Surface and structural design of nanocompounds using molecular dynamics simulations for desalination processes

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**SURFACE AND STRUCTURAL DESIGN OF
NANOCOMPOUNDS USING MOLECULAR
DYNAMICS SIMULATIONS FOR
DESALINATION PROCESSES**

KIEU TRUNG HIEU

INTERDISCIPLINARY GRADUATE SCHOOL

**NANYANG ENVIRONMENT AND WATER RESEARCH
INSTITUTE**

2019

**SURFACE AND STRUCTURAL DESIGN OF
NANOCOMPOUNDS USING MOLECULAR
DYNAMICS SIMULATIONS FOR
DESALINATION PROCESSES**

KIEU TRUNG HIEU

Interdisciplinary Graduate School

Nanyang Environment and Water Research Institute

A thesis submitted to the Nanyang Technological University in partial
fulfilment 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

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Kieu Trung Hieu

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Date

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Adrian Law

Authorship Attribution Statement

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

Chapter 3 has been published as Kieu, H. T., Liu, B., Zhou, K. and Law, A. W. K. Pressure-driven water permeation through multilayer graphene nanosheets. *Physica Status Solidi B* **254**: 1700074 (2017).

The contributions of the co-authors are as follows:

- Associate Professor Law and Associate Professor Zhou provided the research direction and revised the draft of the manuscript.
- Dr Liu gave suggestion about the modeling and calculation.
- I performed the simulation works, conducted data analysis, wrote and revised the draft.

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The contributions of the co-authors are as follows:

- Associate Professor Law and Associate Professor Zhou provided the research direction and edited the draft of the manuscript.
- Dr Liu and Ms Zhang gave suggestion about the model set up and calculation data.
- I performed the simulation works, conducted data analysis, wrote and revised the draft.

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The contributions of the co-authors are as follows:

- Associate Professor Law and Associate Professor Zhou provided the research direction and revised the draft of the manuscript.
- I designed the study, performed the simulation work, analysed the data and prepared the draft.

Jan 7, 2020

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Abstract

The increasing freshwater demand due to population growth, industrial revolution, and climate changes has triggered a critical need for expansion and development of desalination and water treatment industry. Recently, with the rapid advance of nanotechnology, significant improvements have been made to the performance of desalination and water treatment system with the aid from nanomaterials and nanostructures. As the global need for freshwater becomes increasingly important, the search for optimal structural and material design holds a promising potential, which has attracted extensive efforts during the past decade.

To optimize the functionality of the nanocompounds, the understanding of the atomistic behaviors needs to be obtained. Since the macroscopic behaviors of the systems can be very different at the nanoscale, precise techniques are often required to monitor the processes. However, experimental methods are costly and, sometimes, incapable of capturing the dynamic evolution. Hence, detailed information into the underlying mechanism has been lacking, and the selection of material and structure is mainly based on empirical experience, which hinders the speed of the progress.

In the present study, a novel approach for investigating the nanoscale performance of the compounds using computational molecular dynamics (MD) simulations is proposed. Recently, the development of computer science has witnessed a huge development as the computational power is remarkably fastened with new parallel computing architectures. By utilizing the MD approach, one is able to investigate the nanocompounds during the process at a higher speed and a reduced cost compared to experimental testing. Furthermore, MD simulations can provide atomistic insights into the dynamic behaviors of the compounds and propose reasonable structural and chemical improvements to enhance the performance of the system.

The MD approach in this study is then customized to investigate four different environmental processes: (1) pressure-driven water transport through multilayer graphene membrane; (2) water evaporation through a vertically aligned graphene

bilayer with tunable wettability; (3) water evaporation on a corrugated graphene oxide surface with different morphology and (4) non-equilibrium evaporation of a nano water droplet under the effect of vapor pressure. The configuration of the models is based on conditions in membrane desalination and thermal distillation processes. The verification is discussed in each model, which shows good agreement with the measuring data. The dynamic performance of the system is monitored during the simulations, and the underlying mechanism is explained by calculation of intensive and extensive properties of the system.

This work highlights potentials to efficiently utilize computational methods to accelerate the next-generation development of environmental material with nanostructure and surface design to enhance the productivity of desalination and water treatment processes.

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List of Symbols

a	Porous ratio of GE layer
A	Area exposure
A_c	Amplitude
d	Pore diameter
d_c	Capillary distance
d_l	Distance between two adjacent layers of GE multilayer
ε	Energy well of LJ potential
E	Harmonic potential of sampling method
E_k	Kinetic energy
E_p	Potential energy
f	Force magnitude applied to atoms in feed reservoir
$\mathbf{F}$	Sum of forces applied on a particle
h_{fg}	Vaporization heat of water
Δh_{lv}	Liquid-vapor enthalpy change
H	Evaporation enhancement factor
H_{sur}	Expansion of surface area
θ	Contact angle
J, J_0, J_{ref}	Evaporation rate, initial evaporation rate and reference evaporation rate
k	Spring constant
k_B	Boltzmann constant
K	Number of GE layers
κ	Evaporation flux rate constant
κ_p	Pressure change rate constant
L	Channel length
L_x, L_y	Water box size in X and Y dimensions
λ	Wavelength
m	Particle mass
$\dot{m}$	Experimental evaporation flux

n	Number of gaps in GE layer
η	Evaporation efficiency
N, N_0	Number of molecules inside the channel and feed reservoir
N_v	Number of evaporated molecules
O	Gap offset
P	Pressure
ΔP	Capillary pressure difference
P_e	Evaporation potential
P_v	Vapor pressure
P_{sat}	Saturated vapor pressure
ρ	Water density
q	Polar charge
Q	Water flow rate
Q_s	Light intensity
r	Distance between atoms in LJ potential
$\mathbf{r}$	Position vector of a particle
r_w	Gap size ratio
S	Stress tensor
σ	Zero-across distance of LJ potential
σ_c	Condensation Coefficient
σ_e	Evaporation Coefficient
σ_s	Surface tension
t	Time
T	Temperature
v, v_0	Velocity of water molecules inside channel and feed reservoir
V_0	Volume of feed reservoir
w_i	Width of gap i
X	X coordinate
Z, Z_p	Z coordinate

List of Abbreviations

Aqp	Aquaporin
CDI	Capacitive Deionization
CGMD	Coarse-grained Molecular Dynamics
CHARMM	Chemistry at Harvard Macromolecular Mechanics
CNT	Carbon Nanotube
CPS	Capillary Polar Surface
DSMC	Direct Simulation Monte Carlo
ED	Electrodialysis
ELBA	Electrostatics-Based water model
FO	Forward Osmosis
GE	Graphene
GO	Graphene Oxide
ISVG	Interfacial Solar Vapor Generation
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
LJ	Lennard-Jones
MC	Monte-Carlo
MD	Molecular Dynamics
MED	Multi-Effect Boiling
MSD	Mean Square Displacement
MSF	Multi-Stage Flash
NF	Nanofiltration
NVE	Constant volume and energy
NVT	Constant volume and temperature
PA	Polyamide
PE	Potential Energy
PMF	Potential of Mean Force
PPPM	Particle-Particle Particle-Mesh
PSSG	Plasmonic Solar Steam Generation
PTCE	Polycarbonate Tracked-Etched
RO	Reverse Osmosis

TFC	Thin Film Composite
TIP3P	Transferable Intermolecular Potential with 3 Points
VMD	Visual Molecular Dynamics
WHAM	Weighted Histogram Analysis Method

Chapter 1 Introduction

1.1 Motivation

Water scarcity has been a major problem globally during the past decades in the context of population growth, environmental pollution, and climate changes. A recent study in 2014 showed that 40% of the world population is currently living with serious water stress, and the impacts from population growth together with climate change will raise the figure to 60% by 2025 (Schewe *et al.* 2014). Furthermore, it can be seen in Figure 1.1 that in 30-year time, the water stress will be even more severe, with up to 2.8 times increase in the demand for freshwater. The most vulnerable areas include the current high-demand regions, such as Middle East and Western US, as well as the fast-developing regions such as China. North Africa will also witness a significant change in water stress due to the impact of population growth and climate change.

The increasing demand for fresh water has changed the planning of water management all over the world. People have been looking for alternative sources of water beside the traditional sources from rainfall, rivers, and lakes. Since many large cities are located in the coastal areas, it is much convenient to access the oceans for water sources. Hence, desalination has become one of the most vital measures to tackle the issue of water supply over the world. In desalination, high-salinity water, usually from the sea, is treated to remove salts such as sodium chloride (NaCl) to a concentration lower than 1% to meet the requirement for various human uses.

Nowadays, desalination technologies can be categorized into two major groups: thermal desalination and membrane desalination. Thermal desalination utilizes the evaporation and condensation processes to extract fresh water, in which thermal heat and electricity are used as the main energy sources. The dominant technologies in this sector include multi-stage flash (MSF) (Fig. 1.2), multi-effect boiling (MED) and vapor compression (VC).

Figure 1.1. (a) Global water stress in 2010 and (b) projected change in 2040 (Source: Gassert 2013)

On the other hand, membrane desalination uses membranes to selectively separate fresh water from the feed, in which the energy mostly comes from electricity. The most dominant technologies in membrane desalination include reverse osmosis (RO) (Fig. 1.3). Other novel technologies, such as forward osmosis (FO), electrodialysis (ED) and capacitive deionization (CDI), also witness fast development.

Figure 1.2. Schematic diagram of MSF desalination process (Source: Fitchner 2011)

The emergence of desalination and water treatment industry has raised a crucial need to enhance the productivity and performance of the technologies. Recently, nanotechnologies and nanomaterials have been recognized as one of the major focuses of next industrial revolution. Advancements in nanotechnology have shown that with the aid of nanocompounds and nanostructures, the performance of desalination and water treatment processes could be greatly improved. A lot of efforts are now devoted to the design and functionalization of novel compounds and structures, and some improvements have been reported for the development of the next-generation environmental materials. However, due to the high cost of experimental techniques and lack of understanding of atomistic behaviors, the progress has not sufficiently met the demand for development. Therefore, computational modelling of materials is proposed to be the subject of this research.

Figure 1.3. Schematic diagram of RO desalination process (Source: Fitchner 2011)

1.2 Focus of the work

The aim of this research study is to utilize molecular dynamics approach to examine the properties of environmental materials and their behaviors at the nanoscale, and then use the insights from the simulations to guide improvement to optimize their performance. The detailed objectives of the project are to:

- i) Investigate the atomistic and kinetic behaviors of water in pressure-driven desalination and thermal evaporation processes.
- ii) Explore the performance of nanostructures and the effects of environmental factors in the processes.
- iii) Examine and propose modifications of the surface of the materials to optimize their efficiency in pressure-driven and thermal-evaporation desalination.

1.3 Contributions from the research work

In this thesis, the following contributions are made:

- i) A computational study on the transportation of confined water through a multi-layered graphene membrane under pressure condition in RO desalination. The underlying transport mechanism has been revealed, and the effects of structural parameters have been investigated. Several guidelines for the design of graphene multilayer for RO desalination have been provided.

- ii) An atomistic model to investigate the evaporation of water under capillary force. The combined effect of capillary action and surface wettability as well as the influence from temperature have been examined to provide insights for the fabrication of surface for evaporation enhancement

- iii) A study of water evaporation from the surface of graphene oxide for solar steam generation application. The surface morphology effect on the evaporation of water is carefully examined to reveal the realistic behaviors, which contributes useful information for the fabrication of graphene oxide-based compounds for solar evaporation

- iv) A study of non-equilibrium evaporation of a nano water droplet in a closed with effect of vapor pressure using coarse-grained molecular dynamic simulation. By considering the dynamical equilibria of evaporation and condensation, theoretical analysis of the evaporation flux in realistic condition is performed. The results illustrate a novel approach to improve the accuracy of evaporation model.

1.4 Organization of the thesis

The thesis is organized into 7 chapters. In chapter 1, the background information on the significance of desalination and water treatment, together with the research gaps, the focuses of the study and the contribution of the works are introduced. Chapter 2 presents a literature review of the field of study, including the growth in the desalination and water treatment market, the application of nanotechnologies in enhancing the performance, recent progress in the design and fabrication of the compounds, the remaining constraints and the benefits of the computational approach

in the acceleration of the process. The major contributions resulting from this research work are then presented in Chapters 3 to 6 as follow:

i) Chapter 3 introduces the use of MD simulations in examining the structural and chemical design of multilayer GE membrane for pressure-driven water transport. The aim of this work is to provide useful guidelines to the fabrication of GE-based membrane for water permeation in RO and FO processes.

ii) Chapter 4 presents an MD study of water evaporation through a capillary structure under difference surface wettability. The effects of hydrophilicity, temperature and structural parameters on the capillary action and the evaporation flux are thoroughly examined to give insights on the behaviors of water evaporation at the nanoscale.

iii) Chapter 5 describes the investigation of the practical surface morphology effect of GO on the evaporation of water. By revealing the organizing structure of water molecules on different areas of the surface, modifications are proposed that can benefit the evaporation enhancement.

iv) Chapter 6 propose a method to improve the accuracy of theoretical evaporation models of closed systems by considering the effect of vapor pressure. By utilising a coarse-grained MD approach, the dynamic evolution of a nano water droplet reaching saturation is observed, and meaningful insights are presented.

Finally, Chapter 7 summarizes the major findings and accomplishments of this study together with a recommendation for future work.

Chapter 2 Literature review

This chapter describes a summary of the emerging contribution of nanotechnology and nanomaterials for desalination and water treatment industries as well as the current progress of the materials design to enhance desalination efficiency. Two major techniques in desalination and water treatment, namely, membrane techniques and thermal techniques, are systematically reviewed. The present constraints as well as the advancement of computational technique in the design of materials will be presented.

2.1 Development of the desalination market

Despite the challenge of intense energy needed to produce fresh water, there has been an increasing amount of investment into desalination and water treatment technologies over the past few decades. The global desalination capacity has witnessed a surge from 20 to ~95 million cubic meters per day during the period of 2000 – 2020 (Fig. 2.1), together with the significant decrease in the cost of desalinated water (Ghaffour *et al.* 2013, Sood *et al.* 2014, Caldera *et al.* 2017, C. Darre *et al.* 2018). The spatial distribution of the desalination plants across the world in 2018 shows the major contribution from the Middle East and North Africa regions, which account for around 48% of the world capacity. The amount of desalinated water from East Asia and North America regions contribute 18.4% and 11.9% to world production, respectively.

Besides the growth in capacity, desalination technology has also received a lot of attention from scientists and researchers. The total number of publications on the topic of desalination has grown from less than 2000 to approximately 16500 during the 2000 – 2018 period, with the majority of the interest paid to the technological aspect. Fig. 2.2 shows the number of publications on the desalination topic, categorized by the technologies, during the period of 1980 - 2020. There is an exponential increase in research studies on RO and emerging technologies (FO, NF and CDI). Traditional thermal processes, such as MSF and MED, despite the cost-

effective disadvantage, still receive a considerable amount of interest as they are the primary choice in the Middle East due to the abundant energy source from fossil fuel.

Figure 2.1. Trends in global desalination by (a) number and capacity of total and operation desalination facilities and (b) operational capacity by desalination technology (Source: Jones *et al.* 2019)

With the concern of global warming, the utilization of renewable energy sources has been encouraged as an alternative solution for desalination. Such energy sources, with their abundance and environmental sustainability, have attracted a lot of attention from researchers (Alkaisi *et al.* 2017). A recent study in 2017 showed that more than 130 desalination plants using renewable energy source have been established within the last few years (Alkaisi *et al.* 2017). Table 2.1 summarizes the compatibility of the mentioned renewable energy sources with current major desalination technologies.

Figure 2.2. Number of publications by type of desalination technology during the period from 1980 to 2020 (Source: Jones *et al.* 2019)

Among the renewable energy sources, solar energy is the most suitable choice as 70% of the renewable desalination plants utilize this energy source to produce fresh water. Wind, geothermal, wave, and tidal energy are other promising options, but they are facing challenges in the design with conventional operations in terms of scale, establishing methods and geographic location. Another promising source of energy that can be utilized for thermal desalination is waste energy and heat from industrial processes, which has been gathering a lot of attention from researchers for cost-effective operations in thermal desalination technologies (Wang *et al.* 2011, Ammar *et al.* 2012)

2.2 Nanocompounds and nanostructures for desalination

During the past decades, nanotechnology and nanoscience have become a major focus in the revolution of various industries. The development of nanotechnology comes from the need of understanding at the molecular level. In desalination and water treatment technologies, the increase in the global capacity together with the emergence of new desalination technique has attracted extensive research interest in

this area. In the following sections, a brief summary of the application of nanotechnology in membrane and thermal desalination shall be introduced.

Table 2.1. Possible combination of renewable energy and desalination technologies
(Source: Al-Karaghoul *et al.* 2011)

Renewable energy sources	Thermal technologies			Membrane technologies	
	MSF	MED	VC	RO	ED
Renewable technologies	x	x	x	x	x
Solar thermal			x	x	x
Solar PV			x	x	x
Wind	x	x	x	x	x
Geothermal	x	x	x	x	x

2.2.1 Membrane desalination

Several types of materials have been reported to hold promising potential for the next generation membranes, including nanocomposites, aquaporin, nanotubes, and graphene. A number of membranes are approaching commercialization, while others are still under development.

Nanocomposite membranes are created by intercalating nanoparticles into the structure of commercial membranes to obtain more advanced characteristics such as smoothness, porosity and hydrophilicity. They offer an improved permeability at a fixed level of salt rejection, thus reduces the applied pressure requirement and leads to lower operation cost. On the drawback side, they are quite expensive to fabricate due to the cost of supplementary components. Jeong *et al.* (2007) used zeolite nanoparticles to increase porosity and hydrophilicity of thin-film membrane, which increases the permeability of the membrane by up to 80% at 90% rejection rate. Pendergast *et al.* (2013) indicated that the flux enhancement is sensitive to the

reduction of the membrane compaction. Many types of nanoparticles have been brought into the investigation. Hofs *et al.* (2013) used inorganic nanoparticles in the membrane active layer. The membrane yields a permeability flux which is 1.4 times higher to the standard thin-film composite membrane.

