervaporation through GE nanochannels, where while, red, and green sticks represent hydrogen, oxygen, and carbon atoms respectively.¹²¹

Besides the literature on membrane distillation and pervaporation mentioned above, the water vapour transport inside GE/GO nanochannels have also been discussed for gas separation. Kim, et al.¹²² fabricated two types of GO membranes with different stacking methods, where water vapour and other gas molecules transported through the less interlocked GO membrane via Knudsen diffusion and through the highly interlocked GO membrane via molecular sieving, but the membrane structure such as interlayer spacing was not characterized.¹²² The Knudsen number was calculated to be 1–10 for water vapour transport in GE nanochannels with diameter ranging 7.6–50 nm, which was within the regime of molecular flow.⁶⁸ However, molecular sieving, surface diffusion, and Knudsen diffusion all fall into the regime of molecular flow. As such, it remains unclear how GE/GO structure affects the transport behaviour.

2.1.4. Salt rejection in GE-based membranes

In Table 2.1, the salt rejection for GE/GO membranes in pressure-driven desalination is generally not as good as thermal-driven desalination. Several mechanisms of ion rejection have been suggested for GE/GO membranes in pressure-driven desalination, mainly including size exclusion, steric effect of the hydration shell, and electrostatic repulsions (Figures 2.5a-b).⁸² The diameters of hydrated ions are in the range of 6–10 Å as shown in Figure 2.5c, while the diameter of a water molecule is ~2.8 Å as mentioned previously. Theoretically, ions can be selectively rejected if the pore size and interlayer spacing are well controlled. However, high permeation rates were observed for hydrated ions with diameter larger than 9 Å through GO membranes with interlayer distance smaller than 9 Å.¹⁰⁵ Meanwhile, as shown in Figure 2.5d, the permeation rates of ions increase exponentially with respect to interlayer spacing, while it is only linear increase for water molecules, indicating other transport mechanisms exist besides the size exclusion.¹⁰⁵ Abraham et al.¹⁰⁵ used MD simulations to further investigate the ion transport mechanisms. They found that the hydration shells were partially peeled off as ions entered into the GE nanochannels (Figure 5e), posing extra energy barrier for the ion transport.

Electrostatic interactions of ions with GO membranes also play an important role in salt rejections. In Figure 2.5c, Rb^+ and Cl^- are of similar sizes, but the permeation rate of Cl^- through GO membranes is smaller than that of Rb^+ due to the repulsive interaction with the oxidized functional groups carrying

negative charges.¹²³ The electrostatic interactions also account for the membrane structure change in different solutions.¹²⁴ For example, the hydroxyl and carboxyl groups in GO membranes are more ionized in the NaOH solution due to the interactions with OH⁻, resulting in the increased interlayer distance of GO membranes and higher ion permeation rates.¹²⁴ More interestingly, the adsorption interactions between hydrated cations and the aromatic rings in GO membranes (cation- π interactions) can also facilitate the control of interlayer spacing in the fabrication of GO membranes via a drop-casting method.¹²⁵

Figure 2.5. (a & b) Schematic illustrations of the ion rejection mechanisms for nanoporous GE monolayer and GO multilayer membranes respectively;⁸² (c) Experimental results on the permeation rates (p) as a function of hydrated radius (R_H) for different cations (circles) and corresponding Cl⁻ (squares), where the red square represents the Cl⁻ permeability in RbCl solution with similar R_H for both ions;¹²³ (d) Experimental results on the exponential and linear dependence of permeation rates for cations (left axis) and water (right axis) on the interlayer distance respectively, where the horizontal error bars indicate the half-width for the diffraction peaks in interlayer distance characterization, and the vertical error bars indicate the standard deviations;¹⁰⁵ (e) MD simulation results on the decrease of the water molecule number n in the first (solid line) and the second (dashed line) hydration shells as an ion enters in a GE channel with the interlayer distance of 0.7 nm.¹⁰⁵

2.2. Water transport in polyamide layer of TFC membranes

The Polyamide (PA) thin-film composite (TFC) membrane is currently the mainstream product for reverse osmosis (RO) desalination, due to its good stability in various pH as well as exceedingly high water permeability and salt rejection compared with first-generation cellulose RO membranes.^{28,126} A TFC membrane consists of a “dense” PA active layer, a microporous polysulfone support, and a woven polyester substrate, with the PA thin film playing the key role in salt rejection and dictating the water flux. Despite the numerous efforts in improving the performance of PA membrane in the past decades, the fundamental understanding of the underlying membrane structure and transport has been largely empirical, especially at the nanometer or sub-nanometer scale.^{15,29,127} This section reviews the research efforts on water transport mechanisms in the PA layer of TFC membranes from the macroscopic theories to the microscopic observations and MD simulations.

2.2.1. The solution-diffusion model

The PA layer is formed via interfacial polymerization (IP) reaction at the aqueous-organic interface commonly between *m*-phenylenediamine (MPD) in the aqueous solution and trimesoyl chloride (TMC) in the organic solution, as shown in Figure 2.6a. The PA layer is considered as a dense film in the solution-diffusion (SD) model, and the penetration of water consists of three steps, i.e. adsorption, diffusion, and desorption (Figure 2.6b). The diffusion process can be

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described using the Fick's law, which is driven by a chemical potential gradient, mainly concentration differences, as shown in Figure 2.6c. The pressure stays the same inside the membrane, indicating that the pressure is not the direct driving force as stipulated in the pore-flow model.

Figure 2.6. (a) Schematic illustrations of general synthesis method of polyamide (PA) thin-film-composite membranes;¹²⁷ (b) Transport of solvents and solutes through the PA layer follows the solution-diffusion mechanism where molecules partition into, diffuse through, and desorb from the PA thin films;²⁸ (c) Chemical potential μ , pressure p , solvent concentration w , and solvent activity a in a PA layer for pressure-induced diffusion;¹²⁸ (d) Schematic illustration of the nonlinear flux-pressure relationship based on the solution-diffusion model, where insets show concentration profiles in the membrane.¹²⁸

For a binary system consisting of only pure water molecules and a membrane, according to the Fick's law, the water flux across the membrane can be written as¹²⁹

$$\mathbf{n}_1 = w_1(\mathbf{n}_1 + \mathbf{n}_m) - \rho D_{1m} \nabla w_1, \quad (2.1)$$

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where $\mathbf{n}_1$ and $\mathbf{n}_m$ are the mass fluxes of water and membrane respectively, w_1 is the mass fraction of water at any position in the membrane, ρ is the mass density of the hydrated membrane (plus water), D_{1m} is the diffusion coefficient of water in the membrane. The first term on the right of Eq. (2.1) is a convective term which is often neglected when the water content in the membrane is small. But for the more swelling prone membranes with larger w_1 , the convective term can be significant. At the steady state, $n_m=0$. With an unidirectional flow, the Fick's law can be written as

$$n_1 = -\frac{\rho D_{1m}}{1-w_1} \frac{dw_1}{dz}. \quad (2.2)$$

Assuming that ρ and D_{1m} are independent of w_1 , the integrated form of Eq. (2.2) is

$$n_1 = \frac{\rho D_{1m}}{l \langle w_m \rangle} (w_{10} - w_{1l}), \quad (2.3)$$

where w_{10} and w_{1l} are the water mass fractions at the upstream and downstream side of the membrane respectively (Figure 2.6c), l is the thickness of the hydrated membrane, and $\langle w_m \rangle$ is the average membrane mass fraction and can be expressed as¹²⁹

$$\langle w_m \rangle = \frac{w_{10} - w_{1l}}{\ln((1-w_{1l})/(1-w_{10}))}. \quad (2.4)$$

As shown in Figure 2.6c, the water activity in the solution a_{10}^s is the same with the activity in the membrane a_{10}^m at the upstream side. However, at the

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downstream side, the discontinuity of pressure generates different activities in the solution a_{1l}^s and the membrane a_{1l}^m as follows:¹²⁸

$$a_{1l}^m = a_{1l}^s e^{-\bar{V}_1(p_0 - p_l)/RT}, \quad (2.5)$$

where the $\bar{V}_1$ is the average molar volume of water, p_0 and p_l is the upstream and downstream pressure respectively, R is the gas constant, and T is the temperature. Again, in the binary system consisting of only pure water molecules and the membrane, $a_{10}^s = a_{1l}^s = 1$. Assuming solution ideality, the mass fraction can replace the activity in Eq. (2.5) directly, and

$$w_{1l} = w_{10} e^{-\bar{V}_1(p_0 - p_l)/RT}. \quad (2.5)$$

Thus, Eq. (2.3) becomes

$$n_1 = \frac{\rho D_{1m} w_{10}}{l \langle w_m \rangle} (1 - e^{-\bar{V}_1 \Delta p / RT}), \quad (2.6)$$

where the pressure difference is designated as Δp . Eq. (2.6) describes the diffusion process in the membrane, and the partitioning process in Figure 2.6a can be expressed as

$$C_{10}^m = K_1 C_{10}^s \quad (2.7a)$$

$$C_{10}^m = \rho w_{10}, \quad (2.7b)$$

where C_{10}^m and C_{10}^s are the upstream mass concentrations of water in the membrane and solution respectively, and K_1 is the partitioning coefficient. Commonly, the mass concentrations of water in the hydrated membrane and the

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solution at the equilibrium state can represent C_{10}^m and C_{10}^s , respectively.

Therefore, Eq. (2.6) becomes

$$n_1 = \frac{D_{1m} K_1 C_{10}^s}{l \langle w_m \rangle} (1 - e^{-\bar{V}_1 \Delta p / RT}). \quad (2.8)$$

Eq. (2.8) shows that the water flux is not linearly dependent on the pressure difference. Two factors could contribute to the non-linearity, i.e. the convective flow and exponential term. The non-linearity caused by convective flow is raised by $\langle w_m \rangle$, as shown in Eq. 4, which is assumed as 1 if the water content of the membrane can be neglected. If the water content remains unchanged under different pressure, $\langle w_m \rangle$ can also be treated as a constant, which can be excluded from the cause of the non-linearity. If the non-linearity is solely caused by the exponential term, the flux-pressure relationship exhibits the trend in Figure 2.6d, which reaches to a finite plateau eventually. The exponential term can be approximated as a linear expression ($e^{-x} \approx 1 - x + \dots$) when x is small enough. For the water-membrane binary system, the linear approximation is valid unless Δp reaches over 136 atm.¹²⁸ Based on the simplification and assumptions above, the commonly seen linear form of Eq. (2.8) can be expressed as follows:

$$n_1 = \frac{D_{1m} K_1 C_{10}^s \bar{V}_1 \Delta p}{l R T}. \quad (2.9)$$

For saline waters, the separation is achieved by different partitioning and diffusion coefficients in the membrane, as shown in Eq. (2.9). However, the relationship between the adsorption/diffusion coefficients with membrane

structure remains unclear, especially at the molecular level. Besides, understanding the transport mechanisms of water and solutes at the molecular level can provide insight on whether the linear solution-diffusion model is valid.

2.2.2. Polyamide thin films under the microscope

The composition-structure-property relationships of the PA layer has been extensively investigated to improve membrane performance. Microscopic techniques have advanced the characterizations of the PA layer for both chemical compositions and internal structures. The chemical compositions can be obtained from the Rutherford backscattering spectrometry (RBS) and X-ray photoelectron spectroscopy (XPS).^{23,130} One crucial indicator is the O/N ratio, from which the degree of cross-linking (DC) is commonly calculated as follows:

$$\frac{O}{N} = \frac{3x + 4y}{3x + 2y}, \quad (2.10a)$$

$$x + y = 1, \quad (2.10b)$$

$$DC = \frac{x}{x + y} \times 100\%, \quad (2.10c)$$

where x and y represent the fractions of the fully cross-linked ($C_{18}H_{12}O_3N_3$) and linear ($C_{15}H_{10}O_4N_2$) repeating units in the PA structure respectively. Higher O/N results from the larger fraction of linear units and yields lower DC, which allows larger membrane swelling and increased water flux.^{23,29,46}

Positron annihilation lifetime spectroscopy (PALS) characterizations revealed the bimodal pore distributions in PA thin films in Figures 2.7a-b.⁴⁶ The

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bimodal pore distributions are confirmed by the bimodal pKa distributions of carboxylic groups.¹³⁰ Pores in the PA layer were observed using scanning electron microscope (SEM), as shown in Figure 2.7c, but these pores are larger compared to the PALS observations, because they are formed by the void spaces between the polymer “nodules” in the ridge-and-valley structure, as shown in Figure 2.7d.³¹ The interconnected free volume pores contradicts the solution-diffusion model which is based on the non-porous assumption.

Figure 2.7. (a) Free volume hole size distributions of polyamide thin films measured by Positron annihilation lifetime spectroscopy (PALS);⁴⁶ (b) Schematic illustrations of two types of pores in polyamide thin films;⁴⁶ (c) Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images of a polyamide thin film back surface, where the white line on the AFM image indicates the cross-sectional height of the SEM image, and yellow and red colours highlight the conspicuous nodule and pore opening respectively;³¹ (d) Cross-section transmission electron microscopy (TEM) image of a polyamide thin film,³¹ where the red square shows the domain size able to be simulated using molecular dynamics.

Moreover, using the TEM topology images, Pacheco et al. observed open voids at the front side of the PA layer, but none was found at the back side indicating the front side is denser than the back side due to the structure heterogeneity of PA thin films across the depth direction.³¹ In the IP process, MPD molecules diffuse from the aqueous solution to organic solution, and its concentration changes from abundant to insufficient resulting in the depth heterogeneity in oxygen content of PA thin films.¹³¹ The depth heterogeneity had also been reported by Coronell et al.¹³⁰ that O/N at the surface region is 8–46 % higher than the bulk average. The “sandwich structure” of hydrated PA thin films was discovered by Freger²² and Drazevic et al.⁴⁵ that a dense core layer is hidden within more swelling-prone and porous PA structures at the front and back.

2.2.3. Implications from molecular dynamics simulations

MD simulations have also aggressively advanced the understanding of PA structure and transport mechanisms of PA thin films.^{10,48,49,132-134} The ridge and valley structure as well as the void opening formed by nodules in Figure 2.7c commonly cannot be simulated using MD, because the spatial scale of MD is in the range of nanometres. The red square represents the domain size in MD, which is beyond the resolutions of current microscopic imaging technologies. Similar with the PALS results in Figure 2.7a, dry PA structures generated in MD simulations also showed bimodal pore distributions, as shown in Figure 2.8a.⁴⁸ Water molecules occupy the vacancies in the PA structure either discretely or form clusters in Figure 2.8b. Interestingly, Kolev and Freger¹³³ observed only

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unimodal water number distributions around the carboxylic groups in the PA thin film (Figure 2.8c), indicating unimodal pore size distributions. The difference may be due to the polymerization approach or the compositions of the PA films investigated. There is no MD study reporting the composition-structure relationships so far.

Muscatello et al.¹³¹ applied an advanced coarse-grained MD approach to mimic the interfacial polymerization (IP) process. The structure of the generated PA thin films is depicted in Figure 2.8d, exhibiting surface roughness and depth heterogeneity. Their structure characteristics stem from the IP process, where TMC in the organic solution at the top reacts with MPD in the aqueous solution at the bottom and forms cross-linked structures. The diffusion of monomers is halted by the formed cross-linking structures, resulting in the higher concentrations of unreacted O and N at the top and bottom, respectively. The residual O and N atoms appear in the carboxylic and amine groups after hydration, represented by the red and dark blue dots in Figure 2.8d (left). The depth heterogeneity is also apparent in the degree of cross-linking, where the cross-linked amide bonds (cyan dots in Figure 2.8d) are less dense at both surfaces compared to the middle region. The surface roughness resulted from the aggregations of cross-linked PA is comparable to the experimental measurement of smooth PA films (without ridge-and-valley crumples) by Karan, et al.¹³⁵

Figure 2.8. (a) Pore radius distributions of a dry polyamide (PA) thin film generated in molecular dynamics (MD) simulations and (b) the configuration of the hydrated PA thin film;⁴⁸ (c) Distribution of water molecular numbers (N_w) found within 0.7 nm from the carboxylic groups (COOH);¹³³ (d) Front view of the PA structure in coarse-grained MD simulations, where red and blue dots respectively represent O and N atoms in the left image, while in the right image, cyan, red, and dark blue dots represent N atoms in the cross-linked amide bonds, O atoms in the hydroxyls of COOH groups, and N atoms in the amine groups respectively.¹³¹

Continuous efforts have been devoted to identify the water transport mechanisms using MD simulations, with the conclusion that both “jumping” and hydrogen-bonded continuum water transport exist in PA membranes.^{133,136-138} For the jump mechanism, the residence time of water molecules in a cavity before a “successful” jump is 1–2 ns or longer.^{10,127,136} The jump event takes place within only a few picosecond and the length is several angstroms, as shown in Figure 2.9a.^{127,136,139} By contrast, the trajectories of water molecules passing through a relatively straight pore in Figure 2.9b are similar to continuum flow. The jumping mechanism corresponds to the solution-diffusion model, and the continuum-like mechanism to the pore-flow model. However, the fraction of either transport

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mechanism inside the PA layer remains unclear. There is no MD study so far to investigate the influences of atomistic composition and polymer structure on water transport, which is essential in improving membrane design at the molecular level.