Another essential factor that needs to be considered in the fabrication of the membrane is the fouling resistance. Isawi *et al.* (2016) used ZnO nanoparticles to enhance the hydrophilicity of the PA membrane. Anti-fouling test is also conducted. The membrane also showed good water flux, salt rejection and antifouling performance. Al Mayyahi (2018) used TiO₂ nanoparticles to enhance the antibacterial property and organic fouling resistance and of the PA membrane. Other types of nanoparticles have been tested for the antifouling improvement of the membrane (Zhang *et al.* 2013, Ben-Sasson *et al.* 2016, Liu *et al.* 2016, Zhang *et al.* 2017)

Aquaporin (Aqp) membranes consist of protein channels which control the transport of water molecules across the biological cells. They are popular in FO desalination, where the natural osmotic pressure drives the permeation flux, as they allow fast diffusion and high selectivity. In 2012, Wang *et al.* proposed a biomimetic architecture for FO using Aqp Z as the selective layer. The protein is incorporated into ABA block copolymer vesicles, which is then adsorbed on a porous PCTE support under pressure to form the pore-spanning membrane (Fig. 2.3). The membrane exhibits a water flux ranging from 11.3 to 16.4 L m⁻² h⁻¹ depending on the molar ratio of the incorporated AqpZ-ABA vesicle. They indicated that the performance of the membrane can be further improved since only part of the Aqp Z remains functional after the transformation from the vesicles to the planar surface, and the key factor is to maintain their function and stability during the fabrication.

There has also been a huge number of studies focusing on the selection of the protein that can optimize the performance of the membrane in term of permeability and selectivity (Li *et al.* 2015, Tai-Shung Neal *et al.* 2015, Li *et al.* 2017). However, the accuracy of the calculation of permeation in aquaporin membrane has been questioned. Evaluation on the estimation of the permeability of these membranes

showed that the permeability of one or two orders of magnitude large than current membrane can be achieved, although careful considerations are needed (Grzelakowski *et al.* 2015).

Figure 2.3. Schematic diagram of pore-spanning membrane design and synthesis: (a) Incorporation of AqpZ in ABA copolymer vesicles; (b) Surface modification of the PTCE membrane support. PTCE membranes are firstly coated with a 60 nm thick gold layer and sequentially coated with another monolayer of cysteamine through chemisorption. The primary amine residues are converted to acylate residues via conjugating with acrylic acid. (c) Pressure-assisted vesicles adsorption on the PTCE support and (d) the covalent-conjugation-driven vesicle rupture and pore-spanning membrane formation. (Source: Wang *et al.* 2012)

Recently, carbon-based materials such as CNT, nanoporous GE and GO have emerged as the new generation material for membrane desalination. Reports have shown that the transport of water inside the nanochannel formed by CNTs and GE is several orders of magnitude faster than commercial membranes. In addition, it is found that the transport of water inside carbon-based membranes is highly dependent

on the membrane characteristics, which opens a broad range of investigation in order to enhance their capability.

Inukai *et al.* (2015) synthesized a multi-functional RO membrane consisting multi-walled CNT and PA by interfacial polymerization. The membrane exhibits enhanced flow and antifouling property as well as impedes the chlorine degradation. Kim *et al.* (2018) integrated GO flakes into a crosslinked network to mitigate their swelling behavior. The membrane showed a high flux of $33.5 \text{ L m}^2 \text{ h}^{-1}$ with 98% NaCl rejection at a pressure of 10 bar. He *et al.* (2015) reported that the incorporation of GO into the TFC membrane enhances their antimicrobial activity due to both physical and chemical interaction between the GO and the bacteria. Chae *et al.* (2015) found that the size and concentration of GO are critical for the enhancement of the PA thin film composite membrane.

2.2.2 Thermal desalination

A lot of researches published in recent years have brought back the topic of thermal desalination enhancement, particularly with the aid from the sun. The utilization of solar energy to enhance water evaporation and improve desalination performance has received a lot of attention due to the need for sustainability. To facilitate solar evaporation, the nanostructures need to possess the plasmonic property, which enables them to harvest and convert sunlight into thermal energy, providing external heat for the feed body. A number of structures have been proposed recently, which can be classified into two groups: metal and carbon-based.

Metal-based nanostructures have been a traditional option for solar evaporation due to their broad absorption spectrum. In their crystalline structures, the free electrons with high mobility can interact with each other resulting in the regime of plasmon resonance, accelerating the generation of heat (Brongersma *et al.* 2015). Gold is the most preferred metal in light-harvesting experiments due to its strong photothermal property. Such strong plasmonic effect increases the surface temperature of the compounds to higher than the boiling point of water, leading to fast vaporization (Fig

2.4) (Fang *et al.* 2013, Neumann *et al.* 2013). Wang *et al.* (2014) fabricated a free-floating film of Au nanoparticles that can localize the heat transfer at the evaporative surface and reported a fast evaporation rate under laser exposure. Other gold nanostructures, including nanorods (Bae *et al.* 2015) and nanoshells (Zielinski *et al.* 2016) are also tested. However, due to the substantial cost of fabrication, those compounds have yet to be deployed in large-scale applications. To overcome this challenge, cheaper metals with proper structural designs were also proposed (Chen *et al.* 2016, Zhou *et al.* 2016, Sun *et al.* 2017).

Figure 2.4. Schematic of nanoparticle-enabled solar steam generation (Source: Neumann *et al.* 2013).

Carbon-based materials are the new emerging generation of materials for evaporation owing to their natural broad-band absorption, low cost and abundance. The photothermal effect mechanism in carbon-based materials involves the excitation and relaxation of the electron (Kuzmenko *et al.* 2008). Various forms of carbon materials were synthesized and examined in lab-scale evaporation experiments, including graphite (Ghasemi *et al.* 2014), carbon spheres (Zeng *et al.* 2011, Zeng *et al.* 2014) and carbon superhydrophobic gauze (Liu *et al.* 2015). Recently, nanostructures of carbon, such as CNT (Wang *et al.* 2016), GE and GO (Li *et al.* 2016, Hu *et al.* 2017, Wang *et al.* 2017), have also been brought into the examination. These structures were able to achieve a conversion efficiency from 65 to 85% (Dao *et al.* 2018), which makes them advantageous over traditional metal compounds.

In addition, when incorporated in a complex steam generation system, carbon-based materials show a wide range of flexibility. Liu *et al.* (2017) introduced a bilayered structure of GO cast on microporous wood, which provides mechanical stability and thermal insulations for heat localization. Wang *et al.* (2017) used polyethyleneimine to connect reduced GO sheets and porous cellulose esters substrate in a double-layer system. Other polymers such as polyurethane (Wang *et al.* 2017), polytetrafluoroethylene (Zhang *et al.* 2017) and polystyrene (Shi *et al.* 2017) also showed good compatibility.

2.3 Material designs and characterization

2.3.1 Membrane desalination technology

Membrane technology has become more and more dominant in the world desalination market due to the reduced energy cost to desalinate water compared to thermal processes. Academia and industries keep improving the membrane design over the years, and new structures and materials are continually proposed. In RO desalination, great efforts have been devoted to improve the permeability and selectivity as well as the fouling resistance of the membrane. In fact, it is necessary to understand the underlying mechanisms during the process to achieve the optimal performance, including the transport of water inside the membrane nanochannels, the blockage of ion and most importantly the behaviors of water at the nanopores. In CNT membranes, to achieve high permeability, it is suggested that the CNTs must be aligned and packed at a high density, and the pore size must be lower than 6 to 10 Å to enable selective transport (Majumder *et al.* 2005). In addition, the tip of the CNT should be functionalized with hydrophilic groups to reduce the entrance energy barrier, thus increasing the flux, stability and fouling resistance (Majumder *et al.* 2011).

For graphene-based membranes, since the filtration mechanism is mostly based on size-exclusion and electrostatic repulsion, the trade-off between the permeation flux

and salt rejection has been mentioned in the fabrication of the laminar structure. It is reported that high permeance can be achieved while maintaining the rejection by modifying the surface morphology of the inner channel inside the membrane, usually by intercalating nanocompounds such as CNT (Gao *et al.* 2015, Han *et al.* 2015), copper hydroxide (Huang *et al.* 2013), and TiO₂ nanoparticles (Xu *et al.* 2013) into the interlayer space. Researchers are still working on the design of a proper layer separation to fully utilize the low-friction flow of water through the structure of the membranes.

Membrane fouling is also a critical problem that hinders the advances of RO technology. It is caused by the presence of defects and impurities which interact directly or indirectly with the membrane surface. Fundamental studies indicated that the concentration polarization occurs at the feed side of the membrane due to the accumulation of the blocked ions. Excessive accumulation eventually forms a layer on the surface of the membrane, narrowing or even blocking the membrane pores. The most common way to strengthen the antifouling effect of RO membrane is to incorporate inorganic compounds, usually metal nanoparticles, to the membrane surface (Van Hooijdonk *et al.* 2013), but more future efforts are needed since each type of compounds has its specific targeted species.

2.3.2 Thermal desalination technology

Although being surpassed by membrane technology, thermal desalination still accounts for more than 30% of the world's capacity and is the main contributor of water supply in the Middle East and other arid regions. The emergence of renewable energy desalination as well as the development of novel plasmonic solar steam generation (PSSG) systems have brought back great research interest in enhancing thermal desalination efficiency. However, the number of publications is far from sufficient satisfaction due to the wide range of available materials and nanostructures. Several recent review papers have pointed out some basic principles to optimize the performance of a PSSG system (Deng *et al.* 2017, Dao *et al.* 2018, Tao *et al.* 2018).

Generally, the performance of a PSSG system can be estimated using the method of Chen *et al.* (2015):

$$\eta = \frac{\dot{m}h_{fg}}{Q_s A} \quad (2.1)$$

which η represents the evaporation efficiency (%), $\dot{m}$ is the evaporation flux of water ($\text{kg m}^{-2} \text{h}^{-1}$), h_{fg} is the vaporization heat of water (2.257 MJ kg^{-1} at 1 atm), Q_s is the intensity of sunlight (kW m^{-2}) and A is the area of exposure (m^2).

To date, there are two main categories of PSSG systems that have been reported in the literature. The first is called suspending or nanofluid systems in which the plasmonic component is mixed into water, and the converted energy is used for heating up the whole body, leading to faster evaporation (Chen *et al.* 2017). The advantage of this system is that it focuses only on the working compound, and thus is simple to deploy in the water body. In this system, the solar absorption of the materials is the key factor for evaporation enhancement. The material needs to possess a broad-band of absorption in the solar spectrum. Noble metals such as gold and silver have a strong plasmonic effect, but their absorption band is narrow. A lot of attention has been put on carbon materials since they offer a broader band of absorption and a more affordable cost. Composites of carbon and other materials are also examined for additional functionalities, such as easy recycling with magnetic particles (Zeng *et al.* 2011) or self-cleaning with TiO_2 nanoparticles (Lou *et al.* 2016). Besides the high absorption property, low thermal emittance needs to be considered. Cao *et al.* (2014) showed that reducing the thermal emittance of the absorbers would minimize the energy loss due to thermal radiation. In addition, the concentration of the absorbers in the nanofluid also plays a significant role. It is found that under the same illumination condition, the increase of concentration results in a higher bulk temperature, up to a critical value before the temperature starts decreasing (Wang *et al.* 2017). Hence, an optimal concentration needs to be determined to achieve cost-effective nanofluid evaporation.

The second type of PSSG system is called floating systems. In this system, the materials are assembled in an integrated structure that can naturally float on the water surface. The structure of the device in this system may consist of single or multiple layers of materials (Fig. 2.5). In single-layer structures, the plasmonic compounds are disposed directly on the water surface, while in multi-layer systems, they are cast on the top of a supporting layer, which provides them with mechanical stability and water supply. Water is subsequently transported through the porous structure of the substrate to the top layer where they receive heat and evaporate. This type of system localizes heat converted in the top layer of the water body where evaporation occurs, thus avoiding unnecessary heat loss to the water body. However, the fabrication of floating systems is more complicated compared to the nanofluid systems.

Figure 2.5. Schematic illustration of (a) single-layer and (b) double-layer floating PSSG system.

It has been recently pointed out that there are three main factors that govern the performance of a conventional floating PSSG device: the plasmonic properties, the heat localization, and the transportation of water. Firstly, the materials at the top layer must have a strong plasmonic property and broadband absorption to capture the most of incident light. Besides the improvement mentioned in the previous section, in two-layer systems, the efficiency of metallic absorbers can be further enhanced with the aid from the supporting substrate. Tightly packing the metal particles in a porous thin film could make their plasmon resonance effect overlap each other, leading to broadband absorption (Zhou *et al.* 2016, Wang *et al.* 2017). Furthermore, the thermal emittance can be reduced by using an infrared-reflective layer as an intermediate layer between the absorbers and the substrate (Tao *et al.* 2018).

Secondly, the system should have a high thermal insulation to prevent heat transfer from the top layer to the underlying water body, thus optimizing the conversion efficiency. In two-layer systems, the heat loss is mainly by conduction from the substrate layer. Therefore, the material choices for this component often have low thermal conductivity or porous structure. Chen *et al.* (2014) presented a double-layer structure constructed from exfoliated graphite as the absorber and carbon foam as the thermal insulator substrate (Fig. 2.6). Their results showed that the evaporation rate of the double-layer structure is much higher compared to the stand-alone graphite layer, indicating the significance of thermal insulation in solar steam generation.

Figure 2.6. (a) Schematic illustration of the double-layer structure for solar steam generation; (b) The structure consists of an exfoliated graphite layer (5-mm thick) cast on a carbon foam (10-mm thick), both layers are hydrophilic to promote the capillary rise of water to the surface (Source: Chen *et al.* 2014).

However, there are still challenges in managing the heat localization with thermal insulation materials, mostly due to the behaviors of the structure in the water environment. The porous carbon foam in the previous study exhibits excellent thermal insulation with a thermal conductivity of $0.117 \text{ W m}^{-1} \text{ K}^{-1}$ when dry. However, when being exposed to water, its conductivity increases dramatically to $0.426 \text{ W m}^{-1} \text{ K}^{-1}$. This phenomenon is attributed to the fact that the air inside the open pores is replaced by water, leading to the increase of thermal conductivity.

The concept of evaporation with heat localization has attracted a lot of interest from scientists. Various types of materials have been brought into examination, including cellulose (Chang *et al.* 2016, Li *et al.* 2017), silicone (Wang *et al.* 2017), and polymers (Ni *et al.* 2016, Sajadi *et al.* 2016, Chala *et al.* 2018). Besides the material selections, some efforts are dedicated to designing water pathway that can further insulate heat transfer. Li *et al.* (2016) developed a scalable device that effectively enhances solar steam generation with 2D water pathway. The device uses a foldable graphene oxide film as the absorber and cylindrical polystyrene foam as the insulator (Fig. 2.7). Water is driven by the capillary force through the cellulose channel wrapping the insulator foam to the top layer where they receive heat from the absorber and evaporate. This 2D pathway reduces the occupancy of water in the insulator, thus mitigating the change of thermal conductivity due to wetting process and providing better heat localization. Moreover, since the device can float naturally on water surface, the absorber layer is not in direct contact with bulk water, thus all the converted heat is focused on concentrated in the 2D pathway. The device achieved to obtain 80% of evaporation efficiency under 1 sun illumination condition.

The third factor that affects the performance of a floating PSSG system is the transport of water from the liquid into the system and their evaporation from the top surface. For water pumping purpose, porous materials are desired since they can utilize capillary force. For the evaporation of water, it should be noted that the interfacial region where evaporation occurs should be well designed to enable the most effortless evaporation path. The wettability of surface plays a critical role, and usually hydrophilic surfaces are preferred (Ghasemi *et al.* 2014).

The geometry of surface also contributes to evaporation behaviors. Canbazoglu *et al.* (2016) set up evaporation experiments with carbon foam-based micro-diameter porous compounds. By considering a simple model of flow through a circular pipe (the capillary pressure difference ΔP is indicated to be related to pore diameter d and surface tension σ_s ($\Delta P \sim \frac{4\sigma_s}{d}$), a small pore diameter was found to result in a large capillary pressure, and thus faster evaporation. In addition, an enhancement in the hydrophilicity of the surface due to chemical treatment was found to increase the

evaporative thin-film region of water in capillary pores, as the meniscus shape of water profile became deeper (Fig. 2.8), leading to an encouragement of evaporation.

Figure 2.7. Design of 2D water pathway for enhanced evaporation: (A) Schematic diagram of a conventional solar steam generation with direct water contact. (B) Schematic diagram of solar desalination device with suppressed heat loss and 2D water supply. (C) Flow chart for the fabrication of solar desalination device: polystyrene foam, cellulose coating, and GO film on the top surface. (D) Physical map of polystyrene foam (left), cellulose wrapped over the surface of polystyrene foam (middle) and GO film on the top surface (right) (Source: Li *et al.* 2016).

Figure 2.8. (a) Variation of evaporative mass loss with time as a function of increased hydrophilic character of carbon surface; and (b) inferred variation in the meniscus shape indicating increased evaporative thin-film region. [I.M. (Intrinsic meniscus), E (evaporating thin film) and N-E (non-evaporating region) regions are shown] (Source: Canbazoglu *et al.* 2016).

Although hydrophilicity can aid water pumping of PSSG systems, research has shown that not all hydrophilic surfaces are suitable for evaporation enhancement. Excessive water aggregation may occur if the surface is too hydrophilic, leading to extra energy loss for vaporization (Zhang *et al.* 2015). Several studies have proposed a two-component structure, comprising a hydrophobic top layer and a hydrophilic supporting layer (Xu *et al.* 2018, Yang *et al.* 2018). This concept allows flexible designing of the two components to obtain fast water supply at the hydrophilic part while avoiding water accumulation at the surface of the absorber. Another solution is to control the wettability of the floating system through coating of hydrophobic absorber on a hydrophilic skeleton to ensure precise contact of water and heating region (Zhang *et al.* 2015). However, in those studies, the detailed behaviors of water at the hydrophobic interface has not been revealed.

2.4 Remaining constraints

The development of nanomaterials has revealed a huge potential in improving the performance of desalination technologies in recent decades. Researchers have been looking for novel compounds and structures that can benefit the performance of those

processes in terms of productivity and efficiency. Various compounds and structures were proposed and showed improvements in benchmark scale. However, the search for suitable materials has been experiencing several challenges, which can be listed as below:

i) Generally, the progress is relatively slow. The selection of materials is mainly based on the results from literature. To be specific, the development of a new compound or structure is often an improvement of some reported structure. This approach helps retain the desirable properties of the previous material, but it may prevent the progress from making a breakthrough improvement. In addition, the number of studies that provides guidelines for the synthesis and fabrication of materials is far from satisfaction. Hence, it is believed that many promising materials are still yet to be realized.

ii) The limitation in monitoring ability has hindered the understanding of mechanism at the nanoscale. Experimental methods can be adopted to examine the characteristics and properties of the structures, but dynamic behaviors of the complex system consisting of the material and surrounding water are challenging to be observed during the experiments.

iii) Although nanotechnology has been progressing fast recently, some synthesis methods are still having difficulties in fabricating nanocompounds and materials with precise characteristics and functionalities. Impurities and defects inside the nanostructures may cause the materials to be degraded, which affects the prediction of performance.

2.5 Computational study

In addition to the experimental investigation, theoretical simulation approach also contributes tremendously to the development of nanomaterials for desalination and water treatment processes. The insights of underlying mechanism which cannot be observed in experiments can be realized computationally. Furthermore, with the

improvement of the computational power, simulation methods can support the examination of compounds and structure in a dynamical perspective, providing useful guidelines for the design of nanostructures that benefits the device performance. This approach can significantly reduce the experimental cost and shorten the time scale.

To investigate the performance of materials in an aqueous environment, it is necessary to consider the molecular interactions between atoms in the nanostructure and water molecules during the process. Molecular dynamics (MD) simulation is a powerful technique to study the dynamic movement of an atomic system and has been adopted substantially in desalination and water treatment applications. The calculations in MD are based on Newton's second law, by treating the atoms and molecules as spherically symmetric particles

$$\vec{F} = m \frac{d^2 r}{dt^2} \quad (2.2)$$

where $\vec{F}$ is sum of the forces applied on a particle by the others in the system, r and m are its position vector and mass, respectively, and t is time. The main task of molecular dynamics simulations is to determine the force vector at the left-hand side of the equation (2.2), which represents the intermolecular interactions. Appropriate intermolecular potential models need to be adopted, usually from experiments or quantum mechanics calculations. After the driving forces applying on the molecules are determined, their velocity and position are updated subsequently over the time steps (Fig. 2.9).

The MD approach has been utilized extensively in membrane desalination, particularly for RO processes. In the last decade, numerous efforts have been devoted to investigating the transport mechanism of water inside nanostructured channels, especially for CNT and GE-based. It is recognized that the transport of water through CNT and GE membranes exhibits a frictionless slip movement, which explains their ultra-high permeation rate of 4 to 5 order of magnitude faster than classical Hagen-Poiseuille prediction (Majumder *et al.* 2005, Wei *et al.* 2014, Sun *et al.* 2015). Moreover, the structure of water in CNT membrane varies depending on the diameter

of CNTs, from a single-file structure to a spiral-like chain along the CNT axis as the diameter increases (Noon *et al.* 2002, Liu *et al.* 2005). For GE and GO membrane, it is found that interlayer distance is the dominant factor that determines the layered structure of water inside the nanochannels (Liu *et al.* 2016).

Figure 2.9. Schematic of procedures of a MD simulation to reveal the characteristics and properties of a nanoscale system.

In evaporation and steam generation applications, however, the investigation of atomistic behaviors of water molecules at the evaporative interface and their evaporation mechanism has not received sufficient attention, although the design of the evaporative interface is realized as an important factor in the fabrication of the materials. In 2012, Wang *et al.* first used MD simulations to investigate of a tiny water aggregation on a solid surface with controllable wettability. The surface is made hydrophilic by inducing partial polarity in its lattice (Fig. 2.10a-b). The results showed that the evaporation rate is facilitated when the surface becomes more hydrophilic due to the spreading of the droplet, thus expanding the interface. However, when the surface is too hydrophilic, the attraction towards the water molecule starts to interfere with the evaporation.

Figure 2.10. Computational of water evaporation on nanostructured surfaces: (A-B) Evaporation of water aggregation on a solid surface with controllable wettability and the dependence of evaporation rate on the surface polarity. (C-D) Evaporation of water on a patterned surface and the effect of inhomogeneity on the evaporation rate (Source: (a-b) Wang *et al.* 2012, (c-d) Wan *et al.* 2015).

To overcome this restriction, Wan *et al.* (2015) studied the evaporation on a patterned surface containing both hydrophilic and hydrophobic regions (Fig. 2.10c-d). They concluded that the patterned surface enables faster evaporation compared to a homogeneous surface due to a considerable amount of evaporation occurs when the water molecules near the border diffuse from hydrophilic regions to hydrophobic regions. In their next study, the effect of temperature is considered, and it is found that the evaporation rate depends not only on temperature but also the rotation of water on the substrate (Guo *et al.* 2018).

The abovementioned studies have demonstrated the opportunity to accelerate the development of novel compounds and structure for desalination and water treatment technology. However, the insight obtained is far from satisfaction so far, and more efforts are needed to reveal the fundamental understanding of the dynamic evolution

in these processes. Therefore, molecular dynamics approach is adopted in this research study to speed up the progress in the selected areas.

Chapter 3 Water permeation through multilayer graphene

The content of this chapter is extracted from a research article*, which developed a molecular model using molecular dynamics approach to study the permeation of nanoconfined water inside a graphene multilayer membrane containing nanoslits. As graphene-based membranes exhibit excellent potential in separating ions and contaminants for water purification applications, noticeable efforts have been devoted to studying the water permeation behaviors across these membranes. The transportation of water inside the graphene (GE) membrane follows a tortuous path and is highly affected by its geometrical features. The simulations study the effects of the driving pressure magnitude as well as the multilayer configuration parameters, including the number of GE layers, their porous ratio, the gap width and offset, and the interlayer distance.

3.1 Background

Nanofiltration membranes are now widely applied for molecular sieving and separation in desalination and water treatment processes to achieve low operation pressures, high permeation fluxes and relatively low operation and maintenance costs (Lu *et al.* 2002, Hilal *et al.* 2004). Recently, with their ultimate thinness, high flexibility, high mechanical strength and porous microstructure, graphene (GE) derived functional membranes have been shown to be outstanding potential candidates for nanofiltration membranes (Nair *et al.* 2012, Kim *et al.* 2013, Joshi *et al.* 2014, Mi 2014). A number of studies have focused on investigating the performance of nanofiltration process with nanoporous GE (Cohen-Tanugi *et al.* 2012, Cohen-Tanugi *et al.* 2016). They indicated that several structural parameters, including the chemical functional groups bonded to the edge of the pore and the

*This chapter is written based on Kieu, H.T., Liu, B., Zhou, K. and Law, A.W.K (2017). Pressure-driven water permeation through multilayer graphene nanosheets. *Physica Status Solidi B*, 254: 170074.

pore diameter, play a critical role in affecting the filtration performance and water permeability of the nanoporous GE membrane. However, to fabricate such membranes, it is challenging to create the nanopores with desired sizes and distribution. Hence, more attention is now devoted to the few-layered GE-derived functional thin films such as the GE oxide (GO) membranes. When dry, GO membranes made by vacuum filtration can be tightly packed to form highly ordered layered structures with nanochannels formed between two GO layers. The gaps between the adjacent GO nanosheets/nanoflakes provide the natural pores for permeation. Besides, the GO membranes can be intercalated with various nanoparticles to obtain the appropriate void spacing such that water molecules can permeate through, but larger-sized species are blocked (Joshi *et al.* 2014). For example, water desalination requires the interlayer distance of the GO membrane to be less than 0.7 nm to sieve the hydrated Na^+ ions from water. This small interlayer distance can be achieved by partially reducing GO to reduce the interlayer separation caused by the hydrated functional groups on the GO surface, or by covalently bonding the GO layers with small molecules to overcome the hydration repulsion between the layers (Mi 2014).

Previous experimental studies have shown that the water permeation rate of an ultra-thin chemically converted GE nanofiltration membrane can reach as high as $21.8 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, which is much greater than the commonly used polymeric membranes. Meanwhile, the membrane shows extremely high retention ($\sim 99\%$) for organic dyes and moderate retention ($\sim 20\text{-}60\%$) for ion salts (Han *et al.* 2013). This fast water permeation through the nanochannels in the GE-derived membranes has been attributed to the capillary driving force of the two-dimension capillaries formed between the GE layers and the almost frictionless surface of the GE.

Recent MD studies have demonstrated that water permeation behaviors through the GE-derived membranes can be more complicated and is significantly affected by the detailed atomistic structure and configuration of the membrane. For example, it has been demonstrated that the fast water transport through the nanochannels inside the GO membranes can be impeded by a prominent side pinning effect at the interfaces

between pristine GE and oxidized GE domains (Wei *et al.* 2014). The MD study conducted by Liu *et al.* (2016) also showed that the water transport behaviors inside a nanochannel formed by GE bilayers is significantly influenced by the structural parameters of the channel such as the channel thickness and the channel length.

Most of the previous simulation studies of the water permeation through the GE-derived membranes only focus on the water transport behaviors inside the nanochannels formed by two GE nanosheets or nanoflakes. The simultaneous water permeation in the direction normal to the surface of the multi-layer GE-derived membranes has not been well explored. Recently, Jordan *et al.* (2016) conducted MD simulations to study the water permeation across the double-layered GE membranes. They found that the water molecules do not pass through the membrane as a hydrogen-bonded chain but form well-mixed fluid regions inside the membrane. Yoshida *et al.* (2016) promoted a continuum model to predict the water flow across the multi-layered GE membranes. The validity of their model depends on the choice of the relevant parameters. However, in both works, only a few geometrical parameters were considered, and the effect of the geometry of the membrane has not been fully explored.

In this chapter, MD simulations are performed to examine the transport of water molecules across a multi-layer GE membrane with its geometry effect fully investigated. Each layer of the membrane consists of multiple GE nanosheets separated with a proper gap. The effect of the structural parameters, including the inter-layer distance, the number of layers, and the gap width, distribution, offset, and their hydrogenation effect, are comprehensively explored.

3.2 Simulation model

The simulation model consists of a GE membrane in the middle of two reservoirs of water molecules. The GE membrane is formed by multiple layers of pristine GE nanosheet with the bond length of 1.42 Å and parallel to the XY plane. The sizes of the two water reservoirs are both set to be $60 \times 29 \times 24.5 \text{ Å}^3$, and 3204 water

molecules are placed inside each reservoir so that a water density of 1 g cm^{-3} is obtained. In each GE layer, several gaps are created by removing carbon atoms of the GE layers to allow the permeation of water molecules through the membrane. The distance between the center of an entering gap and that of its nearest exiting gap is defined as the gap offset. The configuration parameters of the GE membrane are the number of GE layers K , the number of gaps in one layer n , the width of each gaps w_i ($i = 1, 2, \dots, n$), the offset of the gaps O , the total length of the channel L and the distance d_l of adjacent GE layers (Figure 3.1).

Figure 3.1. Atomistic configuration of the simulation model. The GE membrane consisting multiple GE layers is set in between two water reservoirs. Gaps are created in each GE layers to allow the permeation of the water molecules through the membrane.

The MD simulations are performed by using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package (Plimpton 1995). The boundary condition along the three dimensions are all set to be periodic to replicate the steady and continuous water flow across the GE multilayer. The transferable intermolecular potential 3P (TIP3P) water model (Price *et al.* 2004) is adopted to describe the water molecules. By using this model, the partial charges of O and H atoms are set to be $-0.834 e$ and $0.417 e$, respectively. Both the bonding and non-bonding atomistic interactions between the O and H atoms are described using the CHARMM27 force field (MacKerell *et al.* 1998). By using this force field, the total energy of a system can be expressed as

$$E_{total} = E_{bonds} + E_{angles} + E_{dihedrals} + E_{impropers} + E_{Urey_Bradley} + E_{vdW} + E_{elec} \quad (3.1)$$

The first five terms at the right-hand side of the equation specify the short-range intramolecular interactions, while the last two terms specify the long-range intermolecular interactions. During the calculation of the long-range electrostatic interactions (last term in Eq. 1), the particle-particle particle-mesh (PPPM) method is used, with a cut-off distance of 12 Å and a root mean square accuracy of 10^{-4} . Meanwhile, the van der Waals interactions are described by the 12-6 Lennard-Jones potential as

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3.2)$$

where r is the distance between two atoms, ϵ is the energy well reflecting their interaction strength, and σ is the zero-cross distance of the potential. Specifically, the interaction between the water molecules is determined by the van der Waals interactions of the H-O, H-H, and O-O atom pairs, with the value of ϵ and σ adopted as $\epsilon_{O-O} = 0.1521 \text{ kcal mol}^{-1}$, $\sigma_{O-O} = 3.15 \text{ Å}$, $\epsilon_{O-H} = 0.0836 \text{ kcal mol}^{-1}$, $\sigma_{O-H} = 1.77 \text{ Å}$, $\epsilon_{H-H} = 0.0461 \text{ kcal mol}^{-1}$ and $\sigma_{H-H} = 0.40 \text{ Å}$. The interaction between the GE multilayer and water molecules is determined by the van der Waals interaction between the C and O atoms with the values of ϵ and σ adopted as $\epsilon_{C-O} = 0.0937 \text{ kcal mol}^{-1}$ and $\sigma_{C-O} = 3.19 \text{ Å}$ according to the CHARMM27 force field (Werder *et al.* 2003).

The constant volume and temperature (NVT) ensemble is applied in all simulations. By using Nosé–Hoover thermostat, the temperature is kept at 300 K. To obtain a good correlation between the configuration parameters of the GE multilayer and the water transport behavior, the GE layers are kept rigid during the simulations to prevent their lateral movement and the closing of the gaps. Moreover, this rigid treatment would also guarantee the stability of the GE membrane though there are dangling bonds at the gap edges. A pressure condition to push the water molecules upside-down to enter the GE multilayer is reproduced by applying a force f along the Z direction to each

oxygen atom in the upper water reservoir (Zhu *et al.* 2002). The force is calculated as

$$f = -\frac{PL_xL_y}{N_0} \quad (3.3)$$

where P is the desired pressure on the water molecules, L_x and L_y are the lengths of the water reservoir along the X and Y dimensions, respectively, and their product represents the cross-section area of the GE multilayer; N_0 is the number of water molecules in the upper water reservoir, which is constantly updated every time step. The minus sign denotes the downward direction of the force along the Z direction. This method has been proven effective to investigate the flow properties of confined water in nanochannels in various previous studies (Hilder *et al.* 2009, Su *et al.* 2012, Wei *et al.* 2014). The time step of the simulations is set to be 0.5 fs, and the thermodynamics information is recorded every 0.5 ps. The pressure-driven simulation is conducted for 250 ps to reach a steady state and another 200 ps for data collection.

3.3 Results and discussion

3.3.1 Water flow rate

Figure 3.2a shows the evolution of the number of water molecules inside the channel over time. The number of water molecules increases with time before reaching a saturated value. This evolution indicates that the water molecules first fill the space inside the multilayer before penetrating the GE membrane and entering the bottom water reservoir.

As the transport of water molecules through the GE multilayer reaches its steady state (*i.e.*, the void inside the multilayer is filled by water molecules), both of the number of molecules and their velocity become almost constant with small fluctuations (Fig. 3.2b). At this state, the influx of water molecule entering the multilayer from the top reservoir is approximately equal to the exit flux on the other side. Therefore, the water

flow rate Q can be calculated as the number of water molecules that transmitting through the gaps in the top or bottom GE layer per unit time per unit area. However, the water molecules that are pushed through the gaps inside the GE nanosheets would re-enter the channel through diffusion, making it difficult to track the net number of water molecules being transmitted across the membrane. Hence, Q is estimated alternatively as

$$Q = \frac{vN}{d_l L_x L_y} \quad (3.4)$$

where v and N are the average velocity and number of the water molecules inside the channel, (the product of $d_l L_x L_y$ accounts for the volume of the channel). It is noted that some of the water molecules inside the channel with a certain distance from the gaps may have negligible velocity components along the Z direction.

Figure 3.2. (a) Time evolution of the number of water molecules and (b) the average velocity along the Z direction of the water molecules inside the GE multilayer.

To validate the method, the water flux in the top water reservoir is calculated as $v_0 N_0 / V_0$ and compared with the Q estimated by Eq. 4. Here, v_0 and N_0 are the average velocity and number of the water molecules inside the feed water reservoir and V_0 is its volume. The comparison shows that the water flux in the top water reservoir and that inside the channel are almost the same. Hence, Eq. 4 is adopted for all the calculations of the water flux. Fig. 3.3a shows the dependence of the flow rate Q on the applied pressure P , for the case of $d_l = 7$ Å and two gaps in each GE layer with both of their width $w = 10$ Å and their offset $O = 15$ Å.

Figure 3.3. (a) Linear dependence of flow rate Q on applied pressure P and (b) declining effect of number of layers on flow rate Q . In (a), the number of GE layer is set to be 2; in (b), the pressure is set at 200 MPa.