Since the PA thin films are highly cross-linked and heterogenous, it is very difficult to compute the free energy profiles of water transport in MD simulations. Gao et al.¹³⁶ computed the free energy change of water transport through a relatively straight pore and found that a high energy barrier of 63 kcal mol⁻¹ must be overcome for the water molecules to be transported to the centre of the membrane. Araki et al.³³ used a different approach to calculate the Gibbs free energy change $\Delta G(z)$ from the density profiles using the following equation.

$$\Delta G(z) = -k_B T \log[\rho(z) / \bar{\rho}] \quad (2.11)$$

where k_B is the Boltzmann constant, T is the temperature, $\rho(z)$ is the water density along the z direction, and $\bar{\rho}$ is the average water density in the membrane. The calculated energy barrier in Figure 2.9d is one-order-of-magnitude smaller than 63 kcal/mol reported by Gao et al.¹³⁶ However, Eq. (2.11) is based on the assumption of no pressure change across the membrane in the solution-diffusion model, which has not been proven by MD so far. The difference could be a consequence of neglecting the pressure change or different PA structure investigated.

Overall, while MD simulations have been useful to study the transport mechanisms, the implications to the macroscopic theories and the guidance for

structure optimization are still limited. The randomness of PA compositions and structures generated in MD should be resolved to investigate the composition-structure-property relationships. The solution-diffusion model should be re-examined using MD simulations.

Figure 2.9. Trajectories along the z direction of selected water molecules transporting through (a) a dense PA film and (b) a PA film with relatively straight pore under 3.0 MPa pressure gradient, obtained from molecular dynamics (MD) simulations;¹³⁶ (c) Density profiles of water and a PA thin film along the flow direction in MD simulations;³³ (d) Free energy changes along the flow direction of water and NaCl.³³

2.3. Molecular dynamics simulations of membrane transport

As discussed above, MD simulations have become a suitable tool to explore the transport mechanisms for desalination membranes as well as to optimize the membrane structure so as to enhance the desalination performances.

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Examples have been given in Sections 2.1 and 2.2. This section summarizes the methodologies of MD, including the fundamental equations, force fields, and commonly computed transport parameters. Validations of MD models are also highlighted.

2.3.1. Fundamentals of molecular dynamics simulations

MD is basically a computational method to calculate the movement of atoms using the numerical integration of the Newton's equation of motion as

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = - \frac{dV}{d\mathbf{r}_i}, \quad (2.12)$$

where m_i , $\mathbf{r}_i$, and V are the mass, coordinate, and potential energy of the i th atom.

The potential energy includes externally imposed potential field as well as bonded and non-bonded interactions as follows

$$V = V_{\text{external}} + V_{\text{L-J}} + V_{\text{Coul}} + V_{\text{Bonds}} + V_{\text{Angles}} + V_{\text{Dihedrals}} + V_{\text{Impropers}}, \quad (2.13)$$

where the first three terms account for the non-bonded interactions, including external potential field V_{external} , Lenard-Jones potential $V_{\text{L-J}}$, and Coulumbic potential V_{Coul} , respectively, while the other four terms account for the bonded intramolecular interactions from bonds, angles, dihedrals, and impropers, respectively.

There are a variety of potential energy functions, or force fields, which are developed experimentally or theoretically and in different forms. Commonly used force fields include CHARMM,¹⁴⁰ AMBER,^{141,142} and OPLS¹⁴³ which are

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geared to large molecules (polymers and biomolecules) in the condensed phase, as well as REBO¹⁴⁴ and AIREBO¹⁴⁵ which are suitable for hydrocarbon systems. These force fields are empirical functions validated by thermodynamic properties and quantum mechanical calculations, and they allow no bond breaking. Reaxff,¹⁴⁶ instead, is able to simulate chemical reactions through bond breaking and forming based on the bond order functions, but it is only suitable for systems with one or two thousands of atoms. For larger and more complex systems such as biomolecules, it is sometimes of interest to look at the bigger picture with longer durations, so coarse-grained force fields are necessary to simplify the molecular structures and accelerate the computation at the expenses of accuracy and transferability.

The integration of Eq. (2.12) in this study follows the Velocity-Verlet scheme¹⁴⁷ which predicts the coordinate $\mathbf{r}_i$ and velocity $\mathbf{v}_i$ over a time step δt and can be expressed as

$$\mathbf{r}_i(t + \delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t) + \frac{\mathbf{a}_i}{2} \delta t^2, \quad (2.14a)$$

$$\mathbf{a}_i(t + \delta t) = -\frac{1}{m} \frac{\partial V}{\partial \mathbf{r}_i(t + \delta t)}, \quad (2.14b)$$

$$\mathbf{v}_i(t + \delta t) = \mathbf{v}_i(t) + \frac{\mathbf{a}_i}{2} (t + \delta t) \delta t. \quad (2.14c)$$

The Velocity-Verlet algorithm has been the most commonly adopted scheme because it is simpler, faster and requires less computer storage space. The standard implementation of this algorithm is as follows:

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- (1) Given $\mathbf{r}_i$ and $\mathbf{v}_i$ at a certain time step, computing $\mathbf{a}_i$ based on the force fields;
- (2) Updating $\mathbf{r}_i(t + \delta t)$ using Eq. (2.14a);
- (3) Computing the force fields at the new coordinate $\mathbf{r}_i(t + \delta t)$ and updating $\mathbf{a}_i(t + \delta t)$ using Eq. (2.14b) based on the force fields;
- (4) Calculating $\mathbf{v}_i(t + \delta t)$ using Eq. (2.14c).

The thermodynamics of MD systems can be described using a statistical-mechanical ensemble, so that the macroscopic thermodynamic properties can be computed by the evolutions of the MD system. In the microcanonical (*NVE*) ensemble, the total atom number, volume and energy are constant while the temperature may change, which corresponds to an adiabatic system without any heat transfer. The canonical (*NVT*) ensemble conserves the atom number, volume and temperature, allowing heat exchanges with the environment. In the isothermal-isobaric (*NPT*) ensemble, the amount of atom, pressure and temperature are conserved, where a barostat is needed in addition to a thermostat. The *NPT* ensemble is closest to the laboratory experiments conducted under ambient pressure and temperature.

2.3.2. Computing membrane transport properties

MD simulations of membrane-based desalination processes are conducted in both thermodynamic equilibrium or nonequilibrium conditions. The difference between the equilibrium MD (EMD) and nonequilibrium MD (NEMD)

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simulations is whether the simulation is to eliminate the chemical potential gradient or to maintain the chemical potential gradient. In other words, the EMD should be used for self-driven process, and NEMD for externally-driven process. Specifically, for membrane-based desalination, EMD is helpful to investigate the intrinsic membrane properties and self-diffusivities of solvent and solutes inside the membrane, while NEMD is necessary to obtain the membrane transport properties under externally imposed driving forces.^{35,148}

The most commonly investigated transport property in EMD is the self-diffusivity D_s , measuring the translational mobility of atoms. The self-diffusivity is linearly related to the increase of mean square displacement (MSD) over time. To reduce statistical errors, D_s of a species j is defined from averaging Einstein's equation over a large enough number of atoms, N , and a long enough sampling duration t as¹⁴⁹

$$D_s = \left(\frac{1}{6N}\right) \sum_{i=1}^N \lim_{t \rightarrow \infty} \frac{1}{t} \left\langle \left| \mathbf{r}_i(t) - \mathbf{r}_i(0) \right|^2 \right\rangle, \quad (2.15)$$

where $\mathbf{r}_i(t)$ is the position of the i th atom of species j at time t compared to the initial position $\mathbf{r}_i(0)$, and N is the total number of sampled atoms of species j . In contrast, the transport diffusivity D_t is defined in the Fick's law under nonequilibrium conditions where a macroscopic concentration or chemical potential gradient is present as

$$J = -D_t \nabla C_j, \quad (2.16)$$

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where J is the flux of species j under the concentration gradient ∇C_j . The transport diffusivity can be obtained directly from NEMD simulations with concentration gradient, typically driven by an external perturbation.^{150,151} Under certain circumstances, especially when gas is involved, it is difficult to compute the concentration (or partial pressure) in MD, so other methods are necessary to compute D_t , such as the statistical analysis of transmission probabilities¹⁴⁸ and the thermodynamic corrections of D_s from EMD simulations.^{152,153}

As discussed in Section 2.3.1, the movement of atoms is under the control of the potential energy. As such, the interaction energy between the solvent/solute molecules with the membrane is critical to understand the dynamics of transport behaviours.^{40,154,155} By mapping the potential energy surface (PES), Tocci et al.¹⁵⁵ found that despite the similar structure of graphene and boron nitride, the interaction energy of water molecules with the boron nitride is more corrugated compared to graphene, which explains the low friction of water transport along the graphene surface. With respect to the free energy analysis of transport behaviours within the investigated system under certain driving force, the computation of potential of mean force (PMF) in NEMD should be conducted, which dictates the transport speed and selectivity.^{136,156,157} Various methods have been established to compute PMF, including adaptive biasing force, steered molecular dynamics and umbrella sampling.

Static local characterizations, such as radial distribution functions (RDF) and mass density distributions, are also necessary to interpret the influence under

the nano-confinement of membrane structures. For example, RDF describes the density variation as a function of distance from a reference atom, which can be used to analyse the portioning of solvent/solutes around the reference. Kang, et al.¹⁵⁸ compared the RDF curves of Na^+ around O atoms at two types of graphene nanopores, and explained the different selectivity of the nanopores. Similarly, the water density distributions inside the membrane, as shown above in Figure 2.9, not only give the direct information of water content but also play the crucial role in understanding other physical processes such as surface adsorption and phase transitions at the interface.

2.3.3. Validation of MD simulations

Numerical simulations of the physical world always involve certain degree of approximation and idealization, thus requiring validation to guarantee the reliability of the numerical methods. With the growing use of MD simulations in academic and industrial research, it is of vital importance to conduct validation. However, most MD simulations cannot be completely validated via the experimental data, especially when they address problems that are not clear and concrete. van Gunsteren et al.⁴³ summarized that under such circumstances, the quality of MD simulations should be considered and reported in terms of the accuracy of the force fields, convergence of thermodynamic properties, statistics of sampling, as well as the reliability of the software used. When experimental data are available for comparison with MD results, care should be taken with respect to the uncertainty and error of the experimental measurements,

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configurational dependence of MD results, as well as the time and spatial scale to which the results are averaged.⁴³

In most MD simulations of membrane-based desalination processes, the direct validation of MD results through desalination experiments is impossible because of the idealization and simplifications of the MD configurations. For example, due to the spatial scale of MD, the simulated membrane is limited to nanometres in thickness, and the influence of substrates cannot be assessed. The real membrane structures are sometimes heterogeneous with pores in a certain size distribution, but the MD model is often simplified to a homogeneous structure. As such, MD is typically used to explain experimental observations, and for now there is no report for MD-guided experiments for membrane-based desalination processes. However, there are still several ways to enhance the utility of MD results, including using realistic and dynamic membrane structures, validation of membrane material properties, analysing the statistics of sampling, applying practical operating conditions, and so on.

As discussed in Section 2.1, the interlayer spacing of multilayer graphene oxide (GO) membranes expands after hydration due to the existence of oxidized functional groups, which largely influences the transport of water and solutes.^{60,80,81} However, in earlier MD simulations, GO desalination membranes were simplified as a slit-pore configuration consisting of rigid and unoxidized graphene (GE) walls with a fixed interlayer distance.^{21,27,113} The absence of oxidized functional groups resulted in overestimated transport dynamics and

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incorrect analysis of pore diameter.^{111,159} Other researchers included more complexity by accounting for the functional groups and flexibility of channel walls, but still without the considerations of membrane dynamics.^{111,115,159} Williams, et al.¹⁶⁰ developed an MD approach to construct GO membranes that are similar to the experimental synthesis via flow-directed self-assembly, accounting for the full complexity of the real materials including the oxidized functional group, membrane morphology, as well as pore tortuosity and connectivity. The MD model was validated in terms of the pore size distributions (PSD) and in-plane tensile modulus, showing a greater consistency with the experimental measurements compared to other idealized MD models.¹⁶⁰

Besides the PSD and mechanical properties mentioned above, other membrane properties that can be applied for MD validation include density, elemental composition, solvent self-diffusivity, surface adsorption, surface wetting, and so on. However, the spatial and time scales of experiments and MD simulations should be considered carefully. For example, to validate the water-graphene interactions in MD via the water contact angles on graphene and graphite, the results are strongly affected by the water droplet size and the number of graphene layers.¹⁶¹⁻¹⁶³ The effect of line tension caused by the small water droplet results in a larger contact angle, which could only be eliminated by using at least 4000 water molecules.^{161,163} Meanwhile, the number of graphene layers to represent graphite should be larger than 6, in spite of the cut-off distance of the force fields, to avoid the overestimation of the contact angle.^{161,162}

Chapter 3. Water and salt transport through graphene nanochannels with electric field in nanofiltration

3.1. Overview

As discussed in Section 2.1, graphene-based membranes show advantages over conventional RO membranes in terms of the ultimate thinness, high mechanical strength, and high water permeability. High surface area and excellent conductivity also make graphene (GE) feasible for the fabrication of electrodes in capacitive deionization (CDI). This Chapter is targeted at a systematic investigation of the transport of salty water through the nanochannel formed by a GE bilayer with different channel thickness, applied pressure as well as external electric field using MD simulations. Interactions among the ions, water molecules and GE are also investigated. The simulation results provide useful guidelines for the design and application of GE-derived material for RO or CDI desalination. Besides, the comparisons between unpractical conditions (high pressure and electric field) and realistic conditions (moderate pressure and electric field) are conducted.

3.2. Simulation model

The MD model consists of a nanochannel formed by the bilayer GE and two water reservoirs at each end of the channel constrained by GE walls, as shown in Figure 3.1. The feed reservoir was initially filled with salty water

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containing 16 Na^+ and 16 Cl^- dissolved with 922 water molecules, and the permeate reservoir containing 954 water molecules. The salinity in the feeding reservoir is 48.6 g/L, slightly higher than sea water salinity (35 g/L). Both reservoirs had the same dimension of $40 \times 20 \times 40 \text{ \AA}^3$. The GE bilayer was parallel to the xy plane with a constant length L 32 $\text{\AA}$, while its thickness d varied from 7 to 20 $\text{\AA}$. The GE constrain walls were set normal to the bilayer plane to restrict water and ion movement.

Figure 3.1. Front and top view of the simulated system consisting of two reservoirs and a nanochannel formed by the GE bilayer.

Simulations were carried out using the large-scale atomic/molecular massively parallel simulator (LAMMPS) package.¹⁶⁴ Boundary conditions were set as periodic in all three dimensions to maintain the continuous feeding. The Transferable Intermolecular Potential 3P (TIT3P) was applied to model water molecules, and partial charges of O and H were -0.834e and 0.417e respectively.¹⁶⁵ Other atomic interactions were modelled using CHARMM force

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field,¹⁴⁰ including Coulombics and van der Waals (vdW) interactions. The long-range Coulombics were computed with the particle-particle-particle-mesh (PPPM) method with a cutoff of 12 Å, and vdW interactions were modelled using Lennard-Jones (LJ) potential with a cutoff at 10 Å. LJ parameters and charges of each atom species are summarized in Table 1 based on previous research studies.^{40,140,166} The LJ pair parameters between species i and j were calculated using the Lorentz-Berthelot combining rules except for C-O and C-H interactions. The energy well ϵ and zero-across distance σ between C and O atoms were set as 0.0937 kcal/mol and 3.19 Å, while ϵ and σ between C and H were set 0.⁴⁰

Table 3.1. LJ parameters and charges used in the simulation

Species	ϵ (kcal/mol)	σ (Å)	q (e)
H	0.0461	0.40	0.417
O	0.1521	3.15	-0.834
C	0.0700	3.98	0
Na ⁺	0.0874	2.74	1
Cl ⁻	0.0356	5.03	-1

The NVT ensemble with a Nosé-hoover thermostat was used to keep the temperature at 300K. The GE nanochannel and constrain walls are treated as rigid body with carbon atoms fixed. The SHAKE algorithm was used to constrain the bond and angle of water molecules to maintain the rigid molecule structure. After all the water molecules were relaxed for 50 ps with a timestep of 0.5 fs to reach equilibrium state, a pressure difference ΔP was applied by adding a force f on all the O atoms in the feed reservoir along the positive x direction. The force f is calculated as⁴⁰

$$f = \Delta P L_y L_z / n, \quad (3.1)$$

where n is the number of water molecules in free reservoir, and $L_y L_z$ is the cross section area shown in Figure 3.1. The simulations were conducted with the pressure difference ΔP ranging from 50 to 300 MPa to obtain data for statistical calculations. The external electric field was added in the channel region and vertical to the xy plane. Because ions and water molecules move very fast due to the high pressure, the applied electric field E was also assigned a large intensity ($1 - 5 \text{ V/\AA}$) in order to obtain distinguishable results. The intensity range here is with the same magnitude of electric field that can break bonds and induce ionization of water molecules,¹⁶⁷ but the rigid structure of water molecules was kept by the SHAKE algorithm. Cases with lower pressures (10 MPa) and lower electric field intensities ($0.05 - 0.20 \text{ V/\AA}$) were also tested, which are discussed in section 3.3. The simulated system reached the steady state within around 100 ps. The simulation was then carried on for another 1.5 ns (2.5 ns when $\Delta P=10$ MPa) to collect data.

3.3. Influence of pressure and channel opening

The number N and average velocity v of water molecules and ions were obtained after the system reached the steady state, where N and v remained constant with slight fluctuations. The number N and average velocity v of water molecules and ions were compared under the pressure difference ΔP varying from 50 to 300 MPa at the channel thickness d of 9 Å, 13 Å and 20 Å, as shown

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in Figure 3.2. The three thicknesses chosen here corresponded to two-layer, three-layer and bulk water structures inside the nanochannel reported by previous studies.^{21,40,168} The one-layer water flow at smaller thickness was not chosen because ions can completely rejected by the channel.^{21,34}

Velocity increased linearly with respect to pressure ΔP for both water molecules and ions in Figure 3.2, when the electric field was not imposed. Under the same channel thickness, the velocities of ions were slightly smaller than the velocities of water molecules. The slight difference of velocities became more apparent when the channel thickness was smaller. At larger channel thicknesses, the velocities of both water molecules and ions increased more rapidly with pressure, suggesting the weaker constraint by the nanochannel. The velocities of water molecules inside the CNTs with diameters of 11 – 16.6 Å at $\Delta P=75$ MPa varied within 2–6.5 m s⁻¹.²⁵ In the present simulations, $\bar{v}$ of water inside the GE nanochannel of $d=13$ Å were 10.6 m s⁻¹ and 16.6 m s⁻¹ at $\Delta P=50$ MPa and 100 MPa respectively, higher than that in the CNTs.

The number of water molecules inside the channel varied little in the pressure range of 50–300 MPa in Figure 3.2c. The number of ions also showed no obvious change at $d=20$ Å in Figure 3.2d. However, at $d=13$ Å, N (ION) reduced under the lower pressure of 50 MPa; at $d=9$ Å, there was a more obvious drop of N (ION). This suggested that the entrance of ions into the nanochannel was more sensitive to pressure changes compared to water molecules, especially at smaller channel thickness. In an aqueous NaCl solution of the same salinity in

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this study, the hydration radii of Cl^- and Na^+ are 3.23 Å and 2.35 Å respectively.^{169,170} The equilibrium vdW distance between water molecules in the first hydration shell and the GE layers is 3.19 Å (equal to $\sigma_{\text{C-O}}$), as illustrated in Section 3.2. Therefore, hydration shell were partly peeled off for ions to enter into the narrow nanochannel at $d=9$ Å, imposing an energy barrier, which could be overcome by higher pressure.

Figure 3.2. Influence of pressure on (a) velocities of water molecules, (b) velocities of ions (average of Na^+ and Cl^-), (c) number of water molecules, and (d) number of ions (sum of Na^+ and Cl^-) inside the GE nanochannel of thickness $d=9$, 13 and 20 Å when electric field is not applied.

The influence of channel thickness on velocities and number of water molecules and ions inside the channel is depicted in Figure 3.3 with a constant pressure difference without electric field. Liu et al.⁴⁰ reported there was a sharp

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increase of $N(\text{H}_2\text{O})$ between $d=8$ Å and 9 Å and a moderate sharp increase between $d=11$ Å and 12 Å. The increase gradient of $N(\text{ION})$ is similar with $N(\text{H}_2\text{O})$. In Figure 3.3c, although $v(\text{H}_2\text{O})$ and $v(\text{ION})$ increased with the similar trend as d gets larger, $v(\text{H}_2\text{O})$ was always larger than $v(\text{ION})$. The velocity difference indicated that the constraining effect of the nanochannel on ions is stronger than that on water molecules. The difference between $v(\text{H}_2\text{O})$ and $v(\text{ION})$ reduced as d increased, indicating a weaker constraining effect of GE nanochannels.

Figure 3.3. Influence of channel thickness on (a) number of water molecules channel, (b) number of ions, and (c) velocity of water molecules and ions (average of Na^+ and Cl^-) inside the channel at constant pressure difference $\Delta P=300$ MPa.

Salt rejection is commonly defined as one minus the ratio of permeate salinity versus feed salinity. In previous MD research, salt rejection was calculated by comparing the number of permeated water molecules and ions to the initial values in the feed reservoir, or by counting the number of permeated ions, regardless of whether that boundary condition is periodic or not.^{34,171-173} Periodic boundary condition enables the water molecules and ions to move from one reservoir to another without passing through the membrane, so that the general definition of salt rejection based on counting numbers is not valid.

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However, under non-periodic boundary condition, another problem arises regarding the time point to count the numbers. Some researches use the time point when certain amount of water molecules or ions enter into the permeate reservoir.^{34,172}

As discussed above, the GE nanochannel influenced the ion transport by reducing the velocities inside the channel as well as the probabilities to enter the channel. These two aspects can be expressed by the comparison of velocity and number between the ions and the water molecules inside the channel. Therefore, in the present study, the salt rejection is defined as

$$\text{Salt rejection} = (1 - KC / C_0) \times 100\% , \quad (3.2)$$

where $K = v(\text{ION})/v(\text{H}_2\text{O})$, which is the ratio of average velocities of ions over water molecules inside the channel; $C = N(\text{ION})/N(\text{H}_2\text{O})$, which is the ion concentration inside the channel, expressed as the ratio of the average numbers of ions and water molecules inside the channel; and $C_0 = N_0(\text{ION})/N_0(\text{H}_2\text{O})$, which is the initial ion concentration, expressed as the ratio of the initial numbers of ions and water molecules in the feed reservoir. The definition of salt rejection here can overcome the limitations of counting numbers under the periodic boundary condition. Each simulation was run until the system reached the steady state, and data were then collected to calculate the average values of each parameter in Eq. (3.2). In fact, given any time period, Eq. (3.2) expresses the same meaning as that of the general definition by integration over time. In this manner, we can ensure that Eq. (3.2) calculates a steady-state salt rejection.

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Indeed, we are not able to obtain large salinity difference at each side of the channel, but under high pressure range, its influence on diffusion could be neglected.

Figure 3.4 shows the salt rejection under the influence of pressure difference ΔP and channel thickness d . Within the investigated range of ΔP , the salt rejection at $d=13$ and 20 Å under different pressure did not vary significantly. When $d=9$ Å, the salt rejection increased at the lower pressures of 50 and 100 MPa. Different from the channel formed by GE multilayers, the salt rejection of porous GE single layer depends greatly on the pressure difference in a similar range from 100 to 225 MPa.⁵⁰ As for the influence of channel thickness, there was a sudden decrease from $d=8$ Å to $d=9$ Å in Figure 3.4, where water molecules inside the nanochannel changed from one-layer to two-layer structure. However, when the channel thickness changed from 11 Å to 12 Å and the layer of water molecules transformed into three, there was only a small decrease. Therefore, $d=8$ Å seems to be the critical d that can block small ions such as Na^+ and Cl^- , but it should be noted that the water flux was also small at this d . In real application, there needs to be a balance of water flux and salt rejection for the design of GE derived membranes. For example, if the salt rejection at $d=9$ to 13 Å still varies little under the applied pressure, it would be better to choose larger d for larger flux. At $\Delta P=200$ MPa, the critical diameter to block the salt ion is 5.5 Å for porous GE monolayer (salt rejection=90% by Cohen-Tanugi and

Grossman⁵⁰) and 10.9 Å for CNT (salt rejection=30–60 % by Thomas and Corry¹⁷³).

Figure 3.4. Influence of (a) pressure and (b) channel thickness on salt rejection of the GE nanochannel. Simulations in (b) is carried out under constant driving pressure $\Delta P=300$ MPa.

3.4. Water and ion transport in the electric field

When the electric field with intensity E ranging from 1 to 5 V Å⁻¹ was imposed vertically to the GE nanochannel, the velocities of both water molecules and ions decreased drastically, as shown in Figure 3.5. The velocities of ions nearly reached zero under large E at channel thickness of 9 Å and 13 Å. More ions were held inside the GE nanochannel with larger E , indicating that ions were trapped inside the channel. Correspondingly, salt rejection yielded higher values and reached nearly 100 % at high E . Also, the channel thickness played an important role on the salt rejection. At $d=9$ Å and 13 Å, salt rejection reached over 90 % when E exceeded 3 V Å⁻¹, while at $d=20$ Å, salt rejection was only 90 % when E was 6 V Å⁻¹. At $d=13$ Å, salt rejection increased rapidly from 56 %

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to 94 % when E increased from 2 to 3 $\text{V } \text{\AA}^{-1}$, and similar result was found at $d=10\text{--}12 \text{ \AA}$.

Figure 3.5. Influence of electric field E ($1\text{--}5 \text{ V } \text{\AA}^{-1}$) on (a) velocities of water molecules inside the channel, (b) velocities of ions (average of Na^+ and Cl^-) inside the channel, (c) number of ions inside the channel, and (d) salt rejection. Pressure difference is constant at $\Delta P=300 \text{ MPa}$.

Ions were driven towards the GE channel walls by the electric field, as shown in Figures 3.6a-c, and ions lost part of the hydration shell. We plotted the radius distribution function (RDF) profiles of chlorine-oxygen (Cl^- -O), sodium-oxygen (Na^+ -O) and oxygen-oxygen (O-O) pairs in Figure 3.7. The first peak of RDF for O-O and Na^+ -O occurred at $r=2.82 \text{ \AA}$ and $2.46 \text{ \AA}$ respectively, consistent with previous research.^{174,175} However, the first peak of Cl^- -O occurred at $r=3.42 \text{ \AA}$, slightly larger than the reported range $3.13\text{--}3.35 \text{ \AA}$.^{176,177} When no electric

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field was imposed, the first RDF peak at $d=13$ Å was always higher than that at $d=20$ Å, indicating the GE nanochannel influenced the hydration structures of ions. The RDF curves also vary greatly with electric field strength, especially for those of the ions.

Figure 3.6. Snapshots of ions inside bilayer GE nanochannel when (a) channel thickness $d=13$ Å, pressure $\Delta P=300$ MPa, and electric field $E=3$ V Å⁻¹; (b) $d=13$ Å, $\Delta P=10$ MPa, and $E=0.1$ V Å⁻¹; (c) $d=20$ Å, $\Delta P=300$ MPa, and $E=3$ V Å⁻¹; (d) $d=20$ Å, $\Delta P=10$ MPa, and $E=0.1$ V Å⁻¹.

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Figure 3.7. RDF profiles of O-O, Na⁺-O and Cl⁻-O inside the channel at channel thickness $d=13$ and 20 Å, driving pressure $\Delta P=300$ MPa, and electric field intensity $E=0-5$ V Å⁻¹, as well as bulk flow outside the channel.

The results indicated that ions were separated from the feed flow and trapped inside the channel by the applied electric field to produce desalinated permeate. The model resembled the electrodes of downscaling capacitive deionization (CDI). Although we did not construct the model of porous GE layers, the results above can still show that layered GE electrodes have the potential for CDI applications.

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However, in practical use or laboratory experiments, the applied pressure and electric field cannot be as high as used in the present MD study. Therefore, cases at lower pressure ($\Delta P=10$ MPa) and lower electric field intensity ($E=0.05\text{--}0.2$ V/Å) at $d=13$ Å and 20 Å were also tested. The results in Figure 3.9 show distinct patterns compared to the results in Figure 3.5. Velocities fell to several m s^{-1} and number of ions was also less than those at the high-pressure range, but the number of water molecules stayed the same. The most obvious difference was that the number of ions decreased as the electric field became stronger, in contrary with the results in Figure 3.5. Meanwhile, the increase of salt rejection resulted from the decreased ion numbers rather than the velocity difference between ions and water molecules, indicating that instead of trapping the ions inside the channel, the GE nanochannel with electric field repulsed ions outside the channel. The ions inside the nanochannel still moved forward along the channel wall as shown in Figures 3.6b&d, and apparently the ions stayed farther away from the GE channel wall compared to Figures 3.6a&c.

From the results in Figures 3.8c&f, it can be observed that, after applying an electrical field of $0.05\text{--}0.2$ V Å⁻¹, the salt rejection rate for the GE bilayer channel with the width of 20 Å increased by 40% at the pressure of 10 MPa. For the smaller width of 13 Å, the increase nearly reaches 100%. The increase of the salt rejection rate can be explained by the results shown in Figures 3.8a&d. As the external electrical field increased, lesser number of ions entered into the channel and the mobility of the ions inside the channel was also reduced,

particularly for a large interlayer width of 20 Å. Therefore, the salt rejection rate increased. With the reduced number of ions inside the channel, the internal channel fouling of the membrane is also expected to be reduced. It can be observed from Figure 3.8b that the velocities of the water molecules inside the channel also reduced for the larger interlayer width of 20 Å at 10 MPa, indicating a reduced permeate flux. But for the smaller interlayer width of 13 Å or a weaker electrical field, the permeate flux is maintained. In summary, by applying the electric field across the GE-based membrane, better permeate quality and lesser ion channel fouling can be expected at the same driving pressure without sacrificing the permeate flux.

Figure 3.8. Influence of electric field E (0.05–0.2 V Å⁻¹) on (a) number of ions (average of Na⁺ and Cl⁻) inside the channel, (b) velocity of water molecules and ions (average of Na⁺ and Cl⁻) inside the channel, as well as on (c) salt rejection. Pressure difference is constant at $\Delta P = 10$ MPa.

3.5. Summary

MD simulations were carried out to study the pressure-driven transport of saline water through the nanochannels formed by a graphene bilayer with vertical electric field. The study aims to better understand the water and ion transport in

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GE derived membranes and electrodes for reverse osmosis desalination and capacitive deionization. When the electric field was not imposed, the salt rejection rate varied slightly in the high pressure range (50–300 MPa), and was mainly affected by the channel thickness. When an electric field with high intensity ($1\text{--}5 \text{ V } \text{\AA}^{-1}$) was imposed vertically, ions were trapped inside the channel. We also conducted simulations under realistic electric field ($0.01\text{--}0.1 \text{ V } \text{\AA}^{-1}$ and $0.05\text{--}0.2 \text{ V } \text{\AA}^{-1}$) and pressure (5 MPa and 10 MPa) and obtained distinct results compared to the high pressure and electric field intensity. Results showed that instead of trapping ions inside the channel, GE nanochannels repulsed ions from entering the channel, indicating improved salt rejection rate and reduced ion channel accumulation. Meanwhile, the GE nanochannel thickness and the operating conditions can be optimized to avoid the reduction of permeate flux.

Chapter 4. Water transport through meso-size graphene channels in membrane distillation

4.1. Overview

Membrane distillation is a thermal driven separation process, with phase transition occurring at the hydrophobic membrane surface and only vapour can pass through the porous membrane. To generate a partial pressure gradient across the membrane, it is not necessary to heat up the feed solution to its boiling point. Thus, lower grade energy, including solar energy, waste heat, and geothermal energy, can be used to enable the phase transition. Meanwhile, a moderate hydrostatic pressure (usually up to several atm) is sufficient to drive the process. The cost of membrane distillation is comparable to reverse osmosis (RO), with additional benefits including high selectivity among small molecules and flexibility to combine with other separation processes.

Despite the advantages, it has been pointed out in several review articles that several drawbacks such as low permeate flux, temperature polarization, heat loss, and membrane wetting have hindered the industrial application of membrane distillation.¹⁷⁸⁻¹⁸¹ Although the state-of-the-art module design has substantially enhanced the efficiency, improving the membranes remains crucial to the final performance.^{178,182} Highly hydrophobic membranes with good thermal and chemical stability as well as appropriate thickness and pore distribution are ideal.¹⁸¹ Organic-inorganic composite nanomaterials via sol-gel

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process have also been developed for the distillation processes.^{183,184} These membranes are engineered with highly ordered and vertically oriented mesoporous cylindrical channels (pore diameter at several nanometers), and they possess good hydrophobicity and allow high permeate flux, in contrast to the commonly accepted practice of using microporous membranes for distillation.

As discussed in Section 2.1, the research interest in graphene for the application of water technology is boosted due to its high thermal stability,^{185,186} mechanical strength,¹⁸⁷⁻¹⁸⁹ feasibility to be functionalized with various chemical groups,^{20,190} and tunable channel geometry.^{20,24,79} In particular, graphene can be aligned vertically to form meso-size channels,^{191,192} which may provide a possible superior structure for water vapour transport. Graphene films are also highly hydrophobic¹⁹³ and possess intrinsic anti-wetting property. Therefore, vertically aligned graphene mesoporous membranes can potentially be a great candidate for membrane distillation.

Non-equilibrium molecular dynamics simulations have been proven to be a useful tool to predict and understand membrane transport behaviours in nanofiltration and RO desalination.^{10,194,195} However, little effort has been made to simulate membrane distillation processes using molecular dynamics, because water evaporation is a “slow” process at the nanoscale. It takes around 1 ns for a water molecule to evaporate from an open area of 1 nm² based on our simulation tests. A meaningful statistical analysis will thus require a long simulation period with substantial computational cost.

To overcome the scale limitations mentioned above, a new coarse-grained molecular dynamics (CG-MD) approach was developed to simulate membrane distillation through meso-size (2–5 nm) graphene channels. Using the CG-MD model, the computation time was reduced by at least one-order-of-magnitude compared to the all-atom molecular dynamics simulation. The validation of the water-graphene interaction parameters in the CG-MD model was conducted via the analysis of the contact angles of a water droplet on graphite and monolayer graphene. Subsequently, the effects of graphene channel size, feed temperature, and hydrostatic pressure on the membrane distillation process were investigated. The evaporation process at the channel entrance as well as the water vapour transport behaviours inside the channel were examined separately to understand the underlying mechanisms.

4.2. Coarse-grained MD model

4.2.1. Force fields and validation

A water molecule was represented as a sphere with a dipole moment using the ELBA model.¹⁹⁶ The pairwise potential U_{ij} of the water molecules was described as the sum of a shifted Lennard-Jones (LJ) potential U_{ij}^{LJ} and a dipole term U_{ij}^{dip} with

$$U_{ij}^{\text{LJ}} = 4\epsilon \left\{ \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \left[6 \left(\frac{\sigma}{r_c} \right)^{12} - 3 \left(\frac{\sigma}{r_c} \right)^6 \right] \left[\left(\frac{r}{r_c} \right)^2 - 7 \left(\frac{\sigma}{r_c} \right)^{12} + 4 \left(\frac{\sigma}{r_c} \right)^6 \right] \right\} \quad (4.1)$$

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$$U_{ij}^{\text{dip}} = \frac{1}{4\pi\epsilon_0} \left[1 - 4\left(\frac{r}{r_c}\right)^3 + 3\left(\frac{r}{r_c}\right)^4 \right] \left[\frac{1}{r^3} (\mathbf{p}_i \cdot \mathbf{p}_j) - \frac{3}{r^3} (\mathbf{p}_i \cdot \mathbf{r})(\mathbf{p}_j \cdot \mathbf{r}) \right] \quad (4.2)$$

where $\mathbf{r}$ and r are the intermolecular distance vector and its magnitude, respectively, r_c is the cut-off distance, ϵ and σ are respectively the depth of the potential well and the intermolecular distance at zero potential energy, $\mathbf{p}$ is the dipole moment vector, and ϵ_0 is the vacuum permittivity. Units and values of these parameters are listed in Table 4.1.