It is noticed that the pressure applied in the simulations is remarkably greater than the pressure used in practical reverse osmosis water treatments. This high pressure is used to save simulation cost, as a low pressure can take a quite long computational time to obtain a steady water flow rate. It is observed that as P increases from 100 MPa to 500 MPa, Q increases linearly. This relation suggests the possibility to obtain the flow Q at smaller P from extrapolation. Linear fitting gives that for $P = 5$ MPa, Q is obtained as $18.889 (\text{ns nm}^2)^{-1}$, which corresponds to a value of $975.5 \text{ L cm}^{-2} \text{ day}^{-1} \text{ MPa}^{-1}$. Previously, it has been reported that the water flux of $129 \text{ L cm}^{-2} \text{ day}^{-1} \text{ MPa}^{-1}$ can be obtained for the porous GE single layer (Cohen-Tanugi *et al.* 2012) with the porosity of 10%. If we only consider the pore area instead of the whole area of the GE single layer, this water flux is equivalent to $1290 \text{ L cm}^{-2} \text{ day}^{-1} \text{ MPa}^{-1}$. Hence, the water flux obtained through the double layer GE membrane in the present study is close to that of the single layer nanoporous GE. Considering the difficulties in creating nanopores in single layer GE nanosheets with controllable sizes and distributions, the multi-layer GE membranes are preferable due to their natural porous structure.

The porous structure of the multi-layered GE membrane is crucial for salt ions filtration, and it can also significantly affect the water flow rate. To investigate such effect, MD simulations are conducted to study the effect of the number of the GE layers K as shown in Fig. 3b. It is observed that as K increases, the water flow rate Q

decreases significantly. A recent MD study on the water permeation through the GE-based membrane has demonstrated that there is a high free energy barrier at the entrance of the gap between the GE nanosheets. Moreover, this energy barrier at the gap is much higher when it is inside the membrane than at the membrane surface, due to the different distribution of the water molecules inside the membrane from that of bulk water near the membrane surface (Muscatello *et al.* 2016). Therefore, as the number of GE layer increases, the number of gaps increases, and they tend to impose high-energy barriers for water permeation.

Since the water molecules do not pass through the membrane as a hydrogen-bonded chain, a larger number of GE layers means a longer path for the water molecules to transmit through the membrane and thus a higher transport resistance. Hence, the multi-layer GE membrane with fewer GE layers would be advantageous for enhancing water permeation. At the same time, to achieve good ion filtration performance and mechanical stability, more GE layers would be desired. Therefore, there would be an optimized thickness of the GE membrane for practical desalination or filtration applications.

3.3.2 Effect of gap configuration

Besides the number of GE layers, the distribution of the gaps together with their size can affect the water flow rate as well as the filtration of the ions. One important parameter that describes the gap distribution is the offset distance. To investigate this effect, MD simulations have been conducted for a GE membrane containing only two GE layers with the interlayer distance of 7 Å. In each GE layer, only one gap with the width of 10 Å is created, and the offset distance between the gaps of the two GE layers varies from 15 to 30 Å with an increment of 5 Å. Both gaps are set to have the same distance to the middle of the simulation system along the *X* direction. The minimum offset distance is set at 15 Å such that there is a small distance of 5 Å between the edges of the two gaps and they do not overlap. On the other hand, the maximum offset distance of 30 Å is set such that it does not exceed half the length of the simulation system. Thus, the length of the most direct path for the water molecules

to permeate through the membrane would be the offset length O instead of $L - O$. It should be noted that the change of the offset of the distance between the entering and exiting gaps will not lead to the change of the gap density since only one gap is created in each GE layer and the periodic boundary condition is applied. If the two gaps (the entering gap at the top GE layer and the exiting gap at the bottom) are taken as one gap pair, the increase of the offset distance only leads to the change of the distance between the gap pairs in the GE membrane.

Fig. 3.4a shows the dependence of the water flow rate on the gap offset distance. Interestingly, as the offset distance increases (*i.e.*, the length of the most direct path for the water molecules to travel from the entering gap at the top GE layer to the exiting gap at the bottom GE layer becomes further), the flow rate increases. This observation is contrary to that reported recently by Muscatello *et al.* (2016) The reason can be attributed to the fact that in their study, there is a significant overlap between the gaps from different GE layers when the offset is small. As a result, the movement of the water molecules along the membrane thickness direction is not blocked by the GE layer, and they can penetrate directly through the gaps, leading to a large water flow rate. In the present simulations, the water flow rate with a zero-offset distance has also been calculated, and its value is obtained to be much larger than those presented in Fig. 3.4.

For each entering gap at the top GE layer, there are one exiting gap at its right and another imaging exiting gap at its left when the periodic boundary condition is considered. Thus, there are two diffusion paths for the water molecules to permeate through the membrane. After passing the entering gap, the water molecules first expand along the two paths. However, when the water molecules reach the nearer exiting gap, the diffusion along this direction is blocked due to the high energy barrier at the gap area. Hence, the water molecules prefer the other diffusion path (with a larger distance to the entering gap) and finally reaches the other exiting gap. Ultimately, they will be pushed out the gap by the water molecules behind. Since the water molecules prefer the longer diffusion path, the water flux is mainly determined by the length of this path. With the increases of the offset distance O , the length of

the longer diffusion path ($L - O$) reduces, and the distances of the entering gap with the two exiting gaps become close to equal. Therefore, the water flux increases with the increases in the offset distance. It should be noted that such conclusion holds only when the resistance to the water molecule diffusion inside the nanochannel does not change significantly as the offset increases.

Figure 3.4. (a) Dependence of water flow rate Q on the gap offset O ; (b) mean-squared displacement (MSD) of water molecules inside the nanochannel over time for the gap offset O of $15 \text{ \AA}$ and $30 \text{ \AA}$ and (c) snapshot of interlayer space during the fulfilment of water molecules. The water molecules at the left of the exiting gap tend to stop expanding until the molecules from the right reach the exiting gap.

To examine the diffusion of water molecules in different gap offset conditions, the driving pressure is turned off and the mean-squared displacement (MSD) of water molecules inside the channel is recorded for 200 ps. Fig. 3.4b shows that the MSD curves over time for $O = 15 \text{ \AA}$ and $30 \text{ \AA}$ do not show significant difference though there exists some discrepancy which may be due to the statistical error. This suggests that the water molecules traveling along the nanochannel of the GE multilayer experience the same constraint regardless of the gap offset, and the flow rate thus depends only on the path length.

Another structural parameter of the GE multilayer that affects the transport of water is its porous ratio a which is defined as the total width of all the gaps in one GE layer divided by its length

$$a = \frac{\sum w_i}{L} \quad (3.5)$$

Figs. 3.5a and 3.5b show the water flow rate and average number and velocity of water molecules for the case of two equal-width gaps in each layer with $a = 1/3$, $a = 1/2.5$ and $a = 1/2$ while $P = 100$ MPa and $d_l = 7$ Å. A rise in both velocity and number of water molecules is witnessed as a increases, thus resulting in a larger flow rate. The fact that more water molecules permeate inside the channel while its internal space remains unchanged indicates that as the gaps become wider, the driving pressure will push more water molecules into the nanochannel inside the GE membrane.

Fig. 3.5c shows the number density profile of the water molecules inside the nanochannel of the GE layers along the X direction for the three gap densities investigated. Again, it is apparent that at the locations of the gaps, the water density is higher than those at other locations. It is also noticed that water molecules at the gap areas tend to form a layered structure, as evidenced by the peaks of the water density at the edge of the gaps. As the gaps are widened by increasing the porous ratio a , more layers of water form near the gaps. Comparing to the layered structure at the entering gaps, those at the exiting gaps are less prominent and closer to that of the bulk water, as indicated by the lower height of the density peaks near the edges of the exiting gaps particularly at their middle regions. As the gap width increases, the energy barrier for water molecules penetrating through them decreases, and more water molecules can enter the gap simultaneously. Therefore, the water flow rate increases.

In real GE-based membranes, the width of the gaps would not be all identical. To further study the effect of the distribution of the gaps, the width of the two gaps in each GE layer is modified to be different with a ratio of $r_w = \frac{w_1}{w_2}$ while the porous

ratio a is kept constant. The simulations show that the layered structures at the gap edges are well preserved. However, the water flow rates for these three cases are close to each other, indicating that it is insensitive to the non-uniformity of the gap sizes though sensitive to the overall porous ratio.

Figure 3.5. (a) Water flow rate Q and (b) velocity v and number N of water molecules at the gap density $a = 1/3$, $1/2.5$ and $1/2$; (c) number density of water molecules along X direction of the channel. In (a), two gaps with equal width are created in each GE layer.

Despite the fact that increasing the porous ratio a can enhance the water flow rate, the filtration of ions requires the width of gaps to be sufficiently small to block the targeted species from permeating through the membrane. This issue can be tackled by creating more narrow gaps on a layer while maintaining the same porous ratio a . MD simulations have been conducted for the cases of 2, 3 and 4 gaps on each GE layer with $a = 1/2$. The width of the gaps in each case is set to be equal. Fig. 3.6 demonstrates the flow rate and the number of water molecule inside the channel for the three abovementioned cases. It is observed that there are mild changes in the flow rate Q and the number of water molecules as the number of gaps n increases from 2 to 3. As n further increases to 4, which corresponds to a gap width of 7.5 Å, both the water velocity and the number of water molecules inside the channel decreases

prominently, indicating that the gaps start to block the transport of water. These simulation results demonstrate that there exists an optional gap density and distribution for the achievement of both high permeation rate and good filtration performance.

Figure 3.6. Water flow rate Q and number of water molecules N inside the channel for different number of gaps n .

3.3.3 Effect of interlayer distance

In a previous study of water transport in the nanochannel of a GE bilayer under a driving pressure condition, Liu *et al.* (2016) demonstrated that the water molecules confined in the nanochannel tend to form a layered structure, and their transport behaviors also significantly depends on the distance of the GE layers. To examine the interlayer distance on the water transport across the multilayer GE, MD simulations have been conducted for the case of two GE layers at the driving pressure of $P = 100$ MPa. The interlayer distance d_l varies from 7 to 12 Å.

Fig. 3.7 shows that the water flow rate increases monotonically with the interlayer distance, which is consistent with the aforementioned study. The number N of water molecules inside the channel between two GE layers and their average velocity are also examined. As the interlayer distance d_l increases, both N and v show an overall increasing trend, thus explaining the increase in the water flow rate.

Figure 3.7. Dependence of (a) the flow rate Q and (b) average N and v (b) on the distance d_l .

It is interesting that a jump in the number of water molecules along with a decline in average velocity can be observed when d_l changes from 8 Å to 9 Å, which signals the evolution of the layered water structure inside the channel. Four snapshots of the distributions of the water molecules in the interlayer area for $d_l = 8, 9, 11$ and 12 Å are captured (Figs. 3.8a-d). It is noticed as d_l increases from 8 to 9 Å, the number of water layers inside the channel increases from one to two. At $d_l = 11$ Å, a third layer starts to form between the two original water layers, making the layered structure blurring. As d_l further increases to 12 Å, the water distribution transits to an explicit three-layer structure. Since the transition of the layered structure from two to three as d_l increases from 11 Å to 12 Å is not as sharp as that from one to two when d_l increases from 8 Å to 9 Å, the prominent jump/decline in the water number N or the average velocity v is not observed at $d_l = 11$ Å.

A further evidence for this transition is the spatial distribution of water molecules along the channel thickness direction. Fig. 3.8e visualizes the density profile along the Z direction inside the channel. The peaks that appear in the density profiles represent the layers of water molecules. The most noticeable advance in the evolution is the nearly-three-time jumps in the magnitude of the two peaks when d_l increases from 8 to 9 Å, followed by a two-time jump in the magnitude of the third peak in the middle of the channel when d_l increases from 11 to 12 Å.

Figure 3.8. (a-d) Snapshots of the water distribution inside the nanochannel at the steady state for $d_l = 7, 8, 11$ and 12 Å ; (e) density profile along Z direction of the channel with d_l varying from 7 to 12 Å

3.3.4 Effect of hydrogenated gap

Previous researches have shown that the functional hydrogen groups of the entrance edges can largely affect the energy barrier for water permeation. To investigate such effect, the gaps in the GE membrane are functionalized by assigning hydrogen atoms to the dangling carbon atoms at the edge of the gaps. For simplicity, the GE membrane is still treated as neutral, and the charges of both the carbon and hydrogen atoms are not considered. MD simulations of water permeation through the hydrogenated multilayer membrane are conducted with the gap offset O varying from 15 to 30 Å . Fig. 3.9a shows the remarkable improvement of the water flow rate for the hydrogenated gap compared to that for the pristine gap. The time evolutions of the number of water molecules inside the nanochannel for the both simulations are also plotted for comparison (Fig. 3.9b). When the gaps in the membrane are functionalized, the number of water molecules increases significantly during the first 10 ps with a faster speed than that for the pristine gaps. Subsequently, the rate of permeation approaches the steady state as the number of water molecule inside the nanochannel reach the saturated value.

To understand this effect, the snapshot of the fulfilment of water molecules inside the functionalized nanochannel during the initial 10 ps of permeation is examined (Fig. 3.9d). It is observed that unlike in the pristine gap channel, the water molecules in the bottom reservoir also diffuse into the nanochannel through the hydrogenated exit gap in the bottom GE layer at the early stage of the simulation. This flow of water molecules is then connected to the expanding flow of water molecules from the top reservoir. This phenomenon suggests that the functional hydrogen group at the edge of the gaps facilitates the diffusion of water molecules into the nanochannel with a much lower energy barrier.

To further prove this, the Potential of Mean Force (PMF) (Beutler *et al.* 1994) is calculated. The umbrella sample method (Roux 1995) is performed by choosing a water molecule in the bottom reservoir as a probe and examining its position distribution for the reaction coordinates varying from 30 to 37 Å along the Z direction above the gap area. The width of the umbrella windows is taken as 0.5 Å. A 100 ps simulation was performed for each umbrella window, in which the probe water molecule is restrained in the Z direction using a harmonic bias potential is applied to the probe molecule with the spring constant ranging from 2.3 to 3.0 kJ mol⁻¹ Å⁻².

It is noticed that as the distance to the bottom GE layer (which is located at $Z = 34$ Å) becomes closer, the energy barrier in the pristine gap case increases gradually (Fig.3.9c), while that for the hydrogenated gap shows no significant change and only fluctuates slightly. After entering the nanochannel, the free energy barrier in both cases shows an overall increasing trend. This is due to the fact that the vertical movement of the water molecules are blocked by the upper GE layer, and they start to expand along the horizontal direction. The PMF at the gap ($Z = 34$ Å) for the pristine GE gaps is around 2.5 kcal mol⁻¹ higher than that for the hydrogenated gap. The lower PMF is most possibly caused by the fact that the hydrogen atoms at the gaps forms hydrogen bonds with the water molecules and facilitate their entrance into the nanochannel and thus enhance the overall water flow rate across the membrane.

Figure 3.9. (a) Water flow rate Q and (b) number of water molecules inside the nanochannel over time for the two cases of functionalized gap and pristine gap for different gap offsets O ; (c) PMF along normal direction to the gap, the red dotted vertical line indicates the position of the bottom GE layer; (d) snapshot of the fulfilment of water molecules inside the functionalized nanochannel.

3.4 Summary

This work utilizes molecular dynamics simulations to investigate the pressure-driving permeation of water through a multilayer GE membrane containing staggered gaps. The effects of the configuration parameters of the multilayer including the number of GE layers, the distribution of the gaps such as the gap offset and density, the interlayer distance, and gap hydrogenation are studied. These effects are analysed by examining the water flow behaviors inside the nanochannel formed by two adjacent GE layers, such as the average velocity and spatial distribution of water molecules.

The simulation results show that the water flow rate Q is in a linear relation with the applied pressure P and is close to that obtained for single-layer porous GE. Though a larger number of GE layer would be advantageous for the filtration of ions, the

simulation results indicate that the water flow rate decreases as the number of GE layer increases. Hence, an optimal layer number would be desired to achieve both good filtration performance and high permeation rate. When the effect of the gap offset is considered, it is found that water flow rate increases with the offset, which is counter-intuitive. Such phenomenon is explained by the fact that there are high-energy barriers at the exiting gaps, and the water molecules prefer to diffuse through the interlayer space, which has the longer path. Hence, the water flux is determined by the length of this path.

It is also found that the increase of the porous ratio of the GE layer can significantly enhance the permeation of water. However, the permeation rate is almost insensitive to the number of gaps at the same porous ratio as long as their width is large enough to allow water permeation. This finding suggests the advantage to create a membrane with numerous small-size gaps, which can preserve high water permeation yet preferable for sieving and separating applications. The interlayer distance d_l also influences the flow behaviors in a monotonic manner. The evolution of the layered structure of water molecules inside the multilayer with increasing d_l allows more water molecules to enter the interlayer space, thus increasing the water flow rate. The results also show that the functional hydrogen groups at the edge of the GE gap play a significant role in lowering the free energy barrier at the gap area and allow faster water permeation.

Overall, this study provides a further understanding of the permeation behaviors of water molecules through multilayer GE structures. With the configuration parameters which can affect the permeation being considered comprehensively, useful guidance is provided to the design of GE-based membranes for filtration and purification processes, in which area they are exhibiting a promising potential.

Chapter 4 Capillary evaporation through graphene bilayer

The content of this chapter is extracted from a research article*. Hollow and porous graphene-based nanostructures have drawn intensive attention in thermal desalination and water treatment applications as they facilitate the evaporation of water, which is beneficial to the production of fresh water. The underlying mechanism of water evaporation enhancement through the nanostructures is mainly affected by the capillary effect and surface wettability. In the present work, the evaporation of water through a capillary graphene bilayer with tunable surface hydrophilicity is examined by using molecular dynamics simulations. The effects of temperature as well as the capillary distance are also investigated. This work can help to understand the evaporation mechanism of water molecules under the capillary effect at the atomic scale. It can also provide useful guidance to the design of porous membranes with suitable geometrical and functional configurations to achieve high evaporation efficiency.

4.1 Background

The evaporation of water plays a crucial rule in various industrial applications, including seawater desalination and wastewater treatment (Poulikakos *et al.* 2003), coating and printing (Lee *et al.* 2015, Simovich *et al.* 2015), nanomedicine (Gobin *et al.* 2005, Huang *et al.* 2006) and equipment sanitation (Neumann *et al.* 2013). In these processes, the rate of water evaporation is the controlling factor, and enhancing the evaporation rate can contribute significantly to the process efficiency. Over the last few decades, there has been a great desire to facilitate this phase-change process with the utilization of nanotechnologies and nanomaterials. Plasmonic metal nanoparticles, such as gold and platinum, have attracted a lot of

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attention from researchers in water treatment applications due to their strong photothermal and photoelectric properties (Govorov *et al.* 2007, Lukianova-Hleb *et al.* 2010, Zeng *et al.* 2011, Carlson *et al.* 2012, Neumann *et al.* 2013, Wang *et al.* 2014, Liu *et al.* 2015, Dinh *et al.* 2018). However, the application of such materials is still restricted by the excessive cost of fabrication.

Recently, there have been great efforts devoted to developing hollow and porous nanostructures based on cheap materials that can effectively enhance water evaporation and yet is economically affordable. Assembled in a porous and durable network, the nanostructures have the capability to float against the external forces from surrounding water molecules. Moreover, being porous enables the nanostructures to take advantage of the capillary force, driving water molecules to their subsequent evaporative phase transition. Zhou *et al.* (2016) demonstrated that a porous membrane fabricated from self-assembly of aluminium nanoparticles can achieve high efficiency in solar evaporation enhancement. Wang *et al.* (2016) combined a CNT membrane with a hydrophilic macroporous silica substrate to create a bilayered material and reported great performance in enhancing water evaporation.

Over the last few decades, graphene has attracted intensive attention owing to its excellent thermal and mechanical properties. Remarkable progress has been achieved in the fabrication and characterization of graphene-based nanostructures to achieve specific surface properties and mechanical stability. One of such promising structures is the vertically aligned graphene (Liang *et al.* 2011, Zhang *et al.* 2016), which comprises multiple graphene sheets being stacked together. The spacing between the graphene layers can be controlled to form meso-size channels and thus encourage capillary evaporation. Moreover, the graphene sheets can be decorated with various chemical groups to acquire a preferable surface property. Therefore, vertically aligned graphene can be a suitable candidate for evaporation enhancement application.

There has been great interest in experimentally studying the effect of capillary force on the water-air interface at the microscale (Dai *et al.* 2013, Canbazoglu *et al.* 2016, Lu *et al.* 2016, Li *et al.* 2017). As typical examples, Canbazoglu *et al.* (2016)

conducted evaporation experiments with carbon foam-based micro-diameter porous compounds and reported that a small pore diameter results in a large capillary pressure in the structure, and thus faster evaporation. A similar observation was also reported (Li *et al.* 2017) for the capillary evaporation of water through a two-dimensional nanochannel. However, further experimental study of capillary evaporation of water at the nanoscale is still quite a great challenge, and time-consuming. Thus, numerical simulations are now significantly explored in parallel to speed up the research.

To examine the behaviors of water molecules when being brought into contact with different surfaces at the atomic scale, various insights have been made via the approach of MD simulations. It has been found that many surface properties such as morphology and polarity can significantly influence the transport process (Liu *et al.* 2016, Kieu *et al.* 2017). Wang *et al.* (2012) conducted MD simulations of water evaporation on a polar substrate of which the wettability can be adjusted. The results showed that the evaporation rate increases when the substrate is tuned from being hydrophobic to hydrophilic due to the increased area of the water-air interface caused by the spreading of water molecules on the surface.

Wan *et al.* (2015) studied the enhancement of water evaporation on the hydrophobic-hydrophilic patterned substrate and observed that the majority of evaporation flux comes from the hydrophilic region. In those studies, the evaporation of water is enhanced mainly due to the horizontal spreading of water molecules over the hydrophilic areas of the surface. However, when being confined in a mesoporous structure, the evaporation of water molecules is strongly affected by the capillary effect, which, to our knowledge, has yet to be comprehensively revealed. Therefore, in this chapter, we perform MD simulations to examine the evaporation of water through the capillary channel formed by a graphene bilayer at the atomic scale. The effects of the polarity and hydrophobicity/hydrophilicity of the graphene surface, the capillary distance, and the temperature are also explored. In the following, we shall first present the simulation approach before discussing the results obtained.

4.2 Simulation model

The simulation model examines the evaporation behaviors of a water body lying above a solid substrate, with the effect of a hydrophilic capillary wall. The initial water body consists of 6243 water molecules generated to create a box size of $10.0 \text{ nm} \times 5.4 \text{ nm} \times 4.0 \text{ nm}$. A graphene layer is used as the underlying supportive substrate and another one is placed above the water body with a large distance of 10.0 nm to prevent the water molecules from crossing the top boundary of the simulation box. A third graphene layer (edge functionalized with hydrogen atoms) with the size of $5.4 \text{ nm} \times 5.2 \text{ nm}$ is placed vertically at the centre of the simulation box normal to the X direction, and the periodic boundary condition is applied in all three dimensions (Figure 4.1). By using this configuration, the vertical graphene layer and its periodic image form a meso-sized capillary polar surface (CPS).

The capillary distance, d_c , can be adjusted by changing the box length of the system in the X direction. On the CPS, positive and negative charges are assigned to the carbon atoms at certain positions, following the method of Wang *et al.* (2009). The numbers of positive and negative charges on each graphene sheet are equal so that the total charge of the surface is maintained as neutral. Previously, Schwierz *et al.* (2010) reported that the wettability of a CPS depends strongly on the spatial polarity distribution instead of the total charge. Hence, by tuning the charge q of the atoms, the CPS can be used to mimic surfaces with different polarity and wettability (Talpin *et al.* 2007, Titov *et al.* 2008, Chan *et al.* 2011).

The rigid TIP3P water model (Jorgensen *et al.* 1983) is adopted to describe the partial charge and geometrical structure of the water molecules. The particle-particle particle-mesh (PPPM) method is adopted to treat the long-range electrostatic interaction, with a cut off distance of $12 \text{ \AA}$ and a root mean square accuracy of 10^{-4} . The intermolecular interactions between the atoms in the system are described by the 12-6 Lennard-Jones (LJ) potential as indicated in the equation (2.4). The corresponding values of these parameters are subtracted from the CHARMM27 force

field (MacKerell *et al.* 1998) and listed in Table 4.1. The Lorentz-Berthelot mixing rule is adopted to determine the interaction parameters for the atomic pairs.

Figure 4.1. Atomistic configuration of (a) the water evaporation model and (b) side view of the polar surface. In (a), the yellow dashed line indicates the periodic boundary along the X direction. Due to the periodic boundary condition, the distance between the CPSs equals the X length of the simulation box. The blue and red atoms in (b) denote the negative and positive charges assigned to the carbon atoms, respectively.

All the simulations are conducted using the LAMMPS package (Plimpton 1995) with a time step of 2 fs. The trajectories of the simulations are visualized by the VMD package (Humphrey *et al.* 1996). The system is kept at a constant temperature during the whole simulations by applying the NVT ensemble using the Nose-Hoover thermostat. In order to investigate the capillary effect of the CPS on the water molecules, all the graphene layers are kept as rigid during the simulation. Initially, the water body is relaxed by performing an equilibrium simulation of 10 ns. Afterward, a vapor phase region is defined as the space with a distance larger than 2 nm above the top edge of the CPS to monitor the evaporation behaviors. An upward force of 1 kcal mol⁻¹ along the Z direction is applied to any evaporated water molecules that enter this region to keep them from returning to the water body. The simulation is then continued for another 5 ns for data collection.

Table 4.1. LJ parameters for atoms in the simulations (MacKerell *et al.* 1998)

Atom	q (e)	ε (kcal/mol)	σ ($\text{\AA}$)
O	-0.834	0.1521	3.15
H	0.417	0.0461	0.4
C	0	0.0700	3.98

4.3 Results and discussion

4.3.1 Wettability of the CPS

Since the polar charges are the main controlling factor, it is necessary to validate their effect on the wettability property of the CPS. In order to tell whether a surface is hydrophilic or hydrophobic, one traditional method is to calculate the contact angle of a water droplet on that surface (Shi *et al.* 2009, Scocchi *et al.* 2011, Weijs *et al.* 2011, Vanzo *et al.* 2012). By examining the geometry shape and the kinetic properties of the droplet, clear visualization of the surface wettability can be drawn. Separate MD simulations were thus conducted in which a half-cylindrical water slab is placed horizontally on a graphene substrate with the same partial polarity as the CPS (Vanzo *et al.* 2012). Both the substrate and the slab are periodical in the Y direction, and the length of the substrate along the X direction is large enough to ensure that the borders of the slab do not cross the boundaries of the simulation box (Figure 4.2).

After an equilibrium simulation of 5 ns at room temperature, the density distribution of the water slab on the XZ plane is collected and a contour map of the density is plotted based on which the water-vapor interface is defined at the locations with half the water density of the bulk water. The contact angle is then calculated from the best circular fit of the interfacial line. Considering the fact that the size of the water slab may affect the contact angle (Werder *et al.* 2003, Wei *et al.* 2014), MD simulations

are performed for both a small and a large number of water droplets with 1600 and 4500 molecules, respectively, for comparison.

Figure 4.2. Simulation model for the calculation of the contact angle of a half-cylindrical water droplet on the CPS.

Figure 4.3 shows the liquid-gas interface of the water slab on the surface and the fitting circular curve with $q = 0.1, 0.4$, and $0.6 e$ for both cases of 1600 and 4500 water molecules. The fitted curves match well with the interface profiles. As q increases, the shape of the water slab becomes flattened, indicating that the surface becomes more hydrophilic and the water molecules can spread out on the surface due to the enhanced electrostatic interactions between the water molecules and the charged atoms on the surface. The calculated contact angle at different q is plotted in Fig. 4.4a. The curves for both small and large water droplets show similar decreasing trends with q although there is a slight difference at $q = 0.6 e$. This is because as the water slab spreads out on the surface, a larger number of water molecules can maintain a larger thickness of the water slab and thus result in a larger contact angle. The mean square displacement (MSD) of the water is also plotted for the case of 1600 molecules (Figure 4.4b). The slope of the MSD curve versus time could be related to the diffusion coefficient of the water molecules in three dimensions through the relation

$$MSD(t) \approx 6Dt \quad (4.1)$$

where D denotes the diffusion coefficient and t is the time (Berezhkovskii *et al.* 2002, Liu *et al.* 2016).

Figure 4.3. Evolution of the shape of the water slab containing 1600 molecules (a-c) and 4500 molecules (d-f) placed on the CPS at $q = 0.1, 0.4$, and $0.6 e$.

As the surface turns more hydrophilic at larger q , the MSD curve becomes lower, indicating that the water molecules are less mobilized due to stronger attraction from the polar charges on the surface. The reduced mobility of water molecules is important for the understanding of the effect of surface charges on enhancing the evaporation flux as shall be discussed in the following.

4.3.2 Evaporation rate and evaporation enhancement

Once evaporated, the water molecules are kept in the vapor region at the top of the simulation box so that their number can be counted. A simulation period of 5 ns shows that when the system reaches the equilibrium state, the number of evaporated molecules increases linearly with time. Therefore, the evaporation rate, J , is defined as the mass of evaporation per unit time, divided by the projected area of the water

surface on the XY plane. The projected area is constant and equals to the area of the graphene substrate of the water body. For comparison, MD simulations are performed in which the water body is left to evaporate without the presence of the CPS (referred to as the normal case hereafter), and the corresponding evaporation rate is defined as J_0 . The evaporation enhancement factor, H , is thus determined as

$$H = \frac{J - J_0}{J_0}. \quad (4.2)$$

Figure 4.4. (a) Dependence of the contact angle of the water slab on the polar charges of the CPS and (b) MSD of the water molecules over time at various surface polar charges for the case of 1600 molecules.

Figure 4.5 shows the variation of the evaporation flux and the enhancement factor (inset) at different q for the temperature $T = 60^\circ\text{C}$ and capillary distance $d_c = 10$ nm. The temperature of 60°C is chosen due to the fact that in multi-stage thermal desalination, the temperature of the feed water usually ranges from 60°C to 90°C (Ammar *et al.* 2012). It can be observed from the figure that when q increases from 0.1 to 0.2 e, the evaporation rate J only shows a slight increase. However, a significant jump occurs for J when q further increases to 0.3 and 0.4 e. At $q = 0.4$ e, J reaches the maximum value of $0.62 \text{ molecules ns}^{-1} \text{ nm}^{-2}$ with an enhancement factor of 15%.

Interestingly, as q further increases, J starts to decrease, showing an overall nonmonotonic dependence on the hydrophilicity of the CPS. This behavior is quite similar with that results reported by Wang *et al.* (2012) in their evaporation model of

a droplet on a surface, despite the fact that the enhancement factor in their study is much higher. This is because, in their simulations, the water molecules are not confined in the mesopore and thus can spread easily over the large surface area of the substrate, which significantly increases the liquid-vapor interface. It is also noted that the evaporation rate calculated in their study is lower than that in this study. This increase can be attributed to the large temperature difference which strongly affects the kinetic energy of the water molecules and thus their evaporation rate.

Figure 4.5. Dependence of the evaporation rate J and the evaporation enhancement factor H (inset) on the polar charge q of the CPS.

To understand the dramatic increase in the evaporation rate at $q = 0.3$ and 0.4 e , the liquid-gas interface is extracted by using the same method for the investigation of the wettability of the CPS. Since the water box is periodical in the Y direction, the density profile is averaged along this direction and plotted in the XZ plane. Figure 4.6 illustrates the effect of q on the liquid-gas interface profile and the expansion percentage of the water body surface area, H_{sur} , in comparison with the surface area of the normal case. The interface profiles at $q = 0.1$ and 0.2 e do not show remarkable differences from the interface for the normal case. At $q = 0.3$ e , the water molecules start to climb up on the CPS due to their interaction with the charged atoms, and the interface begins to form a meniscus shape. For $q = 0.4$, 0.5 , and 0.6 e , the meniscus shape becomes more apparent, and the water molecules can even climb to the top of the CPS, leading to a significant expansion of the surface area of evaporation.

The expansion in the evaporation surface area with the formation of the meniscus interface plays a central role in increasing the evaporation rate when q increases to 0.3 and 0.4 e . In addition, the increase in the hydrophilicity at a larger q also leads to stronger interactions between the water molecules and CPS. Such enhanced interaction prevents the water molecules near the CPS from escaping from the CPS and evaporating. Consequently, the evaporation rate shows a decreasing trend at $q = 0.5$ and $0.6 e$.

Figure 4.6. (a) Evolution of the liquid-gas interface to form a meniscus shape and (b) expansion of the evaporation surface area H_{sur} in correspondence with the variation of q .

Theoretically, evaporation occurs when a water molecule at the interface gains sufficiently high kinetic energy through collision with other molecules to surpass the surface free energy barrier due to the formation of hydrogen bonds. Therefore, it is important to investigate the kinetic property of the water molecules at the liquid-gas interface region. To examine such kinetic property, the MSD is calculated for the water molecules near the interface between two density contours of 25% and 75% of the bulk density as indicated by the green and blue lines in Fig. 4.7a, respectively. Due to the meniscus shape, the mobility of the water molecules along the interface is not uniform along the X direction. Hence, four small areas of $0.2 \times 0.2 \text{ nm}^2$ on the XZ plane with distances of 0.9, 2.2, 3.6, and 5.0 nm from the CPS in the X direction (as

indicated by the red dotted lines in Fig. 4.7a) are selected to examine the spatial effect of the MSD. The last position refers to the middle of the liquid-gas interface.

Figure 4.7. (a) Location of the selected areas to calculate the MSD, which are 0.9, 2.2, 3.6 and 5.0 nm from the CPS and (b) the MSD over time for the selected water molecules.

Since the water molecules obtain their kinetic energy by interacting and colliding with each other, the evaporation possibility P_e of a water molecule at the liquid-gas interface can be related to its mobility and the number of its surrounding molecules. Hence, the possibility P_e can be correlated with the diffusion coefficient D and the density ρ as

$$P_e \propto D(x)\rho(x) \quad (4.3)$$

In the four chosen areas for the calculation of the MSD, the water density ρ can be considered to be the same, and thus P_e mainly depends on D . As shown in Figure 4.7b, the MSD curve for the position nearest to the CPS shows the lowest slope, which indicates that the water molecules here are least mobilized, and the stronger interaction energy with the CPS reduces their chance to evaporate. As the distance from the CPS increases, the MSD reduces but the reduction is not monotonic. The water molecules at the two intermediate positions (*i.e.*, 2.2 and 3.6 nm from the CPS) are more mobilized than the water molecules at the centre point (*i.e.*, 5.0 nm from the

CPS). The variance of curvature of the liquid-vapor interface at different positions may be a possible reason for the nonmonotonic reduction.

To further understand the water evaporation behaviors, the free energy barrier is investigated by calculating the potential of mean force (PMF) along the reaction coordinate of evaporation (*i.e.*, the Z direction). During the calculation, an umbrella sampling method (Roux 1995) is used, and a random water molecule is chosen as a probe and attached to a harmonic potential described by

$$E = \frac{1}{2}k(z_p - z_0)^2 \quad (4.4)$$

where k is the spring constant and Z_0 is the equilibrium position ranging from 20 to 70 Å above the substrate. The coordinate profile of the probe molecule is collected along the Z direction by a simulation of 4 ns, with a step of 0.5 Å, and then analysed using the weighted histogram analysis method (WHAM) (Grossfield). Similar to the calculation of the MSD, three different positions with the distances of 1.0, 3.0 and 5.0 nm from the CPS are selected to consider the spatial dependence of the free energy barrier.