The graphene sheets were simulated by coarse-graining four carbon atoms into one sphere bead following Ruiz, et al.¹⁹⁷. The intramolecular interactions include bonds, angles, and dihedrals, details of which can be found in Ruiz et al.¹⁹⁷ Since the pristine graphene has no charge or dipole, the original 12-6 LJ potential below was used to describe the intermolecular interactions between the CG carbon beads as

$$U_{ij}^{\text{LJ}} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (4.3)$$

The LJ parameters and cut-off distance are listed in Table 4.1.

Table 4.1. Parameters of the coarse-grained force field

	σ (Å)	ϵ (kcal/mol)	p (D)	r_c (Å)	M (g/mol)	Reference
ELBA water	3.05	0.55	2.6	12	18.015	Orsi ¹⁹⁶
CG carbon	3.46	0.82	-	12	48.044	Ruiz et al. ¹⁹⁷
Water-CG carbon	3.52	0.26	-	12	-	This study

Similarly, the water-carbon interaction was described using Eq. (4.1). However, the water and CG carbon interaction parameters ϵ and σ needed to be

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examined, because the Lorentz–Berthelot mixing rule was not secure after the coarse-graining. Molecular dynamics simulations were performed using the LAMMPS package¹⁶⁴ and the simulation parameters for the all-atom model were taken from our previous work^{40,198} to obtain the equilibrium distance (3.17 Å) and adhesive energy (1.37 kcal/mol) between one water molecule and a large enough graphene layer ($\sim 4 \times 4$ nm²). In CG-MD, such equilibrium distance and adhesive energy should be reproduced. We calibrated the parameter σ first, since the equilibrium distance between the water molecule and the graphene layer was the function of σ . Afterwards, the parameter ε in the CG-MD model was determined by plotting and calibrating the adhesive energy as shown in Figure 4.1a. The obtained water-carbon LJ parameters for the CG-MD model are given in Table 4.1.

Figure 4.1. (a) Calibration of the Lennard-Jones potential well depth ε between coarse-grained water and carbon spheres via adhesion energy; (b) contact angle of water droplet on graphite and graphene.

We validated the force field between water and CG-carbon by comparing the contact angles of a water droplet on graphite and monolayer graphene. As

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discussed above, the hydrophobicity consideration is crucial for membrane distillation. The water droplet contained 5250 water molecules, and the graphene layer consisted of 936 CG-carbon beads with an area of around $10 \times 10 \text{ nm}^2$. Graphite was modelled by 6 layers of graphene with the interlayer distance of 3.4 Å. After the system was relaxed for 25 ns at the timestep of 5 fs, the interface profile of the water droplet was captured (Figure 4.1b). The contact angles from Figure 4.1b on graphite and graphene were measured to be $93 \pm 0.5^\circ$ and $101 \pm 0.9^\circ$ respectively, in agreement with previous reports via experimental measurements and molecular dynamics simulations as shown in Table 4.2. Such agreements demonstrated the validity of the CG-MD parameters obtained.

Table 4.2. Contact angles of a water droplet on graphene and graphite

Graphite	Graphene	Method	References
90.6°		Experiment	Rafiee et al. ¹⁶²
90.6°		Experiment	Raj, et al. ¹⁹⁹
98.3±5.1°	127±4.0°	Experiment	Wang, et al. ²⁰⁰
93°		Molecular dynamics	Rafiee et al. ¹⁶²
90.2±0.3°	100.7±0.4°	Molecular dynamics	Taherian et al. ¹⁶³
89.6°		Molecular dynamics	Raj et al. ¹⁹⁹
93±0.5°	101±0.9°	Coarse-grained molecular dynamics	This study

4.2.2. Simulation model

The membrane distillation model consisted of two water reservoirs, repeated channels formed by adjacent graphene layers, and two graphene pistons as shown in Figure 4.2a. The channel was two unit cells stacking at the z direction. Each unit cell consisted of one layer of graphene with an area of $L_x L_y = 58.9 \times 39.7 \text{ Å}^2$. Salts were not included in the CG-MD simulations because the

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salt rejection of membrane distillation process is generally very high. Each water reservoir initially contained 946 to 2618 water molecules depending on the channel opening d (20–50 Å), and the reservoirs were confined by 1 atm pressure imposing on the pistons. The pressure was realized by applying a force to each piston CG bead. The height of the piston relied on the channel opening, ranging at 17.2–47.2 Å.

The hydrostatic pressure was imposed by increasing the force magnitude imposed on the piston CG beads at the feed side and remaining the pressure at the permeate side constant at 1 atm. Periodic boundary conditions were applied in all three directions. A large vacuum was put in front of the permeate side in the x direction to eliminate the interactions between the system and its image under periodic boundary conditions. Temperatures of the feed and permeate reservoirs were maintained constant at 310–360 K and 300 K respectively by the Langevin thermostat with a damping parameter of 100 fs (same parameter was applied for all the thermostat in this work). The edges of the channels parallel to the y direction were constrained by attaching the beads to their initial position with a spring potential. The rest of the channel was allowed to move freely. The simulation was first conducted at the timestep of 5 fs for 10 ns for system relaxation, and then continued for 75 ns for data collection. Each simulation was repeated three times. Meanwhile, AA-MD simulations for $d=20$ Å were conducted with the feed containing saline water, and no salt penetration occurred

(details in Appendix A). The computational time was reduced by one order of magnitude.

The membrane distillation process can be divided into three sub-processes, i.e., the evaporation process of water molecules from the interface, the transport process along the graphene channel, and the condensation of the water molecules to the permeation side. The first two processes were dominant in the overall distillation efficiency. To quantify the contributions of the evaporation process and the transport process with ease, another two models in Figures 4.2b and 4.2c were constructed. The condensation process was assumed to require considerably less effort and was neglected in this study.

Figure 4.2. Configurations of (a) membrane distillation model, (b) evaporation model, and (c) vapour transport model.

In the evaporation model, the permeate side was initially empty. An artificial accelerating zone was added next to the liquid-vapour interface layer (Figure 4.2b). The liquid-vapour interface was defined based on the density profile of the water as shown in Figure 4.3. From the liquid phase to the vapour

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phase, the water density gradually decreased to 0 within around 10 Å. The interface was defined at the position where the density was half of the value of the liquid phase. Once a water molecule moved across the starting line and entered the accelerating region, an acceleration along the x direction was applied to force its moving to the permeate side. In this way, the evaporation process was assessed under the minimal influence of channel transport. The temperature in the feed reservoir was varied from 300 K to 360 K at $d=20\text{--}50$ Å, and the permeate reservoir was maintained at 300 K. The simulation was first conducted at the timestep of 5 fs for 10 ns for system relaxation, and then continued for 75 ns for data collection. Each simulation was repeated three times.

Figure 4.3. Density profile along the x direction at the entrance of the graphene channel. The liquid-vapour interface was defined as the central line of the interface layer.

In the evaporation model, the potential of mean force (PMF) of one water molecule across the interface at 350 K was computed using the adaptive biasing force method implemented in LAMMPS-COLVARS package.²⁰¹ The reaction coordinate (RC) was along the x direction from -10 to 10 Å, covering the liquid-

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vapour interface layer. The motion of the water molecule in the xy plane was not restricted. Four non-overlapping windows of equal width of 5 Å were used to sample along the RC. In each window, calculations were performed with the same conditions of the evaporation model described above for 75 ns to ensure sufficient sampling. We also computed the mean square displacement (MSD) of the interface water molecules ($X=-4-6$ Å) over 1 ns. Each simulation was repeated five times to obtain the average curve for the calculation of the diffusivity of interface water. Moreover, the interaction energy profiles between the graphene channel walls with interface water molecules were computed over 5 ns, and each simulation was repeated three times.

The transport model in Figure 4.2c included only a channel and a water molecule. According to Malek and Coppens¹⁴⁸ transport diffusivities are distinctly different from self-diffusivities, especially under condensed loads. Therefore, instead of computing MSD and calculating the self-diffusivity, the following approach was applied to evaluate the transport diffusivities. The water molecule was released at the starting line (Figure 4.3) with an initial velocity ranging from 0 to 0.008 Å fs⁻¹ in the x direction after thermostated at 300–360 K, and the region after the finishing line was thermostated at 300 K. In all three models in Figure 4.2, only the CG-beads before the starting line and those after the finishing line (reservoir regions) were thermostated, while the middle channel region was not thermostated, so that the transport dynamics of water molecules inside the channel would not be affected by the thermostat.

The transport time of the water molecule was recorded once it hit the finishing line, which was defined similarly with the starting line. Since the one-time diffusion or transport of the water molecules inside the channel was random, the simulation was repeated for 300 times so that a probability distribution of the transport time can be obtained. For each channel thickness, the results were fitted into the Weibull distributions, and the suitability was verified by the modified Kolmogorov-Smirnov tests. The timestep of the transport model was set as 1 fs to better capture the movement of the water molecule inside the channel.

4.3. Influence of temperature and channel opening

After the system was relaxed in the beginning 10 ns, the number of water molecules N in the permeate reservoir was recorded for another 75 ns. As shown in Figure 4.4a, the number increased linearly with time ($R^2 > 99\%$). The slope of the increase $\frac{dN}{d\tau}$ was taken to describe the flux J ($\text{mol m}^{-2}\text{s}^{-1}$) in the membrane distillation process as:

$$J = \frac{1}{N_A A} \frac{dN}{d\tau}, \quad (4.4)$$

where N_A is the Avogadro constant and A is the cross-section area of one channel formed by two adjacent graphene layers and can be obtained as $A = L_y d$. The calculated flux was on the order of $10,000 \text{ L m}^{-2} \text{ h}^{-1}$, which was three-order-of-magnitude higher than the average flux of dozens of $\text{L m}^{-2} \text{ h}^{-1}$ in practical applications.¹⁷⁸ We note that the enhancement should be considered together with

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the fact that the current model was ideal. The graphene membrane had perfect structure and thickness, and the distillation process took place in the absence of air. Meanwhile, the temperatures in the feed and permeate reservoirs were maintained constant. In other words, the heat loss caused by the membrane and air conduction, and temperature polarization etc. was not considered. Despite the idealisation, the results demonstrated the huge potential of using graphene for membrane distillation. The results were in agreement with the findings from the upright cup evaporation experiments by Celebi et al.⁶⁸ that the water vapour transmission rate through a 400-nm-pore graphene membrane was four-order-of-magnitude higher than that through polymer membranes.

Figure 4.4. (a) Increase of water molecule number in the permeate at $d=30$ Å with feed temperature at 350 K; (b) Permeate flux through different channel opening d with feed temperature at 350 K; (c) Permeate flux at feed temperature ranging from 310 to 360 K

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at various d , and (d) Influence of hydrostatic pressure on permeate flux at $d=30$ Å and feed temperature of 350K. Results in (b-d) were taken from the averages of three repeated simulations with the permeate temperature at 300 K, and the error bars indicate the standard deviations.

With the validated model, the influence of channel opening (20–50 Å) was investigated in the absence of hydrostatic pressure with the feed and permeate temperatures at 350 K and 300 K respectively. Interestingly, the flux exhibited a non-monotonic dependence on the channel opening size and reached its maximum value at the smallest opening of $d=20$ Å as shown in Figure 4.4b. After a drop from $d=20$ Å to $d=30$ Å, the flux was enhanced as the opening further increased beyond $d=30$ Å. To confirm that this nonmonotonic dependence was not a special case for the specific temperature considered, simulations under different feed temperatures were also conducted. Results in Figure 4.4c proved that the dependence of flux on the channel opening did not vary with temperature, and the permeate flux at $d=20$ Å remained the largest for all the temperatures investigated. This important finding contradicted with the common perception that higher permeate fluxes in membrane distillation can be obtained when membranes possess larger pores. In other words, higher permeate fluxes do not necessarily require the compromise of lower wetting pressure.

As discussed above, we had focused on the two dominant processes, i.e. evaporation and transport, in the membrane distillation process, while assuming that the effect of condensation was relatively minor. Therefore, only the resistances of evaporation and transport were considered. The abnormally high flux at $d=20$ Å can possibly be explained from two aspects: either the evaporation

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rate was high or water transport inside the channel was fast, which will be discussed in detail in Sections 4.4 and 4.5.

Research on the hydrostatic pressure had focused on the liquid entrance pressure (LEP), below which the effect of hydrostatic pressure on membrane distillation is not clear yet.¹⁸² In molecular dynamics simulations, hydrostatic pressure can be easily adjusted via changing the force imposed on the piston wall. In the present model, increasing the hydrostatic pressure to more than 5 MPa was beneficial for permeate flux, as shown in Figure 4.4d. The reason of the enhancement is discussed in Section 4.4. However, when the pressure was raised above 20 MPa, the enhancement became less apparent. Furthermore, when the pressure increased from 53 MPa to 54 MPa, channel wetting occurred, and water molecules filled in the whole channel, indicating the LEP at $d=30$ Å was between 53–54 MPa. The high LEP was due to the hydrophobicity of graphene as well as the small channel opening.

In practical applications, if the hydrostatic pressure is raised to the same level as in RO desalination process, membrane distillation will no longer be energy-effective, and wetting may happen. Hence, the hydrostatic pressure is typically maintained at several atmospheres. Simulations were also conducted for cases with low hydrostatic pressures of 0.25, 0.5, 0.75, and 1 MPa. The results showed that there was no enhancement at 0.25 and 0.5 MPa; while at 0.75 and 1 MPa, the permeate flux increased by only ~20 %. Therefore, raising the hydrostatic pressure is not energy efficient, both in the high and low hydrostatic

pressure range. Recently, Keulen, et al.²⁰² reported a membrane distillation setup against a hydrostatic pressure of around 0.12 MPa, demonstrating that the influence of hydrostatic pressure on membrane distillation is trivial in practical applications, which are consistent with our finding.

4.4. Water evaporation into meso-size graphene channels

The evaporation process was examined by accelerating the water molecules which escaped from the liquid-vapour interface layer, using the model shown in Figure 4.2b. The number of water molecules in the permeate increased linearly with time, and thus the evaporation flux J_e (mol m⁻²s⁻¹) can also be calculated using Eq. (4.4). In reality, an evaporated water molecule has the probability to condensate back into the liquid phase. Accounting for this backward condensation into, Knudsen^{203,204} defined the evaporation coefficient as the ratio between the final number of molecules transferred to the vapour phase with the total number of molecules emitted from the liquid-vapour interface. Due to the acceleration treatment in the simulation, the backward condensation of the water molecules was prohibited, and the evaporation flux obtained in the present study represented the escaping flux only. In other words, the evaporation coefficient was assumed to be 1.

Figure 4.5. (a) Variation of evaporation flux J_e with channel opening of $d=20$ – 50 Å at the feed and permeate temperatures of 350 K and 300 K, respectively, with no hydrostatic pressure; (b) Linear relationship of $\ln J_e$ vs $1/T$ at $d=30$ Å. The error bars indicate the standard deviations.

As can be observed from Figure 4.5a, the evaporation flux was highest at $d=20$ Å and reached over 1100 mol m⁻²s⁻¹. In addition, the evaporation flux decreased monotonically as the channel opening increased. The high evaporation flux corresponded well with the high permeate flux at $d=20$ Å (Figure 4.4b). When d increased to the range of 30–50 Å, the evaporation flux decreased with the channel opening, which was in opposite to the permeation flux (Figure 4.4b). Therefore, for larger channel openings, the transport process inside the channel was more prominent in determining the membrane distillation performance. For even larger d beyond 50 Å, evaporation flux leveled off and no further improvement was observed as confirmed by the simulation results at $d=100$ Å.

In general, the evaporation flux can be expressed by the Arrhenius equation as

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$$J_e = C \exp\left(\frac{-\Delta E}{RT}\right), \quad (4.5)$$

where C is the pre-exponential parameter ($\text{mol m}^{-2}\text{s}^{-1}$), ΔE is the energy barrier which a water molecule must overcome to be evaporated (kcal mol^{-1}), R is the gas constant ($1.99 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1}$), and T is the temperature (K). To calculate ΔE and C , the logarithm of the evaporation flux $\ln J_e$ was plotted against the reciprocal of the temperature, as shown in Figure 4.5b. The linear fitting of $\ln J_e$ with respect to $1/T$ gives ΔE and C as listed in Table 4.3 for different channel openings. The results showed that both ΔE and C were dependent on channel opening d . Interestingly, the energy barrier at a larger channel opening was only slightly lower, and the evaporation flux was dominated by the pre-exponential parameter C , accounting for the collision frequencies among the water molecules. The enhanced evaporation at smaller channel openings was likely caused by the elevated mobility of water molecules due to stronger Van der Waals interactions with the channel walls, resulting in higher frequencies of collision and larger probabilities to be bumped out from the bulk water.