Figure 4.8 shows the PMF and the number density profile along the Z direction at the three selected positions. The increase of the free energy along the Z direction corresponds well to the decrease in the number density of water. For the water molecules at the centre and the intermediate position (*i.e.*, 3.0 and 5.0 nm from the CPS), the free energy rises from ~ 1 kcal mol⁻¹ of the bulk water body to a peak of about 6.5 kcal mol⁻¹. The difference of around 5.5 kcal mol⁻¹ could be regarded as the energy needed for a water molecule to escape from the bulk water via breaking the hydrogen bonds among its neighbouring water molecules. For the water molecules near the CPS, this energy barrier is higher, up to about 6.5 kcal mol⁻¹. This might be due to the fact that the interaction energy between the water molecules and CPS also contributes to the free energy barrier, which makes the water molecules here more difficult to evaporate.

Figure 4.8. (a) PMF and (b) the number density of the water molecules along the Z direction at three distances of 1.0, 3.0 and 5.0 nm from the CPS.

4.3.3 Temperature effect

In multi-stage thermal desalination processes, the feed water is usually heated up to 90-110°C and let to evaporate through a number of stages, in which the temperature decreases gradually (Wang *et al.* 2011, Ammar *et al.* 2012). Since the temperature affects the kinetic energy of the water molecules directly, it is important to have a full understanding of the effect of temperature on the enhancement of capillary evaporation. Figure 4.9a shows the improvement of the evaporation rate J as T increases from 60 to 90°C for $q = 0.1$ and $0.4 e$. As can be seen from the figure, the high temperature boosts the mobility of the water molecules as expected, and the evaporation rate at 90°C is 2.3 times faster than that at 60°C. It should be noted that

this remarkable increase is contributed by both the capillary effect and the rise in the kinetic energy of the water molecules.

To investigate how much is the contribution of the former effect, the enhancement factor H as defined in Eq. 2 is calculated. An enhancement factor of ~45% can be achieved at 90°C for the case of $q = 0.4 e$, and this factor is only ~15% at 60 °C (Figure 4.9b). For $q = 0.1 e$, H also reaches 35% at 90 °C, despite showing a value around zero at 60°C. Overall, these results indicate that a high temperature not only accelerates the mobility of water molecules but also strengthens the capillary effect of the CPS, leading to faster evaporation.

To further understand the influence of temperature on the capillary effect, the density profiles along the XZ plane for the two cases of 60 and 90°C are examined (Figures 4.9c-d). It is found that at the higher temperature of 90°C, the water molecules can climb higher on the CPS, even though the interaction between the water and CPS remains unchanged. This behavior can be explained as that when the water molecules are mobilized at an ascending temperature, they are easier to be attracted by the polar charges of the CPS. The increase of the climbing height, on the other hand, also leads to the increase of the liquid-gas interface area (*i.e.*, the cyan region). As a result of the combined effect, the evaporation rate increases.

4.3.4 Interlayer distance effect

Previous studies of capillary-induced evaporation through a porous medium with pore diameter at the microscale have reported that the evaporation rate is sensitive to the change of the pore diameter (Canbazoglu *et al.* 2016). However, the dependence of evaporation rate on the size of the pore could be very different at the nanoscale. To study this effect, MD simulations are performed with different distance d_c between two adjacent CPSs. Since the system is periodic along the X direction, the change in the length in this dimension is equivalent to the change of d_c . Figure 4.10 shows that the variation of the enhancement factor H as d_c increases from 4 nm to 14 nm at $T = 60^\circ\text{C}$ and $q = 0.4 e$. It is observed that when $d_c < 6$ nm, H is negative, which indicates

that too small capillary space could lead to evaporation suppression instead of enhancement. As d_c increases from 6 to 12 nm, H increases monotonically to reach a maximum value of 24% and then starts to decline as d_c further increases to 14 nm. It is also found that the water surface area does not show a significant expansion when $d_c < 10$ nm. When d_c increases to 12 nm, the water surface area increases dramatically by around 23%, but it decreases as d_c further increases from 12 nm.

Figure 4.9. (a) Dependence of the evaporation rate J on the temperature T at $q = 0.4$ and 0.1 e (inset); (b) variance of the improvement factor H of evaporation with the temperature; (c-d) density distribution profiles of the water molecules along the XZ plane at $T = 60$ and 90 °C.

To understand this interesting nonmonotonic behaviors, the liquid-gas interface profile is examined (Figure 4.11). As can be observed, at $d_c = 4$ nm, the interface profile does not show a considerable change compared to the normal case without the capillary effect. However, as the distance d_c becomes larger than 8 nm, the climbing of the water molecules on the CPS and thus the formation of the meniscus water surface can be clearly observed, implying the presence of the strong capillary effect.

The climbing height of the water molecules reaches a saturated value at $d_c = 12$ nm beyond which the shape of the meniscus water surface does not show apparent changes.

Figure 4.10. Variation of the enhancement factor H and surface area expansion H_{sur} with d_c increasing from 4 to 14 nm.

The capillary effect of CPS is mainly induced by the van der Waals and electrostatic interactions between the CPS and water molecules. Such interaction would help the CPS attract the water molecules. At a small distance d_c , the attraction effect of both the CPSs facing each other remains strong throughout the whole capillary channel length direction. As a result, they compete in attracting the water molecules and thus suppress the capillary effect and the expansion of the meniscus water surface.

As the distance d_c increases, the competition between the two CPSs reduces and they only affect the water molecules near the surfaces. Hence, the capillary effect is promoted, leading to the increase of the water surface area and thus the evaporation rate. Further increase of the distance does not change the interaction between CPSs and the water molecules near them and thus does not contribute to increasing the evaporation rate. Consequently, a decreasing trend in the enhancement factor is observed in both the water surface area and evaporation rate. These results indicate that an optimum channel width exists that can fully capitalize on the advantage of the capillary effect in enhancing water evaporation at the nanoscale.

Figure 4.11. Transformation of the liquid-gas interface in comparison with that of the normal case with d_c increasing from 4 to 14 nm.

4.4 Summary

MD simulations hold the promises as a numerical approach that can help to accelerate the development of nanostructures towards the enhancement of evaporative flux which is critically important in numerous industrial applications. In this study, simulations are performed to examine the evaporation of water under the capillary effect created by two polar vertically aligned graphene surfaces. The influence of surface wettability is examined by changing the magnitude of the polar charges assigned on the CPS. The effects of temperature and capillary distance on the evaporation behaviors are also studied. The underlying mechanisms are investigated by exploring the evaporation rate of water molecules and their kinetic properties, the change in the liquid-gas interface profile, and the interaction energy between the water molecules and CPS.

The evaporation enhancement factor, H , defined as the percentage improvement in the evaporation rate between the two cases with and without the presence of the CPS, shows a nonmonotonic dependence on the charge q . It is found that H increases slightly as q increases to $0.2e$, before jumping up and reaching a peak at $q = 0.4e$. This dramatic increase is explained by the expansion of the liquid-gas interface to form a meniscus shape that encourages the evaporation. When $q > 0.4e$, H starts to decrease due to the high interaction strength between the climbing water molecules and CPS. This interaction strength leads to a high free energy barrier for the water molecules near the CPS to evaporate, as evidenced by PMF.

To investigate the effect of the meniscus interface on the enhancement of evaporation, the spatially dependent diffusion dynamics of the water molecules along the liquid-gas interface is examined by evaluating the MSD. It is found that the water molecules in the intermediate area between the CPS and the midpoint of the meniscus are the most mobilized, and the evaporation occurs predominantly from this area.

The study of the temperature effect shows that a high temperature leads to a significant increase in the evaporation of water as expected, and facilitates the capillary effect as evidenced by the largely augmented enhancement factor of 45% at 90°C . The enhanced capillary effect is caused by the growth of the meniscus-shaped interface as the water molecules are more mobilized and easier to be attracted by the polar charges on the CPS. The results also show that the capillary distance d_c between two adjacent CPSs can affect evaporation behaviors in a nonmonotonic manner. When $d_c < 8$ nm, the interaction strength between the water molecules and the CPSs suppresses the capillary effect and the formation of the meniscus water interface. As d_c increases, the space between the CPSs is widened, the influence from the CPSs is reduced, and the capillary effect is promoted, leading to an increase in the evaporation rate.

Overall, this study provides an understanding of the evaporation behaviors of water being confined in a capillary graphene channel. The utilization of hollow and porous nanostructures to accelerate the evaporation of water has drawn intensive attention

recently. The results from this study show that the main factor associated with the enhancement of evaporation is the geometry of the liquid-gas interface, which can be modified by various parameters including the size of the capillary space, feed temperature and also the wettability of the capillary surfaces. It is hopeful that the findings can be translated to the design and application of vertically aligned graphene and porous nanostructures in water distillation and other evaporation-based applications in the future.

Chapter 5 Water evaporation on graphene oxide surface

The content of this chapter is extracted from a research article*. In the present work, we study the evaporation of water on a corrugated GO surface by using MD simulations. GO nanostructures have drawn intensive attention in thermal desalination and water treatment applications as they can utilize solar energy to enhance the evaporation of water. The surface structure of GO normally contains wrinkles during its synthesis, which significantly affects the evaporation behaviors but yet to be investigated so far. By using MD simulations, it is found that the surface roughness can play a vital role in the contact distribution of the water molecules, thus leading to the further enhancement of evaporation flux compared to a flat surface. The effects of the water drop size and distribution of the oxidized groups are also examined. The results from this work provide helpful information for the design of graphene oxide nanostructures in evaporation and steam generation applications.

5.1 Background

The enhancement of water evaporation aided by surfaces of novel materials has attracted a lot of attention in recent years. The intense interest on this topic arises from many industrial and research applications. For example, thermal desalination technologies can boost the recovery ratio to compete with fast dominating membrane desalination (Subramani *et al.* 2015). Various applications, such as solar-driven evaporation (Tao *et al.* 2018), power generation (Elsafi, 2015, Aurousseau *et al.* 2016, Dinh *et al.* 2018, Dinh *et al.* 2019), printing and coating (Lee *et al.* 2015, Simovich *et al.* 2015), equipment sanitation (Maamari *et al.* 2016) and other steam-generation-involved processes, can also be improved.

*This chapter is written based on Kieu, H.T., Zhou, K. and Law, A.W.K (2019). Surface morphology effect on the evaporation of water on graphene oxide: A molecular dynamics study. *Applied Surface Science*, 488: 335-342.

To facilitate the evaporation of water on a surface, the most fundamental method is to provide external energy, usually heat, to the water molecules. The thermal energy

excites the kinetic motion of water molecules at the surface, leading to a higher possibility to break the interactions between them, providing faster evaporation. Because of this reason, metal-based (Govorov *et al.* 2007, Zhou *et al.* 2016) and carbon-based (Liu *et al.* 2015, Canbazoglu *et al.* 2016) materials are two common selections for the fabrication of the surface due to their plasmonic property, which enables them to convert optical energy, harvested from the sun, into heat (Neumann *et al.* 2013). The potential of metal-based materials has been well recognized in the literature, while carbon-based materials have emerged as a new generation of material over the last few years. Compared to the traditional metals, carbon-based materials offer an affordable alternative yet exhibit excellent plasmonic performance. In addition, carbon-based materials are flexible since they can be assembled with other components in a system to further achieve the functionality desired.

Recently, the size scale of the compound structure has been reduced, and much effort has been devoted to the fabrication of carbon-based nanostructures that can effectively enhance solar evaporation (Wang *et al.* 2016, Wang *et al.* 2016). However, the solar conversion efficiency has reached a plateau. Dao *et al.* (2018) summarized the performance of several carbon-based compounds that were tested in the last few years. The majority exhibits an efficiency ranging from 65% to 80%, with the graphene-based nanostructures showing a higher efficiency compared to the macroscopic compounds. It is challenging to achieve a higher conversion efficiency due to the inevitable energy loss to the external environment.

A novel concept has been proposed that is to enhance the evaporation through the distribution of water molecules on the nanostructure surface (Fedorov *et al.* 2014, Languri, 2018). The surface structure of the nano-compounds is characterized so that water molecules can be collected at areas where the evaporation conditions are favored. Canbazoglu *et al.* (2016) conducted evaporation experiments with carbon foam-based micro-diameter porous compounds. They reported that the utilization of capillary force can significantly enlarge the liquid-vapor interface, leading to faster evaporation. The evaporation behavior also shows a dependence on the wettability of the surface. This approach, which utilizes the plasmonic mechanism of the materials,

can still achieve evaporation enhancement when the supply of external energy is not abundant. Thus, its adaptation is vital for thermal desalination processes with low-grade energy such as waste heat.

The surface of materials is normally either hydrophobic or hydrophilic. The formation and distribution of water molecules on the surface is thus important for evaporation, especially at the nanoscale, as discussed above. Wang *et al.* (2012), using MD simulations, showed that a small number of water aggregates to form a droplet shape similar to the macroscopic scale on a hydrophobic surface. It then spreads into a thin layer when the surface is tuned from hydrophobic to hydrophilic. This behavior expands the liquid-vapor interface and enables more evaporation. However, when the surface becomes too hydrophilic, the water-surface interaction becomes too strong as it prevents the water molecules from evaporating. To effectively make use of this mechanism, Wan *et al.* (2015) proposed a heterogeneous surface which comprises both hydrophilic and hydrophobic areas, and their simulation results showed that a significant amount of water molecules evaporates from the transition areas between the hydrophobic and hydrophilic regions, which can be explained by their diffusion from a high energy site (hydrophilic) to a lower energy site (hydrophobic). This amount combined with the evaporation from the hydrophilic area results in a higher evaporation rate compared to that on a homogenous surface.

Graphene, a derivative of carbon, has attracted a lot of attention over the last decade, particularly in desalination and water treatment (Liu *et al.* 2016, Kieu *et al.* 2017, Boretti *et al.* 2018, Dao *et al.* 2018, Zhang *et al.* 2018). The combinations of high surface area, excellent thermal conductivity and strong plasmonic potential make it a promising candidate for evaporation and steam generation. Its oxidation form, GO, is cheaper and can be synthesized on a large scale. The surface of GO consists of two main parts: oxidized graphene, where the aromatic carbons are attached with oxidized functional groups (-OH, -COOH, -O-), and pristine graphene. The oxidized part is hydrophilic while the pristine part is hydrophobic, making GO an ideal surface for evaporation enhancement.

MD simulations of water evaporation of a flat GO surface shows that the spreading of water molecules and thus the evaporation is strongly dependent on the scale of the oxidized and pristine regions (Wan *et al.* 2017). However, in practice, the surface of GO is not perfectly flat but typically contains wrinkles, which can be controlled during its synthesis. The wrinkles are shown to be beneficial for solar steam generation, as they are able to trap solar energy through a radiative and convective reabsorption mechanism (Hong *et al.* 2018). Potentially, such wrinkles should also have considerable effects on the spreading behaviors of water molecules, and the evaporation on the corrugated GO surface should be different from a perfectly flat surface. However, a systematic study on the wrinkle geometry on the evaporation enhancement has not been reported so far.

In this chapter, we perform MD simulations to investigate the evaporation of water on a corrugated graphene oxide surface. The effects of surface structural parameters on the evaporation enhancement are thoroughly explored. They include the surface morphology, the distribution of functional groups and the thickness of the water body. Since the morphology and functional distribution of GO surface can be characterized via many physical and chemical techniques (Qiu *et al.* 2011, Dong *et al.* 2013, Han *et al.* 2015), the results from this study can also provide useful guidelines for the design of the GO surface structure in the future. In the following sections, we shall present the simulation model configuration and discuss the results obtained.

5.2 Simulation model

The simulation model which investigates the morphology effect of GO surface on water evaporation is shown in Fig. 5.1. The water body consists of 6235 water molecules generated to create a thin layer that has the initial size of $20\text{ nm} \times 4\text{ nm} \times 1\text{ nm}$. The underlying GO sheet has a surface area of $20\text{ nm} \times 4\text{ nm}$, and its morphology is adjusted by tuning the coordinate of the carbon atoms Z_c in the lattice corresponding to a wave function

$$Z_c = A_c \sin(2\pi X_c/\lambda) \quad (5.1)$$

in which A_c is the amplitude, X is the coordinate of the carbon atom along the X direction, and λ is the wavelength. The ratio of A_c/λ thus represents the roughness of the GO surface. On the graphene sheet, hydroxyl groups are assigned randomly on both sides of the graphene basal plane (He *et al.* 1998). In practical conditions, the graphene oxide surface consists of hydroxyl, epoxy and carboxyl groups. However, since those functional groups have a similar effect on the hydrophilicity of the surface, the GO sheet is functionalized with only hydroxyl groups for simplification in this study. The oxidation state of the GO surface is described by the ratio of the number of hydroxyl groups over the number of carbon atoms in the graphene sheet. In this study, the oxidation state is chosen to be 20%, which is the typical condition of GO (Kim *et al.* 2012). A flat GE sheet with the same dimensions is placed on top of the box to prevent the water molecules from passing through the vertical periodic boundary of the simulation box.

The simulations are conducted using the LAMMPS package (Plimpton 1995). Periodic boundary conditions are set in all three dimensions of the simulation box. Water molecules are constructed using the rigid TIP3P (Price *et al.* 2004) model. The particle-particle particle-mesh (PPPM) method, with a cut-off distance of 12 Å, is adopted to calculate the long-range electrostatic interaction. The intermolecular interactions are determined by the 12-6 LJ potential described in equation (3.2).

Table 5.1 summarizes the parameters for all the species in the simulations. The interaction parameter for the atomic pair is determined by the Lorentz-Berthelot mixing rule (Zhu *et al.* 2014). The carbon atoms attached to the hydroxyl groups have their polar charge set at $0.265e$ so that the GO surface is neutral. The parameters of oxygen and hydrogen atoms in the hydroxyl groups are adopted from the OPLS-AA force field (Jorgensen *et al.* 1996).

Figure 5.1. Atomistics configuration of (a) the simulation model, (b) the distribution of hydroxyl groups on the GO surface, (c) the morphology of the GO sheet described by the two parameters A_c and λ , and (d) the snapshot of the system during evaporation simulation. The green honeycomb lattice represents the carbon atoms in the graphene structure, and the red and white spheres represent the oxygen and hydrogen atom, respectively. In (b), the hydroxyl groups are assigned randomly on both sides of the graphene sheet. In (d), the evaporated molecules are kept at the top of the simulation box.

The simulations are conducted with a time step of 2 fs. Constant temperature is maintained by applying the NVT ensemble using the Nose-Hoover thermostat. After an equilibrium of 10 ns, a vapor region is introduced as the space region at 5 nm above the water-vapor interface. Any evaporated water molecule reaching the vapor region is kept at the top of the simulation box by applying an upward force of 1 kcal mol⁻¹ along the Z direction. This method had been adopted earlier in the literature based on an assumption that the water molecules evaporate to an infinite space where they have no interaction with the liquid body (Zhakhovskii *et al.* 1997). To study the effect of surface morphology on the evaporation, the graphene sheet is kept rigid

during the whole simulation, but the hydroxyl groups are allowed to fluctuate on the graphene surface. The simulation is then continued for another 5 ns for data collection. All the trajectories are monitored using the VMD package (Humphrey *et al.* 1996).

Table 5.1. LJ parameters for atoms in the simulations of water evaporation on graphene oxide surface (Jorgensen *et al.* 1996).

Atom	q (e)	ε (kcal/mol)	σ (Å)
C	0	0.0700	3.98
O _{OH}	-0.683	0.170	3.12
H _{OH}	0.418	0.0461	0.4
O _w	-0.834	0.1521	3.15
H _w	0.417	0.0461	0.4

5.3 Result and discussion

5.3.1 Wettability of corrugated GO surface

The natural oxidized functional groups provide the surface of GO with partial polarity, enhancing its hydrophilicity. Such effect allows the water molecules to spread on the oxidized regions of the GO surface, leading to the extension of the vapor-liquid interface. However, when the surface is not ideally flat, the spreading behaviors of water is expected to be impeded depending on the level of roughness. We investigate the effect of morphology on the wettability of the surface by calculating the contact angle of a water slab placed on the GO sheet in a separate model shown in Fig. 5.2. The water slab is periodical along the Y direction, and the X dimension of the GO sheet is large enough so that water molecules do not cross the periodic boundary. During the simulation, the density distribution of the water slab

on the XZ plane is collected, and the vapor-liquid interface is determined as the contour where the water density drops to half of the bulk value. The contact angle is then calculated from the best circular fit of the interface line.

Figure 5.2. The simulation model for the calculation of the wettability of the corrugated GO surface. A water slab is introduced and allowed to relax on the surface until equilibrium. The vapor-liquid interface from the density profile is used to determine the contact angle.

The simulation is carried out for 5 ns, and the contact angle is calculated every 500 ps to capture the spreading behaviors of the water slab for different surface roughness. Fig. 5.3b shows the evolution of the contact angle corresponding to the increase of roughness, with λ set at 30 Å, and A_c varying from 0 to 5 Å. The values at $t = 0$ are calculated from the density profile of the water slab right after energy minimization. It can be seen that the contact angle increases from around 35° to 70° when A_c increases from 0 to 5 Å, indicating that the GO surface becomes more hydrophobic with the surface roughness. It is also observed that during the simulation, the contact angle shows a decreasing trend toward a steady-state value at $A_c = 0$ to 3 Å, confirming the spreading behaviors of the water slab. For the cases of $A_c = 0$ and 1 Å, the spreading of the water slab is fast, occurring mostly in the first 500 ps, while for the cases of $A_c = 4$ and 5 Å, the contact angle shows a minor fluctuating trend around 70°.

Figure 5.3. (a) The calculation of the contact angle θ from the interface contour, and (b) the evolution of θ over time corresponding to the increase of surface roughness. Due to the corrugation of the GO surface, the contact angle in (a) is calculated based on the reference plane formed by the peaks of the GO sheet.

When examining the trajectories of the water slab on the corrugated GO surface, we observed that the water slab tends to accumulate on the space between the peaks of the GO wrinkles covering all the valleys (Fig. 5.3a). Therefore, when the roughness of the surface increases, the area of the valleys between two peaks is also larger, making it more difficult for the water slab to advance to the next peak during the spreading. The decreasing curves of the contact angles for the cases at $A_c = 2$ and 3 Å show the evidence of the spreading behaviors. At $A_c = 2$ Å, the water slab can easily spread to the adjacent peaks but would take more time when A_c increases to 3 Å. When A increases to 4 and 5 Å, the roughness becomes too high that the water slab can no longer advance to the surrounding valleys, thus the contact angle only shows minor fluctuations. This aggregation of the water slab on the corrugated GO surface is crucial to the change in the evaporation mechanism which shall be discussed in the following sections.

5.3.2 Effect of surface roughness on the evaporation flux

As discussed above, in the evaporation simulations, a thin water layer is placed on top of the GO surface and allowed to relax for 10 ns. During the relaxation, the liquid water distributes itself on the surface toward an equilibrium state in which the liquid-

vapor interface is stable. After the relaxation, any water molecule evaporating from the liquid is kept at the top of the simulation box, so that the total number of evaporated molecules N_v can be counted. In this study, the evaporation flux J is defined as the number of evaporated molecules per unit time per unit area. A non-equilibrium simulation of 5 ns shows that the number of evaporated molecules increases linearly with time (Fig. 5.4a), and the evaporation flux J can be determined as the slope of the regression fit of N_v versus time. When the time scale is doubled to 10 ns, the evaporation flux shows an insignificant difference of 0.8%. Therefore, for the sake of computational cost, we use the time scale of 5 ns in all our simulations.

Fig. 5.4b shows the change of the evaporation flux J when A_c increases from 0 to 5 Å for the two cases of $\lambda = 30$ and 50 Å, respectively. The red dotted line is the evaporation flux of water on the flat GO surface as the reference. Interestingly, the evaporation flux increases significantly as the surface becomes rougher, up to an enhancement factor of 32%. It should be noted that the temperature of the whole simulation box is kept constant at the room temperature, meaning that there is no additional external energy provided for the system.

The above results show that the enhancement of the evaporation flux is closely related to the distribution of the liquid body on the GO surface. To verify this hypothesis, we investigate the trajectories of the evaporation simulations for each case of A_c and λ . Fig. 5.4c and d show the snapshots of the trajectories for the cases of flat and corrugated ($A_c = 5$ Å; $\lambda = 50$ Å) surface. It is observed that on the flat GO surface, the water body forms an evenly-distributed layer, and evaporation occurs sporadically from the whole interface. On the other side, due to the wrinkles on the surface, water molecules accumulate mostly in the valleys of the corrugated GO, and most of the evaporated molecules also come from these regions with a higher evaporation frequency.

To evaporate from the liquid body, a water molecule needs to gather enough kinetic energy to surpass the energy barrier resulting from the interaction with the surrounding molecules and the surface. Water molecules increase their kinetic energy

by continuously colliding with the surrounding molecules. Therefore, the probability for a water molecule having enough energy to evaporate is the critically important factor that affects the evaporation flux, and any modification to the shape of the water body can result in a change of this factor.

Figure 5.4. (a) The number of evaporated water molecules and its linear fit over time during the simulation, the inset shows the linear fit when the simulation is prolonged to 10 ns; (b) the effect of amplitude A_c on the evaporation flux J in the two cases of $\lambda = 30$ and 50 Å, the red dashed line shows the reference J value for the case of flat GO and two snapshots of the evaporation on flat (c) and corrugated (d) GO.

Fig. 5.5a shows the density distribution of the water molecules inside the valley area of the corrugated GO sheet along the XZ plane. The density profile forms a contour map with the high-density sites located at the bottom points near the GO surface, and the contours correspond to the shape of the valley area. This density profile affects the diffusion of the water molecules toward the centre of the valley, leading to a higher frequency of collision. The average velocity distribution is also plotted in Fig. 5.5b. It can be seen that on the vapor-liquid interface area (bordered by the red dashed rectangle), the water molecules at the two sides of the valley have a high tendency to

move to the centre, which increases their probability of collision. Thus, evaporation occurs mostly from this region.

Figure 5.5. The profiles of (a) density and (b) velocity distribution of the water molecules inside the valley area of the wrinkle.

Another factor that controls the evaporation of water is the evaporation energy barrier. This barrier is contributed by the interaction energy among the water molecules and the electrostatic interaction between the water molecules and the surface. In the previous study, we have shown that while increasing the water-surface interaction energy may enhance the diffusion of water on the surface, the evaporation of water will also be retarded if this energy becomes too high (Kieu *et al.* 2018). Since this interaction is determined by the distance between the GO surface and the outermost water molecules, the change in the surface morphology has a significant influence on this interaction energy.

To examine this effect, the potential energy (PE) between the GO surface and the water molecules at the outermost region of the interface is calculated for the two aforementioned cases. A water molecule is used as a probe to scan the lateral surface of the GO sheet along the XY plane. The PE is then plotted in a contour map. Fig. 5.6 shows the PE maps of the surface at a Z coordinate corresponding to the position of the water molecules at the outermost layer for three cases of $A_c = 0, 3$ and 5 Å. The black and dashed lines represent the starts of the valley and peak regions, respectively. It can be seen that there are blue and red regions which represent

attractive and repulsive energy, respectively. They distribute randomly in the PE maps due to the random distribution of the hydroxyl groups on the graphene surface.

Figure 5.6. Potential energy map of the water molecules at the vapor-liquid interface from the surface of GO when at $A_c = 0$ (a), 3 (b) and 5 (c) Å. The space between the dashed lines in (b) represents the valley area of the wrinkle.

Compared to the flat surface ($A_c = 0$ Å), the PE map of the corrugated surface ($A_c = 3$ and 5 Å) is more patterned as the high-energy sites appear mainly at the peak areas. At the valley area (*i.e.*, the space between the two dashed lines), the magnitude of the interaction between the interfacial water molecules and the GO sheets is closer to zero, indicating that the interaction between them here is weak. These low-energy sites favour the mobility of water molecules, and thus evaporation occurs mainly from this region. It is also noted that the increase in the surface roughness can further enhance this effect, which is evidenced by the change in the PE at the valley when A_c increases from 3 to 5 Å.

5.3.3 Effect of water layer thickness

The presence of low-energy sites in the wrinkles of the GO surface can be explained by the fact that water molecules aggregate to cover the space in the valley area, which results in a thicker liquid body. Therefore, the interfacial water molecules here are

located further away from the surface, compared to the even spreading of water molecules on the flat surface. However, this effect can be mitigated when the thickness of the water layer is small. Here, MD simulations are conducted to examine the effect of water thickness on flat and corrugated ($A_c = 5 \text{ \AA}$, $\lambda = 50 \text{ \AA}$) GO surfaces. The thickness of the initial water body is reduced from 10 to 5 $\text{\AA}$. Fig. 5.7 shows a decreasing trend in the evaporation flux for both cases of flat and corrugate GO surface as predicted. Interestingly, despite the similar declining trend, the enhancement of evaporation flux is still maintained consistently on the corrugated surface compared to the flat surface.

Figure 5.7. The effect of water layer thickness on the evaporation of water on flat and corrugated GO surface.

When the trajectories are examined, it is observed that as the water layer becomes thinner, the water molecules tend to reside in areas with high oxidation concentration of the flat GO surface, leaving the low concentration areas uncovered. Therefore, the decline in the evaporation flux can be attributed to the shrinking vapor-liquid interface, besides the increased water-GO interaction energy. On the other hand, although the thin water body increases the potential energy between the surface and the interfacial molecules, the accumulation of water in the valleys of the corrugated GO is preserved. Since evaporation occurs mostly from these regions, the evaporation flux is insensitive to the shrink of the vapor-liquid interface. These results indicate

the considerable benefit of the surface roughness to the enhancement of water on GO compounds.

5.3.4 Effect of oxidized groups distribution

During the synthesis of GO, the wrinkles on the surface can be controllably characterized using specific techniques (Qiu *et al.* 2011, Dong *et al.* 2013, Han *et al.* 2015). Such wrinkles have been shown to reduce the water-surface interaction energy, leading to enhanced evaporation. When the wrinkles are formed on the oxidized region of GO, the hydrophilic functional groups could attract the water molecules to gather inside the valleys of the wrinkles. However, if the surface of the wrinkle is pristine, the spreading of water molecules may be impeded due to the hydrophobic nature of graphene. Recent experimental works have shown that the distribution of the hydrophilic oxidized groups on GO surface is not homogenous, and there is a phase separation of typically 1 to 2 nm between the oxidized and pristine graphene regions. Understanding the effect of this pattern is thus important to the design and fabrication of GO compounds for evaporation enhancement.

MD simulations are conducted to investigate the effect of the patterned GO surface on the evaporation of water in 4 Scenarios. In Scenarios (1) and (2), 80% and 100% of the peak areas are oxidized and the valley areas are pristine, respectively. The opposite is examined in the Scenarios (3) and (4), respectively. Fig. 5.8a illustrates the evaporation flux of water J on the patterned GO surface in all 4 Scenarios. The value for the case of homogenous GO is shown as Scenario (5) for reference. It is observed that when the peaks of the wrinkles are hydrophilic (*i.e.*, Scenarios 1 and 2), the evaporation of water is similar to the case of homogenous GO, and the evaporation flux does not show a remarkable change. On the other side, the evaporation flux is further increased when the oxidized groups are allocated in the valleys of the wrinkles (*i.e.*, Scenarios 3 and 4), up to a factor of approximately 20% compared to that of the homogenous GO. When the evaporation flux of flat GO is considered, the enhancement is around 53%.

Interestingly, the trajectories of the system in Scenarios (3) and (4) show a different behavior from the common results. When the peak of the GO sheet is pristine, water molecules aggregate to form large clusters on the valley areas of the surface (Fig. 5.8b). This behavior is attributed to the hydrophobic property of pristine graphene which prevents the spreading of the water molecules. The accumulation further increases the thickness of the water body, thus reducing the water surface interaction energy.

Figure 5.8. (a) Effect of patterned GO surface on the evaporation flux J in the five scenarios; (b) the formation of water slabs on the valley-oxidized GO surface which increases the thickness of water body; and the potential energy map of the water molecules at (c) 5 Å and (d) 10 Å above the surface.

Fig. 5.8c and d show the PE map of water molecules at 5 and 10 Å above the peaks of the surface. It is noticed that at 5 Å above the surface, the magnitude of the PE is smaller than that of the homogenous GO as shown in Fig. 5.6 by a factor of 5. At 10 Å above the surface, the energy is close to zero, implying that the interaction between the water molecules and the GO surface is insignificant, and the energy barrier of evaporation depends mainly on the water-water interaction. These results suggest a potentially advantageous design of the GO-based compounds that capitalizes on the

oxidation of the wrinkles to effectively improve their evaporation enhancement at the nanoscale.

5.4 Summary

The surface of GO-based nanostructures for evaporation enhancement always contains nanoscale wrinkles, which have not been considered in the investigation of their performance systematically so far. In this study, MD simulations are conducted to examine the effect of the surface morphology on the evaporation of water. The roughness of the surface is tuned by changing the corrugation pattern of the GO sheet. The enhancement mechanism is revealed by investigating the kinetic properties and the allocation of the water molecules on the GO surface, as well as the interaction energy between them.

The effect of surface modification on the distribution of the pristine and oxidized regions on the GO surface is also examined. The results show that the surface roughness impedes the natural spreading of the water molecules, diminishing the hydrophilicity of the GO surface as a result. However, the evaporation flux J shows a monotonical increase with the surface roughness, up to an enhancement of 32% compared to that of the flat GO surface. It is found that the valley areas on the corrugated surface have a critical role in gathering the water molecules inside their concave space and modifying their density distribution. Being surrounded by the high-density area at the sides, water molecules inside the valleys have a higher tendency of moving toward the centre, thus increasing their chance of collision, and leading to a higher probability of evaporation at this area. In term of the evaporation energy barrier, the corrugation of the GO surface also provides low-energy sites at the valleys of the wrinkles that favour the evaporation of water molecules.

In the fabrication of the nano-compounds, the structure of GO is not homogenous. On a macroscopic surface, the size of the water body may differ non-uniformly. MD simulations are performed to investigate the effect of the size of the water body on the evaporation behaviors. The results show a decreasing trend of the evaporation

flux as the initial thickness of the water layer decreases due to the increase in the water-surface interaction. However, the corrugation GO surface still maintains its advantage over the flat surface in terms of evaporation enhancement. This is because on the corrugated surface, evaporation occurs mainly from the valley areas. The evaporation flux is not affected by the shrink of the vapor-liquid interface, which occurs in the case of flat GO surface.

The distribution of pristine and oxidized regions in the corrugated GO surface also has an influence on the evaporation of water. The MD results show that the oxidized valleys and pristine peak pattern further improve the performance of the surface, with the water molecules forming large clusters at the valley areas instead of covering the whole surface, which increases the thickness of the body. This aggregation significantly reduces the water-surface interaction, leading to a higher evaporation flux. Since the wrinkles on the GO surface can be controlled during the fabrication and characterization, it is advantageous to capture the patterning effect in the future design of the compounds to optimize their performance.

Graphene-based materials have attracted intensive attention in steam generation devices in recent years. Since the evaporation of water on nanostructures is a complicated phase-change phenomenon, many structural and external factors need to be examined throughout the process. By considering the effect of the surface roughness, which is one of the important factors in the practical conditions, we believe that the understanding of the evaporation mechanism at the nanoscale has been advanced. In addition, the results from this study shed light on the application of not only graphene-based but also other materials in the design of nano-compounds and nanostructures for effective evaporation and steam generation.