Table 4.3. Arrhenius parameters for water evaporation into graphene channels.

d (Å)	20	30	40	50
ΔE (kcal mol ⁻¹)	8.92	8.88	8.84	8.82
$\ln C$ (mol m ⁻² s ⁻¹)	19.87	19.66	19.54	19.46

For the canonical ensemble (NVT), PMF profiles in Figure 4.6 reflected the Helmholtz free energy change ΔA along a reaction coordinate, and the values are given in Table 4.4. The calculated energy barrier via Arrhenius equation in

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Table 4.3 is the total energy change ΔE , i.e. internal energy change ΔU . Both ΔU and ΔA showed no significant variation, indicating the energy barrier was not the dominant factor in evaporation. The difference between ΔU and ΔA was attributed to the entropy change. In thermodynamics, Helmholtz free energy is defined as $A = U - TS$, where T and S are temperature and entropy respectively. Since the interface was thermostated at a constant temperature, thus $\Delta A = \Delta U - T\Delta S$, in which ΔA and ΔU were obtained from Figure 4.6 and Table 4.3. The entropy change ΔS was then calculated and shown in Table 4.4, which also showed no significant variations.

Figure 4.6. Potential of mean force (PMF) of one water molecule across the liquid-vapour interface at the temperature of 350 K for different channel opening d . The PMF profile reflects the Helmholtz free energy change during evaporation.

Table 4.4. Change of Helmholtz free energy ΔA and entropy ΔS of water evaporation

d (Å)	20	30	40	50
ΔA (kcal mol ⁻¹)	5.82	5.76	5.91	6.05
ΔS (cal mol ⁻¹ K ⁻¹)	8.86	8.91	8.37	7.91

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To further investigate the collision frequency of interface water molecules, which dominated the evaporation process, we computed the MSD of interface water molecules, shown in Figure 4.7a. In three dimensions, diffusivity D can be calculated from the slope of MSD with respect to time via $\text{MSD}=6D\tau$ (Figure 4.7b). According to the Smoluchowski's²⁰⁵ particle collision theory of Brownian motion in a liquid, the collision frequency is proportional to the diffusivity. Therefore, the collision frequency was highest at $d=20$ Å, which was consistent with the conclusion from the Arrhenius fitting in Table 4.3. The interaction energy between interface water and the channel wall is also plotted in Figure 4.7b. As mentioned earlier, the reason of the evaporation enhancement at smaller channels was likely to be the elevated interaction strength. The similar variation of interaction energy to both the diffusivity and evaporation flux confirmed that the stronger interaction resulted in the elevated collision frequency of surface water molecules and eventually led to the enhanced evaporation flux.

Figure 4.7. (a) Mean square displacement (MSD) profiles of water molecules in the interface layer; (b) Diffusivities D of interface water molecules derived from the MSD profiles and the interaction energy of the interface water molecules with the graphene channel wall.

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The effect of hydrostatic pressure on evaporation flux is illustrated in Figure 4.8a. There was only a slight rise as the pressure increased from 0 to 53 MPa. From the liquid-vapour interface portrayed in Figure 4.8b, an increase of the curvature was observed, leading to the larger surface tension under higher hydrostatic pressure. In addition to enhancing the evaporation flux, the hydrostatic pressure also pushed the interface forward by almost 12 Å, hence shortening the transport length of water molecules inside the channel. In particular, under the effect of hydrostatic pressure, the channel entrance effect on the water distillation can be eliminated by forcing the liquid-vapour interface into the channel. This explained the jump of permeate flux from 0 to 10 MPa as shown in Figure 4.4d. However, as commented earlier, it would be uneconomical to apply such a high pressure in membrane distillation, since the enhancement in evaporation is limited and the shortening of transport path can be neglected in longer channels.

Figure 4.8. (a) Evaporation flux and (b) liquid-vapour interface curvature under hydrostatic pressure $P=0$ –53 MPa at $d=30$ Å at the feed and permeate temperatures of 350 K and 300 K, respectively. The error bars indicate the standard deviations.

4.5. Transport of water vapour inside meso-size graphene channels

The transport behaviour of water vapour through the membrane was evaluated by characterizing both the transport resistance and transport time inside the channel. Under the assumption of zero condensation resistance, the permeate flux can be expressed as²⁰⁶

$$J = \frac{J_{e,f} - J_{e,p}}{R}, \quad (4.6)$$

where J is the permeate flux in membrane distillation ($\text{mol m}^{-2}\text{s}^{-1}$), $J_{e,f}$ and $J_{e,p}$ are the evaporation fluxes from the feed and permeate reservoirs ($\text{mol m}^{-2}\text{s}^{-1}$) respectively, and R is the transport resistance of water molecules inside the channel. Values of $J_{e,f}$ and $J_{e,p}$ at different temperatures and channel openings were obtained from the evaporation model as plotted in Figure 4.5, and the overall distillation water flux J is given in Figure 4.4. The transport resistance R was then calculated using Eq. (4.6) and plotted in Figure 4.9. Besides R , the “average” transport time τ_w is also plotted, which is the scale parameter of the Weibull distribution for the water transport time from 300 separate runs using the transport simulation model as described in Section 4.2.2.

It can be observed in Figure that the transport resistance at the channel opening $d=20 \text{ \AA}$ was low, and it increased at $d=30 \text{ \AA}$. However, as d further increased, the transport resistance started to decrease. Both curves in Figure 4.9

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revealed the same variations. The main purpose of using two different approaches to evaluate the transport resistance was to ensure that the results were trustworthy, since the acceleration region setting in the evaporation model was artificial. The same variation via these two approaches can justify that the position of the acceleration starting line was appropriate, although there was no guarantee of the real evaporation coefficients being 1 at the same position in the distillation model.

Figure 4.9. Transport resistance R and transport time τ_w of water vapour inside the meso-size graphene channel.

To understand the mechanisms of water transport at different channel openings, the trajectories of water molecules were recorded and shown in Figures 4.10a-c. The pair-wise potential energy surface between the graphene channel and a probing vapour water molecule in the xz plane was plotted in Figures 4.10d-f, where the black line represents the zero pair-wise potential energy. The nonzero interaction potential energy zone extended into the channel with smaller distances for larger channel openings. As a result, for a narrow channel, the probability of a water molecule interacting with the graphene wall was higher,

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and its transport would exhibit a dominant surface diffusion behaviour (Figure 4.10a). On the contrary, when the channel opening became wide, the probability of the water molecule staying inside the surface region next to the graphene reduced, and its transport along the channel would exhibit the characteristics of the Knudsen diffusion (Figure 4.10b-c).

Figure 4.10. Sequential snapshots with a timestep of 1 ps for a water molecule transporting through the graphene channels at (a) $d=20$ Å, (b) $d=30$ Å, and (c) $d=50$ Å; pair-wise potential energy surface inside the graphene channels at (d) $d=20$ Å, (e) $d=30$ Å, and (f) $d=50$ Å. The black lines indicate zero potential beyond which the interaction between the graphene channel and the water molecule is prohibited due to their large distance.

With surface diffusion, the water molecules were adsorbed onto the highly smooth surface of graphene layers, and they moved on the surface along the lateral direction of the graphene channel. Desorption of water molecules from

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the surface region to the middle region also happened, but the occurrence was less frequent for $d=20$ Å. The transport pattern changed drastically for larger channels, where Knudsen diffusion became more pronounced and surface adsorption-desorption still occurred. For larger channels, surface interaction reduced the kinetic energy and the lateral velocity of water molecules, thus resulting a larger transport resistance or transport time. The transition from surface diffusion-dominated to Knudsen diffusion-dominated transport from $d=20$ to 30 Å can explain the high transport resistance at $d=30$ Å and is the main reason of the significant flux decrease shown in Figure 4.4b. It is worthwhile pointing out that when the channel opening becomes narrower than 20 Å to a certain value, the nonzero interaction potential energy zones of the two graphene walls will overlap with each other, where the transport mechanism will transit to molecular sieving, as reported in previous research.^{21,207}

To obtain a quantitative validation of the above discussion, a surface region was defined within 5 Å from the channel walls, and the time of the water molecule staying inside this surface region was recorded from 300 repeating simulations using the transport model described in Section 4.2.2. The probability of surface diffusion p_s was expressed as the portion of the time when the water molecule stayed in the surface region over the total transport time. For reference, the hypothetical surface diffusion possibility was denoted as $p_0 = 10/d$ with the assumption that the position of the water molecule was uniformly distributed along the channel thickness during its transport. Both p_s and p_0 are plotted in

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Figure 4.11. When the channel opening was smaller than 40 Å, the surface diffusion probability p_s was larger than the hypothetical probability, indicating that the water molecule tended to diffuse along the surface. In particular, at small channel openings, the diffusion probability p_s reached as high as 77%. As the channel opening increased to 50 Å, p_s decreased sharply to only 15%, showing that the water molecule mainly diffused outside the surface region and exhibited the Knudsen diffusion behaviours.

Figure 4.11. Probabilities of the diffusion taking place at the surface region (within 5 Å from the channel walls) calculated from the molecule trajectory record and with the hypothesis of uniformly distributed transport.

Theoretically, the Knudsen number $Kn=\lambda/d$ provides the guidance on the gas transport mechanisms inside the channel. Here, λ is the mean free path of the transport molecules.²⁰⁸ The mean free path of water vapour at 60 °C is 0.3 μm according to the estimation of Chua, et al.²⁰⁹ Hence, $Kn \gg 1$ in this study, and the water vapour transport inside the graphene channel was in the regime of Knudsen diffusion. Following the initial derivation by Knudsen²¹⁰ and the

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extensions to other pore geometries by Smoluchowski²¹¹, Gruener and Huber²¹² summarized the expression of Knudsen diffusivity D_{Kn} ($\text{m}^2 \text{s}^{-1}$) to be

$$D_{Kn} = \frac{1}{3} G \bar{v} \quad (4.7)$$

with

$$\frac{1}{G} = \frac{1}{4L} \int_0^L \frac{o(l)}{A(l)} dl \quad (4.8)$$

and

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}, \quad (4.9)$$

where G (m) is a pore geometric factor determined by the cross-section area $A(l)$ (m^2) and perimeter $o(l)$ (m) along the pore length L (m), and $\bar{v}$ is the mean thermal velocity of the transported particle determined by the gas constant R (8.314 J mol^{-1}), temperature T (K), and particle molar mass M (kg mol^{-1}).

For the 2D graphene channel, the geometric factor G should be

$$G = \frac{2dL_y}{d + L_y}, \quad (4.10)$$

where d is the channel opening and L_y is the width along the Y direction. Because of the 2D shape of graphene, $L_y \gg d$ and G can be expressed as $2d$. Using this geometric factor G , we can probe why the 2D structure is efficient for diffusion. For a cylindrical channel with diameter d , G equals to d according to Eq. (4.8), which makes the diffusivity only half of that inside the 2D channel. Besides, 2D

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graphene channels possess minimal tortuosity and roughness, both of which are factors to reduce G . The Knudsen diffusivity can then be expressed as

$$D_{Kn} = \frac{2d}{3} \sqrt{\frac{8RT}{\pi M}}. \quad (4.11)$$

Therefore, if the transport was simply Knudsen diffusion, D_{Kn} would increase linearly with d from 0.82 to 2.06 mm² s⁻¹ for water molecules inside the graphene channels with $d=2-5$ nm under the average temperature $T=325$ K.

The real diffusivities can be calculated from the transport resistance R in Figure 4.6 via the relationship below,^{206,213} which is derived from microscopic descriptions and applicable for this study, i.e.

$$R = \frac{1}{\eta} = \frac{\bar{v}L}{4D}, \quad (4.12)$$

where η is the transmission probability of water molecules in the absence of air and D is the diffusivity. In the present study, the water vapour diffusivities inside the graphene channels with $d=2, 3, 4$, and 5 nm under the average temperature $T=325$ K were 0.40, 0.24, 0.35, and 0.37 mm² s⁻¹ respectively, lower than the theoretical D_{Kn} . This was consistent with our observation that water molecules inside the channel were not “free”. Thus, the transport cannot be described purely by the Knudsen diffusion. Precisely, at $d=2$ nm, surface diffusion dominated the transport; from $d=3$ to 5 nm, the transport can be described as an activated Knudsen diffusion (also known as activated diffusion) where the surface energy still played a part in the transport. The activated diffusion is determined by both

the interaction strength of the water molecules with the channel surface and their kinetic energy after escaping from the surface.

Although the surface diffusion and activated diffusion are both slower than the pure Knudsen diffusion, these two mechanisms lead to larger variation of diffusivities among different molecules due to the large variation of their interaction energy with the channel.^{208,214} As such, the membrane selectivity of water over another coexisting species, defined by the product of their diffusivity ratio and sorption coefficient ratio, will be higher under surface diffusion and activated diffusion. For membrane distillation, selectivity is an essential property demanded for the next-generation membranes,²¹⁵ particularly to increase the rejection ratio of other contaminants contained in the water. Hence, the larger contrast will also be potentially beneficial for real applications, although a detailed analysis of interactions of the different contaminant solutes with the membrane needs to be carried out for confirmation.²¹⁶

4.6. Summary

A coarse-grained molecular dynamics model was developed to overcome the spatial and time scale limitations and to simulate the membrane distillation process through meso-size (2–5 nm) graphene channels at the direct contact mode. The coarse-grained force fields were validated through the contact angles of a water droplet on graphite and graphene. The computational cost was reduced by at least one order of magnitude. Compared to commonly used microporous

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polymer membranes, the permeate flux through the mesoporous graphene membrane was three-orders-of-magnitude higher. The largest permeate flux was obtained when the channel opening was 2 nm, but the permeate flux did not vary monotonically with the opening size. Moreover, the hydrostatic pressure showed limited effects on distillation flux, and it is thus uneconomical to raise the hydrostatic pressure in membrane distillation.

To understand the mechanisms of the distillation flux variations, we isolated the evaporation and transport processes and examined them separately. Thermodynamics analysis of the evaporation process showed that smaller channel opening was beneficial for evaporation due to the enhanced collision frequency among the surface water molecules caused by the strong interactions with the graphene layers.

The channel opening variation resulted in different water transport mechanisms based on the analysis of water trajectories, potential energy mapping and water transport time as well as the comparisons with previous theoretical models. When the channel opening increased from 2 nm to 3 nm, a transition from surface diffusion-dominated transport to activated Knudsen transport occurred. Although both surface diffusion and activated diffusion are slower than pure Knudsen diffusion, they can potentially lead to higher selectivity caused by the interaction energy differences for different solutes in water (i.e. higher rejection).

Chapter 5. Composition-structure-property relationship of polyamide thin films for RO desalination

5.1. Overview

As introduced in Section 2.2, the polyamide (PA) thin-film composite (TFC) membrane is currently the mainstream product for reverse osmosis (RO) desalination, due to its good stability in various pH as well as exceedingly high water permeability and salt rejection compared with first-generation cellulose RO membranes.^{28,126} Despite the numerous efforts in improving the performance of PA membrane in the past decades, the fundamental understanding of the underlying membrane structure and transport mechanism has been largely empirical, especially at the nanometer or sub-nanometer scale.^{15,29,127} Recent microscopic technologies have been exploited to investigate the internal structure of PA thin films.^{31,45,130} However, it is extremely difficult to experimentally capture the comprehensive internal structure of the PA thin films and to directly observe the motion of solvents and solutes inside.^{7,30} Continuous efforts have been dedicated to the molecular-level design of PA films to pursuit high permeability and selectivity as well as to mitigate fouling.^{135,217-219} Molecular insights into the composition-structure-property relationships would provide guidelines for the tailored design of next-generation membranes.^{28,126}

MD simulations have advanced the understanding of membrane transport mechanisms of PA thin films.^{10,49,132-134} Various methods have been developed

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to build cross-linked PA structures in MD: some started with linear PA chains,²²⁰ and others mixed MPD/TMC monomers homogeneously.^{48,132,133} Muscallato et al.¹³¹ applied an advanced coarse-grained approach to mimic the IP process. Unfortunately, few could reproduce the realistic atomic composition and cross-linking degree,¹³³ and the repeatability was typically not reported. More importantly, the composition and structure of generated PA were not varied in a reliable manner. As such, MD investigations of structures and transport mechanisms of PA thin films have been limited to a particular composition so far. For example, Harder et al.⁴⁸ showed that PA thin films had bimodal pore size distributions, while Kolev and Freger¹³³ observed only unimodal pore distributions. The difference could be attributed to the different strategies of constructing PA as well as the single PA structure examined.

The first objective of this work is to develop a new feasible and repeatable approach of building and hydrating the PA films in MD to reproduce the realistic atomic composition, structure, as well as dry and hydrated membrane properties. Based on the MD approach, the molecular-level relationships of the atomic composition, membrane structure and water permeability were established for PA thin films generated from four MPD/TMC ratios representing insufficient to abundant MPD. The results contribute to the fundamental understanding of depth-heterogeneous PA thin films with varied compositions from back to the surface, and meanwhile provide insights into the molecular-level design of next-generation membranes.

5.2. Building and hydrating PA thin films in MD

5.2.1. Generation of dry PA matrix

We employed the polymerization algorithm *Polymatic*²²¹ to build the PA structure under the environment of LAMMPS¹⁶⁴. *Polymatic* provides adequate equilibration of the system during the bonding to avoid unrealistic conformation and ensure that the cross-linking can reach its largest degree within the limited time scale in MD. The atomic structures of linked and hydrated MPD-TMC (Figure 5.1a) were simulated using the general amber force field (GAFF)²²², and the partial charges were calculated using semi-empirical bond charge correction (AM1-BCC)²²³ in the Antechamber tool. Partial charges and the force fields are summarized in Tables B1-5 (Appendix B).

The generation procedures of dry PA matrix consisted of four steps: polymerization, termination, and compression, as shown in Figure 5.1. For convenience, one hydrogen atom from the amine group and the chlorine atom from the acyl chloride group were removed in the initial packing, and the partial charges of the reactive carbon and nitrogen were assigned as the same in the amide bond. The initial system contained 1000 hexane molecules, 280–310 MPD molecules, and 200 TMC molecules in a periodic box of 903 Å³. Four MPD/TMC ratios: 2.8:2.0, 2.9:2.0, 3.0:2.0, and 3.1:2.0, were initiated for the polymerization. The bonding criteria was set as the distance between the reactive nitrogen and carbon atoms being less than 5 Å. Once an amide bond was formed, the new bond,

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angles, and dihedrals caused by the linking were defined accordingly. The bonding and structure relaxation were handled by *Polymatic* algorithm, detailed in Abbott et al.²²¹

After the polymerization, the unlinked nitrogen and carbon atoms were terminated with hydroxyl groups and hydrogen atoms, representing the hydrolysis of side groups in water. Partial charges were reassigned based on the hydrolysed structure in Figure 5.1a. There existed large void space after the removal of hexane in Figure 5.1b, and the PA structures were compressed and relaxed using the 21-step equilibration process to achieve realistic porous polymer densities.^{221,224} There were still voids remaining in the annealed dry PA matrixes, and the densities of dry matrixes were calculated with the voids included.¹³³ These voids provided space for water uptake in the hydration process.

Due to the randomness of initial packing and polymerization, the whole procedures in Figure 1b were repeated five times for each MPD/TMC ratio. Although the initial packing cell was the same size for all the simulations, the resulting unit cells of equilibrated PA matrixes ended up with different sizes ranging from 43.7 to 44.1 Å.

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Figure 5.1. (a) Atomic structures of an MPD monomer, TMC monomer, MPD-TMC oligomer, and hydrated MPD-TMC oligomer, where white, grey, blue, and red sticks represent H, C, N, and O respectively; (b) Procedures of dry PA matrix generation include: polymerization between MPD and TMC monomers solvated in hexane, termination of the unreacted nitrogen and carbon atoms with hydrogen atoms (-H) and hydroxyl groups (-OH) respectively, and 21-step equilibration. Specifically, the snapshots in polymerization and termination are the initial status, while the snapshot in 21-step equilibration shows the final status.

The degree of cross-linking (DC) was calculated in Eq. (5.1), following the definition by Coronell, et al.²²⁵ as the ratio between the number of actual formed amide bonds and the theoretical maximum number of amide bonds in a fully cross-linked polymer.

$$DC = \frac{N_{C-N}}{N_{C-N}^0} = \frac{N_N - N_{NH_2}}{N_N + N_{COOH}}, \quad (5.1)$$

where the number of amide bonds N_{C-N} was counted in MD and equalled to the number of nitrogen atoms N_N subtracted by the ammine group number N_{NH_2} , and the theoretical number of amide bonds was the sum of N_N and carboxylic group number N_{COOH} . A more widely used expression of the DC assumes that the actual PA structure is a molecule formed by the fully cross-linked ($C_{18}H_{12}O_3N_3$) and linear ($C_{15}H_{10}O_4N_2$) repeating units.^{135,217} The fraction of these two components

is determined from the ratio between oxygen and nitrogen O/N using Eq. (2.10) as described in Section 2.2.2. We did not use the expression because it lacks the molecular precision and excludes the fact that amide groups exist in PA structures.^{131,225} The density of the dry PA matrix was calculated as the total mass in a unit cell over the unit cell volume, including possible voids. The accessible volume fraction to water molecules and the pore size distribution (PSD) were computed using Zeo++^{226,227} with a spherical probe of radius of 1.45 Å and 1 Å respectively.

5.2.2. Hydration of PA thin films

The most common hydration approach^{9,10} is to fill the PA matrix with water molecules to reach the reported experimental water content of 23 wt%,²²⁸ where water molecules could be artificially inserted into the inaccessible cavities.¹³² We instead used the physical PA-water interaction to drive the hydration process in equilibrium MD simulations. The dry PA matrix was 3D periodic, with an infinite replication of the unit cell in Figure 5.1b. We ripped the matrix apart at the x direction by deleting a slab of atoms (2 Å in width) along with the corresponding bonds, angles, and dihedrals, as shown in Figure 5.2a. The altered structure was equilibrated at NPT ensemble (300 K, 1 atm) for 5 ns at the timestep of 2 fs and then put in between two water reservoirs each containing 1612 water molecules, shown in Figure 5.2b. The hydration was performed under the NPT equilibrium at 10 atm and 350 K for 150 ns, which was long enough for hydration (Figure 5.2c). Another 5 ns of NPT equilibration was

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then performed at 1 atm and 300 K. The pressure was under the anisotropic control at the x direction, with the yz cross-section area remained unchanged.

Figure 5.2. Snapshots of the hydration process: (a) converting a PA matrix with 3D periodic boundary to a PA thin film by deleting a slice of atoms and (b) dipping the thin film into a water reservoir; (c) Changes of water content over time during the hydration of the PA thin film generated from MPD/TMC=2.8:2.0. White, grey, blue, and red sticks represent H, C, N, and O in the PA structure respectively. White and red balls represent H and O atoms in water, while yellow and green balls respectively represent Na^+ and Cl^- . The blue square indicates the fixed edges along the Z direction to mimic the attachment on a substrate.

Since the hydration process was computationally costly, we hydrated only one structure for each MPD/TMC ratio. The chosen dry PA structures had the nearest atomic composition compared to the averages. The water content was calculated as the ratio of water density over the hydrated PA density, excluding the interface region of the hydrated PA thin films. We also computed the mean square displacement (MSD) of water molecules in the hydrated PA thin films over 250 ps, and calculated the self-diffusivity D_s from the slope of MSD with respect to time via $\text{MSD} = 6D_s t$. Each simulation was repeated three times.

5.2.3. RO Desalination model

The desalination model is depicted in Figure 5.3. We attached a spring on a 5 Å slab of PA thin films along the z direction at the permeate side to mimic the binding on a substrate. The feed reservoir contained 2527 water molecules, 30 sodium ions, and 30 chlorine ions (salinity of 36 g L⁻¹, close to 35 g L⁻¹ of typical sea water), and the permeate reservoir contained 2585 water molecules. We used a graphene piston at each end to confine the reservoir, and imposed the pressure of 1 atm by applying a force on each carbon atom of the piston. The system was relaxed for 3 ns at the timestep of 2 fs with NVT ensemble at 300 K. Then we raised the pressure on the feed side to 100 atm to push the feed through, and recorded the number of water molecules and ions in the permeate reservoir for 30 ns. To reduce statistical errors, each desalination simulation was repeated on three different machines so that randomness can be introduced by different computer architecture.

Figure 5.3. Snapshot of the desalination model after relaxation for 3 ns. White, grey, blue, and red sticks represent H, C, N, and O in the PA structure, respectively. White and red balls respectively represent H and O atoms in water, while yellow and green balls respectively represent Na⁺ and Cl⁻. The blue square indicates the fixed edges along the Z direction to mimic the attachment on a substrate.

5.3. Composition and structure of dry PA matrix

Table 5.1 gives the average atomic compositions in molar percentage, DC, and densities of the four dry PA matrixes at different initial MPD/TMC ratios. Our results were overall in good agreement with the measurements by Coronell et al.¹³⁰ using Rutherford backscattering spectrometry (RBS). The densities in Table 5.1 were also consistent with the experimental measurements of 1.22–1.28 g cm⁻³ for crumpled PA thin films,¹³⁵ and agreed with the result of 1.25 g cm⁻³ obtained by the previous MD studies.^{131,133} Despite the randomness in packing and polymerization processes, the standard deviations (SD) of the results were within 5 % except for COOH% at 3.1:2.0.

The generated PA thin films of different compositions varying from 2.8:2.0 to 3.1:2.0 can be interpreted as the front to back regions of depth-heterogenous PA thin films in the experimental observations. In the IP process, MPD molecules diffuse through the formed layer and its concentration changes from abundant to insufficient, resulting in the depth heterogeneity in the oxygen content of PA thin films.^{130,131} In Table 5.1, as the amount of MPD decreased from 3.1:2.0 to 2.8:2.0, O% increased and so did the COOH% and the O/N ratio. The heterogeneity was also apparent with respect to the DC and density in Table 5.1. The highest DC was at 3.0:2.0, but still not 100 % cross-linking, because the PA networks formed at the earlier stage hindered the diffusion of the rest unreacted monomers. The insufficiency of either MPD or TMC for the other three ratios accounted for lower DC, and the density was positively correlated to the

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DC. On the other hand, the compositions in Table 5.1 can provide guidance to tune the oxygen content and degree of crosslinking in the molecular design of PA membranes.

Table 5.1. The atomic composition, degree of cross-linking, and density of dry PA matrixes generated from various initial MPD/TMC ratios in comparison to the experimental data

	2.8:2.0	2.9:2.0	3.0:2.0	3.1:2.0	Experimental data
C%	74.30±0.05	74.57±0.02	74.78±0.01	74.94±0.05	71.6-74.2
N%	11.94±0.02	12.22±0.003	12.46±0.002	12.69±0.01	12.4-13.1
O%	13.76±0.07	13.21±0.02	12.75±0.01	12.37±0.06	13.0-14.2
COOH%	0.95±0.08	0.58±0.03	0.29±0.01	0.09±0.06	0.41-0.71
O/N	1.16±0.008	1.08±0.002	1.02±0.001	0.98±0.005	1.00-1.12
DC (%)	91.95±1.17	94.29±0.40	95.40±0.24	95.39±0.90	94.1-96.2
Density (g cm ⁻³)	1.245±0.01	1.255±0.020	1.259±0.010	1.258±0.002	1.22-1.28

The results were expressed as average±SD.

Hydrogen atoms were excluded in the calculations.

The experimental data of atomic compositions and density were retrieved from Coronell et al.¹³⁰ and Karan et al.¹³⁵ respectively.

We found no interconnected pores using a sphere with the size of a water molecule to probe the PA dry matrixes, resulting in zero free volume pores with the size of a water molecules. Thus, we instead used a smaller probe with the radius of 1 Å to obtain the PSD. The results of no free volume pores with the size of a water molecule in the dry PA matrixes seemed to contradict the experimental observations that free volume pores did exist in dry PA layers.^{46,229} However, the experimental measurements were typically conducted after the hydrated PA layers were dried,^{46,229} yielding enlarged free volume pores. Using positron annihilation spectroscopy (PALS), Kim et al.⁴⁶ discovered two types of pores in PA thin films, namely network and aggregate pores, with the pore sizes of 2.1–

2.4 Å and 3.5–4.5 Å respectively. Coronell et al.¹³⁰ supported the bimodal pore size distributions by the bimodal pK_a distributions of carboxylic groups. As mentioned in the introduction, previous MD studies held different opinions over the bimodal pore size distributions. We found that the PA matrixes generated from different MPD/TMC ratios showed different pore structures, as shown in Figure 5.4.

Figure 5.4. Pore diameter size distributions of the four dry PA thin films generated from the initial MPD/TMC ratio of (a) 2.8:2.0, (b) 2.9:2.0, (c) 3.3:2.0, and (d) 3.1:2.0. Each distribution was averaged from five replicates.

Figure 5.4c shows two distinct peaks at the pore size of approximately 3.4 Å and 7.3 Å, indicating the bimodal pore structure of the PA matrix at 3.0:2.0. Two adjacent peaks in Figures 5.4a-b also revealed the bimodal pores at the pore size of 3.6 Å and 5.6 Å for 2.8:2.0 as well as 3.1 Å and 5.3 Å for 2.9:2.0

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respectively, very close to 3 Å and 5 Å reported by Harder et al.⁴⁸ and the experimental observation by Kim et al.⁴⁶ The bimodal pore size distribution disappeared at 3.1:2.0 in Figure 5.4d, and there existed unimodal pores of the size approximately 3.5 Å.

We attribute the bimodal pore size distributions mainly to the carboxylic groups, which are the largest and most polar end groups in the PA matrix. Higher COOH% leads to the two closer peaks and higher second peak, while lower COOH% levels off the second peak. This is confirmed by the PSD of two PA matrixes with the highest and lowest COOH% in Figure 5.5 below (out of the 20 PA matrixes generated). The relationship between COOH% and pore structure can be applied to tune the pore sizes of the PA thin films. In Figures 5.5, dry PA matrixes generated from the initial MPD/TMC=2.8:2.0 possessed high COOH%. The two peaks were at 3.9 Å and 5.2 Å in Figure 5.5a, and 3.9 Å and 5.2 Å in Figure 5.5b, the closest among the 20 matrixes generated. Moreover, the second peak was almost equivalently high compared to the first peak. In contrast, there existed only one apparent peak in Figures 5.5c-d with flatter distribution for pore sizes larger than 5 Å.

Figure 5.5. Pore diameter size distributions of four dry PA thin films generated from the initial MPD/TMC ratios of (a-b) 2.8:2.0 and (c-d) 3.1:2.0.

5.4. Properties of hydrated PA thin films

The hydrated thin films were obtained by ripping the dry matrixes apart and dipping in a water reservoir. The ripping process was presumed to alter the atomic composition and DC of the PA films. We recounted the atomic numbers and the amide bonds, and calculated the atomic composition and DC in Table 5.2 for the four hydrated PA films. Compared to Table 5.1, the atomic compositions barely changed, and the DC decreased by 2 % but remained the same variations, justifying the feasibility of our hydration protocol.

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Table 5.2. The atomic composition and degree of cross-linking of hydrated PA thin films generated from various initial MPD/TMC ratios

	2.8:2.0	2.9:2.0	3.0:2.0	3.1:2.0
C%	74.48	74.58	74.90	74.80
N%	11.84	12.21	12.54	12.71
O%	13.67	13.21	12.56	12.49
COOH%	1.05	0.61	0.27	0.13
O/N	1.15	1.08	1.01	0.98
DC%	90.10	92.87	93.83	93.36
Thickness (Å)	58	54	51	53

Figure 5.6 gives the cluster size distribution of water molecules in the hydrated PA thin films, indicating the accessible pore size of the hydrated membrane. More than half of the clusters consisted of a single water molecule, especially for the case at 3.1:2.0 where pores with the size of a water molecule (diameter around 2.9 Å) comprised 72.2 % of the total clusters. We attribute the high peak to the unimodal pores of the dry PA matrix in Figure 5.4d. The proportion of single water molecule pores dropped for the other three PA films and reached its lowest at 2.8:2.0 as larger water molecule clusters appeared. Similarly, this can be explained by the higher second peaks with larger pores of dry PA matrixes in Figures 5.4.

Figure 5.6. (a) Cluster size distributions of water molecules in the hydrated PA thin films generated from MPD/TMC of 2.8:2.0, 2.9:2.0, 3.0:2.0, and 3.1:2.0; (b) Water density profiles along the X direction in the membrane region.

The occurrence of larger water molecule clusters yielded higher water densities in Figures 5.6b. Besides the amount of water uptake, Figure 5.6b also revealed the variation of water-membrane interface shape caused by the different membrane surface roughness. The water density profiles at the interface showed the slowest and steepest change at 2.8:2.0 and 3.0:2.0 respectively. As shown in Figure 5.7, the PA film generated from MPD/TMC=2.8:2.0 had the roughest surface, while the ones at 3.0:2.0 and 3.1:2.0 presented flatter surfaces. Meanwhile, with the existence of larger water cluster, water molecules formed visible channels at 2.8:2.0 and 2.9:2.0, while the other two PA films possessed no channels (Figure 5.8). The channel morphology and pore connectivity have been well documented by Shen et al.¹⁰, and we will not repeat here.

Figure 5.7. Cross-membrane snapshots of the four hydrated PA thin films generated from the initial MPD/TMC ratios of (a) 2.8:2.0, (b) 2.9:2.0, (c) 3.0:2.0, and (d) 3.1:2.0. White, grey, blue, and red sticks represent H, C, N, and O respectively. Water molecules were removed for a clear view of the surface roughness.

Figure 5.8. Cross-section snapshots of water molecule distribution in a 1-nm slab ($2.1 \text{ nm} \leq Z \leq 3.1 \text{ nm}$) of hydrated PA thin films generated from the initial MPD/TMC ratios of (a) 2.8:2.0, (b) 2.9:2.0, (c) 3.0:2.0, and (d) 3.1:2.0. White and red balls represent H and O in water molecules respectively. Membrane thickness is along the X direction.

Figures 5.9 gives the properties of hydrated PA thin films including density, water content, and membrane swelling. The water content and water density were the highest at 2.8:2.0 and were positively correlated to O%, as shown in Figure 5.9c. But the hydrated membrane density at 2.8:2.0 (1.32 g cm^{-3}) was slightly lower than that (1.34 g cm^{-3}) at 2.9:2.0. The reason lies in the larger density of the dry PA matrix at 2.9:2.0, resulting from the higher DC. The

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swelling volume was also under the influence of DC: compared to 3.1:2.0, the higher water content at 3.0:2.0 did not lead to a larger swelling volume, because the higher DC hindered the stretching of the hydrated structure. As depicted in Figure 5.9d, the swelling volume was linearly correlated ($R^2 > 99.9\%$) to DC and the dry membrane density. Higher DC yields larger dry density and thus leads to lower membrane swelling, which was also disclosed in the experiments by Foglia et al.²⁹ From the molecular point of view, the water cluster size distributions in Figure 5.6a also revealed the rigidity of the PA thin film generated from MPD/TMC=3.0:2.0, because unlike other compositions, clusters larger than 10 water molecules did not exist at 3.0:2.0 due to the high DC.

As discussed in Section 5.3, the depth-heterogeneity of PA thin films reflects in COOH% and DC. In Figure 5.9a, the water content decreased from 2.8:2.0 to 3.1:2.0, indicating that it is also depth-heterogeneous in real PA layers where MPD varies from abundant to insufficient from the back to the surface. However, the smallest swelling percentage occurred at 3.0:2.0 in Figure 5.9a, suggesting that the smallest membrane swelling exists in the middle of real PA layers. This provides the molecular explanation of the “sandwich structure” discovered by Freger²² and Drazevic et al.⁴⁵, where a dense core layer is hidden within more swelling-prone and porous PA structures.

Figure 5.9. (a) Water densities, hydrated membrane densities, water contents, and swelling volume in percentage of the hydrated PA thin films generated from MPD/TMC of 2.8:2.0, 2.9:2.0, 3.0:2.0, and 3.1:2.0; (b) Mean square displacement (MSD) of water molecules inside the hydrated PA thin films generated from the four initial MPD/TMC; (c) Variations of water content and water density in the PA thin films with respect to oxygen content; (d) Linear relationship between membrane swelling and the degree of cross-linking as well as dry membrane density.

Compared to experimental measurements, the swelling percentage in Figure 5.9a, ranging from 5.8 % to 18.4 %, was very close to the AFM-measured thickness increment of 2.7–13.0 % for the hydrated PA layers in RO membranes.^{22,45} The water content in this study was in the range of 4.3–15.6 wt%, consistent with 11.2–12.8 wt% reported by Zhang, et al.²³⁰ The upper bound of the water density ranging 0.05–0.21 g cm^{-3} also agreed well with 0.18–0.23 g cm^{-3} measured via quartz crystal microbalance.⁴⁷ Figure 5.9b shows the mean square displacement (MSD) of water molecules inside the four hydrated PA films over

250 ps. The calculated self-diffusivity D_S , ranging $0.2\text{--}1.6\times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, was highest at 2.8:2.0 and kept decreasing at larger MPD/TMC ratios. D_S at 2.8:2.0 ($1.6\times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) was very close to $1.7\times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ obtained by quasielastic neutron scattering.¹³¹ Overall, the present polymerization and hydration protocols can reproduce satisfactory realistic properties of the hydrated PA thin films. This transferrable approach is also applicable for other monomers to tune the hydration properties of polymers at the molecular level.

5.5. Relationships between water flux and membrane structure

Figure 5.10 shows one set of results on the number increment of water molecules in the permeate over 30 ns. There was a rapid rise of permeated number at the beginning stage (within 3 ns) along with a thickness reduction of around 5 %, indicating that some water molecules were squeezed out into the permeate with the contraction of PA thin films. Different from the nearly perfect linear increment ($R^2>95\%$) of permeance through rigid membrane structures in previous MD studies,^{36,39,231} Figure 5.10a shows apparent fluctuations for all the four compositions. The fluctuations are caused by the dynamic nature of PA structures, where deformable bonds as well as the soft van der Waals and electrostatic interactions result in the flexible and transient channels.^{10,139}

The water flux $J \text{ (L m}^{-2}\text{hr}^{-1}\text{)}$ was calculated using the slope of the number increment in Eq. (5.2), and the results are shown in Figure 5.10b.

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$$J = \frac{M_w}{\rho_w N_A A} \frac{dN}{dt}, \quad (5.2)$$

where N is the number of permeated water molecules within time t , M_w is the molar mass of water (18.015 g mol⁻¹), ρ_w is the density of liquid water at 300 K and 1 atm (0.997 g mol⁻¹), N_A is the Avogadro constant (6.022×10²³ mol⁻¹), and A is the cross-section area (Å²). In addition to fixing the back of PA films, we also tested clamping the sides of the PA film, resulting in less membrane contraction and increased water flux, as shown in Figure 5.10c.

The water flux J can also be written as:¹⁰

$$J = -\frac{P_w(\Delta p - \Delta \pi)}{l}, \quad (3)$$

where $\frac{P_w}{L}$ is the water permeability (L m⁻²hr⁻¹atm⁻¹), P_w is the permeability coefficient (L m⁻¹hr⁻¹atm⁻¹), l is the membrane thickness (nm), Δp is the pressure difference across the membrane (atm), and $\Delta \pi$ is the osmotic pressure (30 atm in this research). The permeability coefficients in this study were calculated to be 0.14–2.93×10⁻⁶ L m⁻¹hr⁻¹atm⁻¹, in the same magnitude (~10⁻⁶ L m⁻¹hr⁻¹atm⁻¹) estimated from the experimental results by Chowdhury et al.²¹⁷ For the high cross-linked (DC>90 %) and defect-free PA thin films examined in this study, we did not observe any salt penetration. In the experiments, PA TFC membranes with DC>90 % can achieve salt rejections higher than 94 %, ²³² and even higher rejection 97.5 % was also reported.²¹⁷ We will generate PA thin films with lower DC in our following work and examine the rejection of salt and other solutes.

Figure 5.10. (a) Number of permeated water molecules as a function of time; (b) Water flux at the hydrostatic pressure of 100 atm through PA thin films generated from different MPD/TMC ratios; (c) Comparisons of water flux, membrane thickness and water content of the PA thin film generated from MPD:TMC=2.8:2.0 by clamping on the back, two sides along the y direction, and four sides along the yz direction (all $5 \text{ \AA}$ in width). (d) Variations of water flux with respect to membrane swelling. Error bars indicate the standard deviations.

The flux in Figure 5.10b dropped from 2.8:2.0 to 3.0:2.0, and then there was a slight decrease from 3.0:2.0 to 3.1:2.0. We plotted the variation of flux with respect to membrane swelling in Figure 5.10d, showing that more swelling-prone membranes allowed larger water flux. The non-linear swelling-permeability relationship previously discovered in experiments^{22,45} showed a similar trend with Figure 5.10d. The flux at 2.9:2.0 was 10 times of that at 3.0:2.0, while the swelling difference was merely 1.6 times. The reason lies in the

different water transport mechanisms through the PA membrane. As mentioned in Section 5.4, there were visible water channels for PA thin films at 2.8:2.0 and 2.9:2.0 due to the existence of large water clusters, water molecules could move like hydrogen-bonded continuum. However, there was no visible channels at 3.0:2.0 and 3.1:2.0, and water molecules relied on temporary on-and-off channels jumping from one cavity to another in the two dense PA films. Further investigations on water transport mechanisms are elaborated in Chapter 6.

5.6. Summary

We developed a molecular dynamics approach to generate and hydrate PA thin films in RO membranes. The digital membrane reproduced the realistic dry and hydrated membrane properties and provided molecular-level explanation of the depth-heterogeneity observed in the experiments, such as the “sandwich structure” of swelling PA. We detailed the methodology to facilitate other researchers to examine various types of monomers and degrees of cross-linking. The generated PA thin films can also be offered as substrates for surface modification and functionalization and the transport investigation of various solutes.

We established the composition-structure-permeability relationships for the PA thin films generated from four initial MPD/TMC ratios representing insufficient to abundant MPD in the polymerization. Higher COOH% was obtained with lower MPD/TMC ratios, and highest DC was achieved when the

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ratio is 3.0:2.0. We discovered that the pattern of pore size distribution in dry PA matrixes relied on COOH%, where low COOH% lead to the unimodal distribution, and higher COOH% yielded bimodal distribution with two close peaks. As a result, after hydration, the PA thin film with the lowest COOH% showed the highest proportion of one-molecule pores in the cluster size distributions of water molecules. PA thin films with higher oxygen content or COOH% possessed higher water content, but not necessarily higher membrane swelling. The membrane swelling was linearly corelated to DC and dry membrane density, and water permeability was positively related to membrane swelling.

The huge flux drop from MPD/TMC=2.9:2.0 to 3.0:2.0 was caused by deviated water transport patterns. There were visible and more persistent water channels in the PA films at 2.8:2.0 and 2.9:2.0, while in the other two denser films at 3.0:2.0 and 3.1:2.0, water molecules relied on the on-and-off channels to jump from one cavity to another. Despite the different transport mechanisms, all the PA thin films exhibited oscillations during the water permeation. Further investigations on water transport mechanisms are required to relate the molecular scale discoveries to macroscopic theories.

Chapter 6. Transport of water through polyamide films

6.1. Overview

Continuous efforts have been devoted to identifying water transport mechanisms in the polyamide (PA) layer of thin-film-composite membranes using MD simulations, which led to the conclusion that both jumping and hydrogen-bonded continuum water transport exist.^{133,136-138} However, the influences of atomistic composition and polymer structure on water transport remain unclear, which is essential in improving membrane design at the molecular level. Moreover, researchers have debated over the solution-diffusion (S-D) model and pore-flow model of PA membranes for decades, and the S-D model has won the support of the majority.⁶⁻⁸ However, recent microscopic observations and MD studies of the porous structures for PA thin films together with the hydrogen-bonded “continuum” water transport have pointed towards the pore-flow model.^{7,17,31,127,136,233} This chapter focuses on the transport mechanisms of water in PA thin films with different atomic compositions and the modification of macroscopic S-D model with molecular details.

6.2. Simulation model

The transport mechanisms were explored by following the trajectories at the x direction of random water molecules and computing their interactions energies with the PA films generated with MPD/TMC=2.8:2.0 and 3.0:2.0 as

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described in Chapter 5, representing two types of PA structures shown in Figure 5.7. To quantify the continuum-like flow, water fluxes were computed using the desalination model in Figure 5.3, but with the entire PA structures fixed by attaching a string to the initial positions. The difference in water fluxes through the relaxed and fixed membranes can be used to identify the flow caused by diffusion and convection.

The influence of pressure on water transport was examined by comparing the water fluxes for the four PA structures generated in Chapter 5 under the hydrostatic pressure ranging 25–150 atm. Although the practical operating pressure in RO desalination commonly does not exceed 80 atm, the high pressure range was also examined in this thesis to capture the full picture of pressure influence and to obtain a better understanding of the S-D model. To eliminate the effects of salinity increase in the feed caused by the water permeation, the simulation duration at 2.8:2.0 and 2.9:2.0 was shortened to 15 ns and remained the same 30 ns as mentioned in Section 5.2.3 at 3.0:2.0 and 3.1:2.0. Each simulation was repeated three times. Mass densities across the PA thin films were also computed to illustrate the different influence of pressure on water transport for the four PA structures.

6.3. Transport mechanisms of water

In Figures 6.1 and 6.2, we depicted the trajectories at the x direction of four random water molecules and their interactions energies with the PA films at

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2.8:2.0 and 3.0:2.0. Water molecules transport in the PA thin films at 3.0:2.0 only by jumping in Figure 6.2, but to our surprise, jump mechanism was also more pronounced at 2.8:2.0 in Figure 6.1. The result was contrary to what reported by Shen et al.¹⁰ that water molecules were transported without jumping at all through a channel in a PA film. Possible reasons include the sampling approach and the structures of PA films between the two studies.

In the dense PA film at 3.0:2.0, the residence time of water molecules in a cavity before a “successful” jump was 1–2 ns or longer, consistent with previous research studies.^{10,127,136} The jump event took place within only a few picosecond and the length was several angstroms, also consistent with previous research studies.^{127,136,139} Accompanying each jump, there was a change, mostly a rise, in the interaction energy with PA structures up to 10 kcal mol⁻¹, as shown in Figures 6.1 and 6.2, and then the energy either stayed at the same level or fell back to the previous value. This indicates that water molecules need to overcome an energy barrier or else flow back to a lower energy state in every jump.

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Figure 6.1. Trajectories along the x direction of four random water molecules inside the PA film generated from MPD:TMC=2.8:2.0 as well as the interaction energy with the PA thin film. The flow direction is along the positive x direction. The red circles indicate the continuum-like transport, while the red rectangles indicate the jumping transport.

Figure 6.2. Trajectories along the x direction of four random water molecules inside the PA film generated from MPD:TMC=3.0:2.0 and their interaction energy with the PA film. The flow direction is along the positive x direction. Water molecules only showed jump transport mechanism as marked by the red squares.

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The dynamic nature of PA structures with deformable bonds, soft van der Waals and electrostatic interactions result in the flexible and transient channels.^{10,139} To examine the influence of the polymer flexibility on water transport, we immobilized the PA structure by applying a spring force (spring constant of $100 \text{ kcal mol}^{-1} \text{ \AA}^{-2}$) on the PA atoms to their initial positions. In Figure 6.3a, compared to the flexible PA structures, water fluxes through the immobilized PA films dropped to zero at 3.0:2.0 and 3.1:2.0, where water molecules relied on the jump mechanism. Once the PA structures were immobilized, the transient channels were permanently off. However, there were visible water channels in PA thin films at 2.8:2.0 and 2.9:2.0, and water molecules could still penetrate along the immobilized channels.

We followed the trajectories of four probing water molecules along the x direction for the immobilized PA structure at 2.8:2.0 in Figures 6.3b-c. They exhibited only continuum-like transport behaviour, proving that convective flow coexisted with diffusive transport, and that the fraction of convective pore flow depended on the PA structure. As discussed in Section 2.2.1, the solution-diffusion (S-D) model has been challenged with the discovery of interconnected pores.^{7,17,31,127,136,233} Figure 6.3 indicates that the convective transport might not be neglectable for less cross-linked PA membranes, with which it remains to be examined whether the S-D model is still valid.

Figure 6.3. (a) Decreased water fluxes in immobilized PA thin films compared to flexible PA films for different compositions; (b and c) Trajectories along the x direction of four randomly selected water molecules inside the PA thin film generated from MPD/TMC=2.8:2.0. The flow direction is long the positive direction of the x -axis. Water molecules mainly showed continuum-like transport mechanism as marked by the red squares.

6.4. Influence of pressure and the solution-diffusion model

Water fluxes through the four PA structures under the driving pressure of 25–150 atm are shown in Figure 6.4a. As mentioned in Section 5.5, the osmotic pressure of the feed saline water was 30 atm, but the permeate flow was not zero under the driving pressure of 25 atm. This stemmed from the artificially increased water density in the feed by the pressure, as shown in Figure 6.4b, which was imposed by adding a force on the piston (Figure 5.3) in this MD study. The feed water density was initially smaller than 1 g cm^{-3} when the pressure on the feed piston was 1 atm ($\Delta p=0 \text{ atm}$) due to the existence of salts, and it reached the permeate water density 1 g cm^{-3} at merely $\Delta p=5 \text{ atm}$. Therefore, smaller pressure was needed to counter the osmotic pressure in this research.

Figure 6.4. (a) Flux variations with respect to pressure difference Δp for the four PA thin films generated from MPD/TMC=2.8:2.0, 2.9:2.0; 3.0:2.0, and 3.1:2.0, respectively. Fluxes increased almost linearly with pressure in the blue region, while the increase slowed down in the red region. Higher pressure in the green region caused the deformation of polymer structures, leading to the rapid rise of water fluxes. The error bars indicate the standard deviations. (b) Water density change in the feed with respect to Δp , where the dash line indicates the pure water density in the permeate at the atmospheric pressure and the room temperature.

Different from the linear flux-pressure relationship in commonly accepted S-D model, the fluxes in this study increased nonlinearly with pressure. As mentioned above, the practical hydrostatic pressure used in the experiments is usually below 80 atm, falling in the linear region marked in blue in Figure 6.4a. In the red region, raising the pressure resulted in only moderate flux enhancement. Paul¹²⁸ reported that the nonlinearity was only significant when the pressure reached 136 atm, while a much lower value of only around 75 atm was needed in this study due to the artificially raised density as mentioned above. Abrupt changes occurred when imposed with higher pressure at 150 atm in the green region, which were likely caused by the deformation of polymer structures. The

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flux-pressure curve resembled Figure 2.6d in Section 2.2.1 except for the rapid increase at $\Delta p=150$ atm.

The influence of pressure on water densities inside the PA thin films has generally been overlooked in previous MD research, possibly because PA membranes were immobilized in previous studies so that water densities stayed the same under different pressure. Water density distributions under the influence of pressure in PA films of 2.8:2.0 and 3.0:2.0 are plotted in Figure 6.5 to highlight the distinctive membrane structures and transport mechanisms. As discussed in Section 5.2.2, the narrower interface region at 3.0:2.0 implied the smaller surface roughness. Besides, in contrast to the relatively symmetric water density distribution inside the PA membrane of 2.8:2.0 (Figure 6.5a), there was a concentration gradient in Figure 6.5b in the membrane region, similar to what is expected in the macroscopic S-D model as shown in Figures 2.6c-d. The concentration gradient was larger under higher pressure difference, thus higher diffusive flux was obtained. Araki et al.³³ reported the opposite concentration gradient inside the PA membrane that the downstream water density was higher than the upstream one under the pressure difference of 5 MPa, the reason of which we are not sure yet. The lack of apparent concentration gradient in the PA film of 2.8:2.0 (Figure 6.5a) further proved the existence of convective flow. At $\Delta p=150$ atm, the PA films were compressed further by around 5 Å, and the shape of density curve was also altered due to the deformation of the PA structure.

Figure 6.5. Water density distributions in the PA films generated from (a) MPD/TMC=2.8:2.0 and (b) MPD/TMC=2.8:2.0 under the pressure difference of 25–150 atm.

As discussed in Section 2.2.1, the nonlinearity of the flux-pressure curve in Figure 6.4a arises from the exponential concentration-pressure relationship and the average membrane mass fraction $\langle w_m \rangle$ due to the unneglectable convective flow.¹²⁸ The nonlinear density-pressure relationship in Figure 6.4b confirmed the first source of the nonlinearity. Since water densities at both sides of the membrane can be easily obtained in MD, the mass fraction of water at the upstream and downstream inside the membrane w_{10} and w_{1l} can be expressed as

$$w_{10} = K_1 \frac{\rho_{10}^s}{\rho} \quad (6.1a)$$

$$w_{1l} = K_1 \frac{\rho_{1l}^s}{\rho}, \quad (6.1b)$$

where K_1 is the partitioning coefficient of water between solution and membrane, ρ_{10}^s and ρ_{1l}^s are the water densities in the feed and permeate solution respectively, and ρ is the hydrated membrane density. Eq. (2.3) can thus be reformulated as

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$$n_1 = \frac{D_{1m} K_1}{\rho_w l \langle w_m \rangle} (\rho_{10}^s - \rho_{1l}^s), \quad (6.2)$$

where n_1 is the water flux ($\text{L m}^{-2}\text{hr}^{-1}$), l is the thickness of the hydrated membrane (nm), ρ_w is the water density at the room temperature and atmospheric pressure (0.998 g cm^{-3}), and D_{1m} is the transport diffusivity of water in the PA membrane ($\text{m}^2 \text{ s}^{-1}$). Water flux with respect to $\Delta\rho^s$ ($\Delta\rho^s = \rho_{10}^s - \rho_{1l}^s$) is plotted in Figure 6.6. Data at $\Delta p=150$ atm were excluded due to the deformation of PA structure. As shown in Figure 6.6, nonlinearity still existed, but with higher R^2 value at 3.0:2.0 compared to 2.8:2.0. It is thus worthwhile to examine the effects of $\langle w_m \rangle$ caused by the convective flow as well as the variations of membrane thickness l under different pressure in Eq. (6.2).

Figure 6.6. Variations of water flux with respect to the density difference $\Delta\rho^s$ between the feed and permeate across the PA thin films generated from (a) MPD/TMC=2.8:2.0 and (b) MPD/TMC=3.0:2.0 at $\Delta p=25\text{--}125$ atm.

The membrane thickness l can be captured from the water density profiles, and the average membrane mass fraction $\langle w_m \rangle$ is defined as the ratio of the water

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density over hydrated membrane density. The values are plotted in Figures 6.7a-b for MPD/TMC=2.8:2.0 and 3.0:2.0. The variations of l were similar for the two PA films, while $\langle w_m \rangle$ barely changed at 3.0:2.0, suggesting the absence of convective flow. Normalizing n_1 in Eq. (6.2) by l and $\langle w_m \rangle$ to eliminate the effects of these two factors, we have

$$n'_1 = n_1 l \langle w_m \rangle = D_{1m} K_1 (\rho_{10}^S - \rho_{1l}^S) / \rho_w, \quad (6.3)$$

where n'_1 is the normalized flux ($\text{L m}^{-1}\text{hr}^{-1}$), depicted in Figures 6.7c-d. The linearity of flux vs density difference improved after eliminating the effects of membrane thickness and membrane mass fraction. Because of the almost linear variations of l , the nonlinearity can thus be mainly attributed to $\langle w_m \rangle$. Taking the slope in Figures 6.7c-d, the permeability coefficient $P_w = D_{1m} K_1$ can be calculated as

$$P_w = \rho_w \frac{dn'_1}{d\Delta\rho_{10}^S}. \quad (6.4)$$

P_w was calculated to be $2.92 \times 10^{-10} \text{ m}^2 \text{ s}^{-2}$ and $1.68 \times 10^{-11} \text{ m}^2 \text{ s}^{-2}$ for the PA thin films of 2.8:2.0 and 3.0:2.0, respectively. Assuming that the partitioning coefficient K_1 remained as the water mass fraction in the hydrated membrane at the atmospheric pressure, the water transport diffusivities D_{1m} in the two PA films were calculated as $8.58 \times 10^{-10} \text{ m}^2 \text{ s}^{-2}$ and $7.64 \times 10^{-11} \text{ m}^2 \text{ s}^{-2}$, in the same magnitude (10^{-11} – $10^{-10} \text{ m}^2 \text{ s}^{-2}$) for commercial PA desalination membranes estimated by Lin et al.⁴⁷ in experiments. As such, the modified S-D model was valid to describe

the water transport in the present MD study, by accounting for the nonlinearity caused by the density-pressure relation and the convective flow.

Figure 6.7. Variations of (a) membrane thickness l and (b) average membrane mass fraction $\langle w_m \rangle$ with respect to the pressure difference $\Delta p=25\text{--}150$ atm. Linear relationships of the normalized flux with water density difference $\Delta \rho^S$ between the feed and permeate across the PA thin films generated from (c) MPD/TMC=2.8:2.0 and (d) MPD/TMC=3.0:2.0 at $\Delta p=25\text{--}125$ atm.

6.5. Summary

The water transport mechanisms were examined in the PA thin films with different compositions. Only jump transport appeared in the highly cross-linked PA membranes based on the trajectories of water molecule movements, corresponding to the diffusive transport described in the classic S-D model.

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However, both jump and continuum-like transport appeared in the less dense PA films, and only continuum-like transport was found when the PA structures were immobilized, confirming the existence of convective flow.

The relationship between water flux and pressure was found to be complex due to the nonlinear pressure-density relation and the convective flow. In the highly cross-linked PA films, the water density gradient drove the diffusive transport, and the water flux was linearly related to the water density difference across the membrane under different pressure. In the less dense PA films, however, the water density gradient was less apparent, further proving the coexistence of diffusive and convective flow. Here, The S-D model was then improved by using the water density difference directly instead of pressure difference, as well as by including the membrane mass fraction to account for the convective flow. The calculated transport diffusivities of water via the modified S-D model were consistent with experimental estimations.

Chapter 7. Conclusions and recommendations

7.1. Conclusions

The thesis is targeted to investigate the relationships between membrane structure and membrane transport using molecular dynamics (MD) simulations for two types of desalination membranes, graphene-based membranes and the polyamide layer in thin-film-composite membranes. Unique MD approaches were developed to assess different research problems. Distinctive transport mechanisms were identified under the influence of membrane compositions and structures as well as operating conditions. Molecular interpretations were gained of the macroscopic transport theories. The major conclusions are as follows.

- Pristine graphene (GE) nanochannels allowed excellent water permeability in pressure-driven desalination. Electric fields vertically applied across GE channels slowed down the water transport inside the GE channels due to the increased interaction between water molecules and GE walls. Ions were either adsorbed on the GE wall or repelled from entering into the channel by the electric field, both resulting in higher salt rejections.
- A coarse-grained MD approach was developed and validated to overcome the scale limitations of all-atom MD in simulating membrane distillation process through meso-size GE channels. The permeate flux through the

GE membrane was three-orders-of-magnitude higher compared to commercial microporous polymer membranes, as the combined result of the evaporation enhancement at the GE-water interface and the reduced transport resistance of water vapour. Two transport mechanisms, i.e. surface diffusion and activated Knudsen diffusion, were identified for different channel opening. The lowest vapour transport resistance was found at the channel opening where only surface diffusion occurred. Besides, smaller channel opening was beneficial for water evaporation at the GE-water interface due to the elevated mobilities of the interface water molecules.

- An MD approach was developed to build and hydrate the PA layer with controlled monomer ratios and realistic membrane properties, which enabled the investigation of the composition-structure-permeability relationships at the molecular level. The variation of pore size distributions in the dry PA structures at different monomer compositions led to the different water cluster distributions and wetting properties of hydrated PA films. Membrane swelling was linearly dependent on the degree of cross-linking (DC), and higher water flux was obtained in the more swelling-prone PA films due to the transition in water transport mechanisms.
- Different water transport mechanisms were discovered in the PA thin films with varied compositions. Only jump transport appeared in the

highly cross-linked PA membranes, corresponding to the diffusive transport described in the macroscopic solution-diffusion (S-D) model. However, both jump and continuum-like transport appeared in the less dense PA films, confirming the existence of convective flow. Water fluxes increased nonlinearly with pressure due to the nonlinear pressure-density relation and the convective flow. The S-D model was modified by directly using the water density difference instead of pressure difference as well as by including the membrane mass fraction to account for the convective flow. The calculated transport diffusivities of water via the modified S-D model were consistent with experimental estimations in the literature.

7.2. Recommendations

MD simulations have become a common practice to explore novel membrane materials and investigate membrane transport mechanisms. Advantages of MD simulations over the numerical methods at smaller scales, such as density function theories and *ab initio* MD, should be emphasized in handling complex systems and dynamic membrane structures. Employing realistic membrane configurations and operating conditions would improve the utility of MD. Validations of force fields should be routinely conducted to guarantee the quality of the results. Moreover, MD results can not only provide

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molecular descriptions of transport behaviours but also supplement macroscopic transport theories.

This thesis is mainly focused on water transport, while the more complicated transport behaviours of various solutes have not been extensively covered. Future work on the solute rejection, including surface interactions and solute transport mechanisms, is recommended to further optimize membrane compositions and structures in MD. Membrane fouling caused by small organics and larger biomolecules can also be investigated based on the membrane structure generated in Chapter 5.

Incorporating nanomaterials into polymeric matrixes to fabricate the mixed matrix membranes (MMMs) is currently the feasible solution to take advantage of the novel membrane transport mechanisms brought by nanomaterials while maintaining the stability and mechanical properties of polymers. In this thesis, nanomaterial membranes and polymeric membranes were separately investigated in MD, but building MMMs is also possible through the approach described in Chapter 5. Future work can include the dynamic interactions of nanomaterials with polymeric matrix to study the composition-structure-property relationships of the MMMs and the unique transport behaviours of solvents and solutes in MMMs.

Appendix A: All-atom molecular dynamics simulations of membrane distillation through meso-size graphene channels

All-atom molecular dynamics (AA-MD) simulations were conducted for only channel opening $d=20$ Å in order to compare the results and computational time with coarse-grained molecular dynamics (CG-MD). The system consists of two reservoirs, one graphene channel wall, and two piston channel walls as shown in Fig. S1. Different from CG-MD model, the feed reservoir is initially filled with salty water containing 15 Na^+ and 15 Cl^- dissolved with 918 water molecules, and the right-hand receiving reservoir with pure water containing 947 water molecules. The salinity in the feeding reservoir is 4.57 g L^{-1} , slightly higher than sea water salinity (3.5 g L^{-1}). The sizes of the graphene channel and the piston walls are the same with CG-MD. The reservoirs were confined by 1 atm pressure imposing on the piston at each side. This pressure was also realized by applying a constant force to carbon atoms of the piston.

Figure A1. All-atom molecular dynamics model of membrane distillation at channel opening of 20 Å.

APPENDIX A

The force fields of graphene were adopted from Patra, et al.²³⁴, and the force fields of other atoms were from our previous work.¹⁹⁸ Periodic boundary conditions were applied in all three directions. A large vacuum space was put in front of the piston at the permeate side in the x direction, to eliminate the interaction between the system and its image along this direction due to the application of periodic boundary conditions. The edges of the channels parallel to the y direction were constrained by attaching the beads to their initial position with a spring potential. The rest of the channel was allowed to move freely. Temperatures of the feed and permeate reservoirs were maintained constant at 350 K and 300 K respectively. The simulation was first conducted at the timestep of 1 fs for 10 ns to allow the system relaxation, and then continued for 75 ns to collect the data, same with the duration in CG-MD. The simulation was repeated three times.

The water molecule number in the permeate also increased linearly with time as shown in Figure A2. The distillation flux calculated from the slope using Eq. (4.4) was $337.6 \text{ mol m}^{-2} \text{ s}^{-1}$, 21% smaller than the CG-MD result $431.9 \text{ mol m}^{-2} \text{ s}^{-1}$ in Table A1. This is consistent with the fact that saline water evaporates slower than pure water. No salt penetration occurred in all three repeated simulations. In terms of computation cost, the total CPU time of CG-MD simulation was reduced by more than one order of magnitude comparing to the AA-MD CPU time, indicating the high efficiency of the CG-MD approach.

APPENDIX A

Figure A2. Increase of the water molecule number with time in the permeate reservoir at $d=20$ Å with feed and permeate temperature at 350 K and 300 K and no hydrostatic pressure imposed.

Table A1. Comparisons between AA-MD and CG-MD

	J (mol m ⁻² s ⁻¹)	CPU time (hour)
AA-MD	337.6±28.6	3820.6±32.5
CG-MD	431.9±19.0	336.5±5.7

Appendix B: Force fields of the polyamide thin films in molecular dynamics simulations

The pairwise potential was the sum of bonded and non-bonded interactions, simulated using the general amber force field (GAFF)²²². The bonded potential included bonds, angles, and dihedrals; the non-bonded interactions included Coulombics and van der Waals (vdW) interactions. The long-range Coulombics were computed with the particle-particle-particle-mesh (PPPM) method with a cutoff of 12 Å, and vdW interaction was modelled using Lennard-Jones (LJ) potential with a cutoff at 10 Å. The partial charges were calculated using semi-empirical with bond charge correction (AM1-BCC)²²³ in the Antechamber package. Water molecules were modelled with the Transferable Intermolecular Potential 3P (TIT3P), and the SHAKE algorithm was used to constrain the bond and angle of water molecules. Table B1 summarizes the partial charges and the LJ potential for each atom type. The LJ pair parameters between two species were calculated using the Lorentz-Berthelot combining rules. Tables B2-5 gives the force field parameters of bonds, angles, dihedrals, and impropers.

Table B1. Partial charges q and LJ parameters of monomers and hexane molecules.

Atom type	Description	Mass (g mol ⁻¹)	q (e)	ϵ (kcal mol ⁻¹)	σ (Å)
N	Unreacted N	14.0100	-0.4621	0.1700	3.2500
BC	C in benzene	12.0100	0.0986	0.0860	3.3997
BH	H in benzene	1.0080	0.1330	0.0150	2.5996
NH	H in amine	1.0080	0.3215	0.0157	1.0691
O	O in carboxyl	15.9999	-0.5761	0.2100	2.9599
C	C in carboxyl	12.0100	0.6797	0.0860	3.3997
LN	Linked N	14.0100	-0.4621	0.1700	3.2500
LC	Linked C	12.0100	0.6797	0.0860	3.3997

APPENDIX B

HC	C in hexane	12.0100	-0.0794	0.1094	3.3997
HH	H in hexane	1.0080	0.0387	0.0157	2.6495

Table B2. Parameters for bonds.

Bonds		Harmonic	
Atom1	Atom2	K (kcal mol ⁻¹ Å ⁻²)	r_0 (Å)
BC	BC	461.1	1.398
BC	BH	345.8	1.086
BC	N	384.2	1.412
NH	N	403.2	1.013
C	BC	345.9	1.491
C	O	637.7	1.218
BC	LN	384.2	1.412
NH	LN	403.2	1.013
LC	BC	345.9	1.491
LC	O	637.7	1.218
LC	LN	427.6	1.379
HC	HC	300.9	1.538
HC	HH	330.6	1.097

Table B3. Parameters for angles

Angles		CHARMM				
Atom1	Atom2	Atom3	K (kcal mol ⁻¹ rad ⁻²)	θ_0 (rad)	K_{UB} (kcal mol ⁻¹ Å ⁻²)	r_{UB} (Å)
BC	BC	BC	66.6	120.02	0	0
BC	BC	BH	48.2	119.88	0	0
BC	BC	N	67.9	120.19	0	0
BC	N	NH	47.6	116	0	0
C	BC	BC	64.3	120.33	0	0
BC	C	O	68.7	122.6	0	0
LC	LN	BC	63.8	123.71	0	0
LC	LN	NH	48.3	117.55	0	0
BC	LC	LN	67.7	115.25	0	0
BC	BC	LN	67.9	120.19	0	0
BC	LN	NH	47.6	116	0	0
LN	LC	O	74.2	123.05	0	0
LC	BC	BC	64.3	120.33	0	0
BC	LC	O	68.7	122.6	0	0
HC	HC	HC	62.9	111.51	0	0
HC	HC	HH	46.3	109.8	0	0

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Table B4. Parameters for dihedrals

Dihedrals		CHARMM					
Atom1	Atom2	Atom3	Atom4	K (kcal mol ⁻¹)	n	d	Weighting factor
BC	BC	BC	BC	3.625	2	180	0.5
BC	BC	BC	BH	3.625	2	180	1
BC	BC	BC	N	3.625	2	180	1
BC	BC	N	NH	0.45	2	180	1
BH	BC	BC	BH	3.625	2	180	1
BH	BC	BC	N	3.625	2	180	1
C	BC	BC	BC	3.625	2	180	1
C	BC	BC	BH	3.625	2	180	1
BC	BC	C	O	1	2	180	1
LC	LN	BC	BC	0.45	2	180	1
BC	LC	LN	BC	2.5	2	180	1
BC	LC	LN	NH	2.5	2	180	1
BC	BC	LC	LN	1	2	180	1
BC	BC	BC	LN	3.625	2	180	1
BC	BC	LN	NH	0.45	2	180	1
BC	LN	LC	O	2.5	2	180	1
BH	BC	BC	LN	3.625	2	180	1
NH	LN	LC	O	2.5	2	180	1
LC	BC	BC	BC	3.625	2	180	1
LC	BC	BC	BH	3.625	2	180	1
BC	BC	LC	O	1	2	180	1
HC	HC	HC	HC	0.18	3	0	1
HC	HC	HC	HC	0.25	2	180	0
HC	HC	HC	HC	0.2	1	180	0
HC	HC	HC	HH	0.16	3	0	1
HH	HC	HC	HH	0.15	3	0	1

Table B5. Parameters for impropers

Improper		Harmonic			
Atom1	Atom2	Atom3	Atom4	K (kcal mol ⁻¹ rad ⁻²)	χ_0
BC	BC	BC	BH	1.1	180
BC	BC	BC	N	1.1	180
C	BC	BC	BC	1.1	180
LC	BC	LN	NH	1.1	180
BC	BC	BC	LN	1.1	180
LC	BC	BC	BC	1.1	180
BC	LN	LC	O	10.5	180

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