Chapter 6 Evaporation of droplet using coarse-grained molecular dynamic simulations

This chapter summarizes the results on utilizing coarse-grained MD approach to study the kinetics behaviors of the evaporation of a nano water droplet in a closed system under the effect of vapor pressure. Computational methods have been playing an important role in investigating various nanoscale mechanisms occurring during the phase-change process, accelerating the progress of novel material characterization and screening. However, due to the limitation in model size and computational cost, such computational studies of water evaporation face a challenge in the accuracy. By assuming constant vacuum evaporation and neglecting the effect from re-condensation, many of such recorded flux values are unrealistically high. In this study, we managed to overcome the computational challenge of accurately capturing intensive thermodynamic properties in a non-equilibrium molecular dynamics study by utilizing the ELBA coarse-grain water model. The entire dynamic change of a nano water droplet reaching saturation in a closed system is observed through non-equilibrium molecular dynamics simulation, and meaningful insights are presented.

6.1 Background

The evaporation process at the air-water interface plays a fundamental role in many natural and industrial processes. For example, the generation of steam utilizing incident solar energy has a huge industrial demand for desalination, fabrication and manufacturing, and equipment sanitation (Chen *et al.* 2019, Zhou *et al.* 2019). The advancement of nanotechnology has also injected new energy to this discipline, and recent laboratory studies at bench scales had been performed to investigate the enhancement of evaporation utilizing novel nanocompounds (Dao *et al.* 2018). These studies demonstrated the potential that the interfacial vapor generation can be facilitated on the surfaces of these compounds at the nanoscale, for example by maximizing solar energy absorption and heat management, to achieve efficiencies that are much higher than natural evaporation (Tao *et al.* 2018). However, despite the

extensive effort so far, the fundamental understanding of the underlying mechanism of nanoscale evaporation remains elusive. Therefore, further studies are essential to continue the development.

Computational modelling with high performance computing has been adopted as an effective tool to investigate the nanoscale evaporation process. Over the last two decades, numerous related studies had been performed using the approach of Monte Carlo (MC) (Sharma *et al.* 2012, Yamashita *et al.* 2017) and Molecular Dynamics (MD) simulations (Zhakhovskii *et al.* 1997, Wang *et al.* 2013, Zhang *et al.* 2013, Wang *et al.* 2014, Hens *et al.* 2015, Xie *et al.* 2016). A vast majority of the configurations in these studies focused on the evaporation of water on solid substrates. Recently, efforts had also been devoted to investigate the interfacial evaporation on specific nanostructures to provide insights for the fabrication of steam generation devices (Yang *et al.* 2017). For example, Ding *et al.* (2017) reported that multilayer graphene with cone-shaped nanopore can remarkably enhance the water evaporation with a large pressure difference. Our recent MD work which coupled the effect of capillary action and surface wettability had also shown that a hydrophilic surface with a rough morphology can extend the liquid-vapor interface formation and thus facilitate the vaporization (Kieu *et al.* 2018, Kieu *et al.* 2019).

The abovementioned computational studies had yielded helpful insights into the nanoscale behavior of interfacial water evaporation. In particular, the behavior of liquid-phase change is highly non-linear at and near the interface, and hydrodynamic equations cannot fully capture the macroscopic variations in this region adequately. The ‘jumps’ in macroscopic behavior in the region have been explained by the presence of the Knudsen layer with a typical thickness of a few mean-free paths (Gusarov *et al.* 2002). Two widely adopted theoretical evaporation models, the Hertz-Knudsen equation (6.1) and the modified Schrage equation (6.2), have also been proposed in the literature to represent the evaporative flux across this layer:

$$J_{HK} = \frac{\sigma_e \Delta P \Delta h_{lv}}{\sqrt{2\pi m k_B T}} \quad (6.1)$$

$$J_{\text{Schrage}} = \frac{\sigma_e \Delta P \Delta h_{lv}}{(2 - \sigma_e) \sqrt{2 \pi m k_B T}} \quad (6.2)$$

where J is the evaporation flux, ΔP is the vapor pressure difference, Δh_{lv} is the enthalpy change from liquid to vapor, m is the molar mass, k_B is the Boltzmann constant, and T is the temperature. Since probing meaningful information in the thin Knudsen layer is very challenging experimentally (Lu *et al.* 2019), computational methods are also commonly adopted.

In the vast majority of the computational work so far, the assumption of vacuum evaporation was generally made as a boundary condition with the evaporation being treated as an irreversible process. Re-condensation, which would exist in a real setting, was normally not taken into account. This omission was mainly attributed to the substantial computational expenses required (Frezzotti *et al.* 2018). However, it limited the studies to the initial non-equilibrium state, and also led to the predictions of very high evaporation fluxes from these simulations compared to laboratory and field measurements reported in the literature. To compensate for the inaccuracy, σ_e is sometimes empirically set to a small value to provide a better match between the predicted and actual evaporation rate values (Persad *et al.* 2016). Some studies also used the simple Lennard-Jones spherical particles to model the fluid behaviour instead, which did not have direct physical representations (Liang *et al.* 2017). Another approach is to calculate the evaporation flux indirectly at equilibrium conditions, where the evaporation and condensation rates are presumably equal (*i.e.*, $\sigma_e = \sigma_c$). Both experimental and computation studies can then be performed to calculate the evaporation coefficient through the condensation route instead, but conflicting values had been reported so far (Hołyst *et al.* 2009, Hołyst *et al.* 2015). Interestingly, although the concept of Knudsen layer is perceived to cater for the jump in macroscopic thermodynamic properties, it had also been shown that simple macroscopic relations such as the Kelvin equation holds to a certain degree at the nanoscale (Factorovich *et al.* 2014).

In summary, due to the typical assumption of vacuum evaporation without re-condensation, no computational literature so far has rigorously examined the kinetic

models of evaporation from the initial evaporative to the equilibrium state to the best of our knowledge. To address this need, we perform non-equilibrium MD simulations to examine the transient thermodynamic properties of a nano water droplet in a closed periodic system, that encompasses vapor pressure and re-condensation for the first time. The entire dynamic changes of the nano droplet and the localized vapor pressures inside the system are monitored quantitatively from vacuum to saturation. We note that the scope of the dynamic simulations in this study is demanding in terms of both computational techniques and resources. Most importantly, the size of the system, timestep and averaging needs to be carefully considered so that the physical occurrences dominate over statistical noises (Meland *et al.* 2003). Advanced computational setup is also developed to achieve the necessary isolation and probing (Smith *et al.* 2006). so that the varying radial extent of the Knudsen layer around the droplet can be determined through the transient pressure and energy distribution spatially, and the dynamical evolution of evaporation inside the Knudsen layer can be revealed. As shall be shown in the following, the results give the quantitative details why some of the classical thermodynamic behaviour of fluids (Clausius-Clapeyron relations) do not contradict with the interface kinetics, and the new understanding can potentially improve the accuracy in predicting the evaporation flux of nanoscale phase-change by computational models. In the following, we shall first present the simulation setup, before discussing the results obtained in detail.

6.2 Simulation model

Traditionally, the simulations of evaporation kinetic behaviour at the liquid-gas/Knudsen-bulk interface are performed by approximating the Boltzmann Transport/Enskog-Valsov equations at the interface (Frezzotti *et al.* 2018). The most popular method is to solve the Boltzmann transport equation through the Direct Simulation Monte Carlo (DSMC) methods. Though computationally cheaper, these statistical methods cannot elucidate the underlying processes which the individual water molecules undergo during the phase change.

In this study, we adopt the detailed approach of MD simulations instead. All MD simulations are conducted using the LAMMPS (Plimpton 1995) package. The

microcanonical ensemble (NVE ensemble) is used as the time integration algorithm with a Langevin thermostat set at 343.15 K. The thermostat is applied to both translational and rotational degrees of freedom to all the water molecules with a damping factor of 100 femtoseconds. Separate simulation runs are also conducted with thermostat set at 333.15, 323.15 and 313.15 K to examine the effect of temperature within this range. The timestep used for the data collection is 0.5 fs. We necessarily choose such a small timestep to ensure sufficient averaging while still capturing the dynamic changes during the non-equilibrium runs.

The box size is $400 \text{ \AA} \times 400 \text{ \AA} \times 400 \text{ \AA}$, and the boundary condition is periodic across all three Cartesian dimensions. A total of 64000 water molecules are initially generated. Energy minimization is then performed, and the system is relaxed for 2 ns before deleting all vapor molecules. A droplet then forms near the centre of the simulation box, and the centre-of-mass of the droplet is computed. Subsequently, we apply a spring force to the centre of the water droplet (all water particles within a radius of $40 \text{ \AA}$) to ensure that the droplet does not fluctuate during the data collection.

In order to examine the radial distribution of the thermodynamic properties from the centre of the droplet, we discretize the regions for pressure calculations to a series of “dynamical shells” as shown in Fig. 6.1. A total of 20 shells with uniform thickness of $2 \text{ \AA}$ starting from inner radius of $75 \text{ \AA}$ are evaluated. The number of vapour molecules in each shell is updated every 10 timesteps. Within the shell, the partial pressure is calculated by summing the diagonal components of the stress tensor as follow:

$$S = - \left[m_a v_a v_b + \frac{1}{2} \sum_{n=1}^{N_{pairwise}} (r_{1a} F_{1a} + r_{2a} F_{2b}) \right] \quad (6.3)$$

$$P = \frac{S_{xx} + S_{yy} + S_{zz}}{3V} \quad (6.4)$$

where V is the sub-volume of the region of interest. The stressed tensor is calculated by summing the virial and kinetic contributions for every dynamic group (Thompson *et al.* 2009). The stress and density calculations are averaged over 10000

instantaneous values for every 100000 timesteps (0.05 ns). The averaging quantities are chosen to balance the computational speed while achieving statistically significant results (Malek *et al.* 2018).

The simulations are performed using the High Performance Computing cluster at Nanyang Technological University on two nodes, with 2 Intel® Xeon® Gold 6142 processors per node. Given the fact that the spatial decomposition partitioning scheme used by LAMMPS is not optimized for inhomogeneous systems, communication bandwidth among the processors is minimized to improve parallelization.

We adopt the ELBA coarse-grained model to examine the non-equilibrium behaviour of the evaporating droplet (Orsi *et al.* 2011, Ding *et al.* 2016). The ELBA model uses the Stockmayer potential for polar fluids, with each particle represented by a Lennard-Jones soft sphere with an electrical point dipole. In our opinion, this model is the best candidate to study short-distance interactions which can realistically reproduce long-distance electrostatic behaviours at the same time. It is also chosen over another popular mW coarse grain model (hydrogen-bonded structure of water modelled through a non-bonded angular dependent term) due to better thermodynamic agreement at higher temperatures (Molinero *et al.* 2009). The OpenMP threadings, as well as hardware specific Intel Math Kernel Libraries and Intel accelerator packages, are used to speed up the computational performance. The entire LAMMPS package is compiled specifically for the Intel® AVX-512 instruction set architecture. In this study, an average computational speed of 15.584 timesteps per second is recorded in the data-collection stage.

Figure 6.1. VMD screenshot of our model configuration. The boundary box of $400 \text{ Å} \times 400 \text{ Å} \times 400 \text{ Å}$ is shown by the black solid lines. The dotted circles are shown to visualize the discretized shells from the droplet. A spring force is applied to all water molecules within 400 Å of the droplet. The small simulation shows the initial condition after all vapor molecules are deleted, and vapor formation is developed dynamically.

6.3 Results and Discussions

6.3.1 Evaporation flux

During the simulation run, the geometry of the water nanodroplet remains nearly identical with a constant curved liquid-vapour interface. To determine whether the system is in equilibrium, the bulk evaporation count is measured with the evaporative region defined as 97 Å away from the centre of the droplet. This specific distance is chosen as it is sufficiently far away from the droplet and the Knudsen layer, as shown in the radial pressure profile to be discussed later on. The variation of the water molecule count is plotted against time in Fig. 6.2a. In all four temperature conditions, the bulk vapour density appears to reach the equilibrium value after approximately 500 ps . We also note that the resulting plot largely resembles a one-phase association equation with zero offset (Box-Lucas model) as:

$$N_v(t) = N_{max}(1 - e^{-\kappa t}) \quad (6.5)$$

where N_{max} is the saturated number of vapour molecules and κ is the evaporation flux coefficient. Therefore, the Levenberg-Marquardt (L-M) algorithm (Moré 1978) is chosen for the regression analysis. The instantaneous bulk evaporation flux J is calculated by taking the numerical derivative of the vapour particles count. Due to the small magnitude of change per timestep, extrapolating meaningful information from the flux is quite difficult. Thus, we take the derivative of the fitted Box-Lucas model instead being the function of evaporated water particles count over time as:

$$J(t) = \frac{\delta N(t)}{\delta t} = J_0 e^{-\kappa t} \quad (6.6)$$

where J_0 is the initial flux at $t = 0$.

The derived equation for the instantaneous evaporation flux is plotted in Fig. 6.2b. Due to the small timestep, the instantaneous state of the closed system might be either net condensation or net evaporation represented by the positive or negative flux values, respectively. The fluctuations shown in the figure highlight such dynamical interplays. It is worth mentioning that κ is largely determined by the size of the system. In consideration of the computational cost, the simulation box size of $400 \text{ \AA} \times 400 \text{ \AA} \times 400 \text{ \AA}$ is judged to be sufficient to highlight such dynamical behaviours within a reasonable timescale.

6.3.2 Vapor pressure and evaporation mechanism

The bulk pressure change in the closed system is computed (shown in Fig. 6.3) following the Box-Lucas exponential growth model as

$$P_v(t) = P_{sat}(1 - e^{-\kappa_p t}) \quad (6.7)$$

where the P_{sat} represents the saturation pressure and κ_p is the pressure rate time constant. P_{sat} can also be estimated by various semi-empirical equations proposed in the literature.

Figure 6.2. The bulk molecule counts N_v (a), as well as the evaporation flux J (b), is shown for 343.15, 333.15, 323.15 and 313.15 K over time. The dotted line for the flux is the derivative of the regression line fitted for the molecule (average $R^2 = 0.914193$). Given these values aren't averaged over time and are instantaneous snapshots of the system, the numerical derivative is too noisy to interpret a meaningful flux relationship.

Here, we compare the fitted values from the simulations with calculated values from the widely adopted semi-empirical Antoine equation (Yaws *et al.* 1989). in Table 6.1. The comparison shows that the MD results agree reasonably well with the calculations. The small differences between them are expected physically, because the Antoine equation does not take into account the effect of a curved liquid vapour interface and the associated effect of curvature on surface tension (Tolman length) (Factorovich *et al.* 2014). Overall, the present results validate that calculating the

virial and kinetic stresses is a relatively accurate method to determine the local non-equilibrium pressure. They also show that the configuration in the present study is yielding atomistic thermodynamic properties that are statistically significant and can be reasonably interpreted in the macroscopic scale.

Figure 6.3. Bulk vapor pressure at 343K, 333K, 323K and 313K. A Box-Lucas regression line is fitted with an average R^2 value of 0.953. The trend show system reaching equilibrium vapor pressure relatively quickly.

Table 6.1. Comparison of saturated bulk vapor pressure P_{sat} between our measured pressure tensor values and values calculated using the Antoine equation.

Temperature	313K	323K	333K	343K
Antoine equation	0.073	0.121	0.196	0.307
Fitted values	0.0758	0.138	0.217	0.327
Relative difference (%)	3.8	14.0	10.7	6.5

6.3.3 Spatial density and radial energy profiles

To further examine the mode of evaporation and determine the interfacial region, a bidimensional density map is computed across the centre of mass along the XZ cartesian plane through discretizing the entire simulation box to 6400 individual

cubes of $5 \text{ \AA} \times 5 \text{ \AA} \times 5 \text{ \AA}$ (Fig. 6.4). The interfacial line is determined as the density contour at half the bulk value (Kieu *et al.* 2018).

Figure 6.4. XZ Bidimensional density maps of droplet interfacial region at $t = 50$ and 500 ps. Slight expansion in the interfacial region is observed. All the values are averaged over every 100000 timesteps.

From Fig. 6.4, it can be observed that the droplet retains its bulk density profile during non-equilibrium evaporation (50 to 500 ps), with the location of the interfacial region confining at around $75 \text{ \AA}$ from the centre of mass. At the same time, there is a noticeable expansion of the interfacial region when comparing the density maps between 50ps and 500ps as shown in Figure 6.4.

The change in the radial profile of average kinetic energy E_k and potential energy E_p per molecule across the interface and Knudsen layer shells is shown in Fig. 6.5 over a duration of 500 ps. A consistent decreasing trend in the slope of average radial kinetic and potential energy profile (E_k and E_p) of the water molecules can be clearly observed. This subtle relaxation in distribution can be attributed to the slight expansion of the interfacial vapour density. Given that the primary interactions of the water molecules are based on pairwise and dipole interactions, the magnitude of E_p is directly related to local density. The shift in the interfacial region is also observed in the relaxation in gradient of E_p as well, which is consistent with the macroscopic thermodynamic behaviour. Overall, the results explain why the thermodynamic assumptions in the Kelvin equation are still valid in nanoscale systems regardless of the difference in length scale and granularity, because both the energy distribution

and density profile are independent of local non-equilibria behaviours. Furthermore, since the thermodynamic properties are the outcomes of atomistic behaviours averaged over ‘macroscopic’ timescales, the steady-state behaviour of the nanoscale system can be extrapolated to more realistic sizes.

Although the water molecules might not have sufficient E_k on average to pass through the energetic barrier (represented by E_p) and move into the bulk vapour phase away from the interface, some of these water molecules can do so by gaining sufficient instantaneous E_k through intermolecular interactions (Nagata *et al.* 2015). Visualizing the extent of this effect can be shown by investigating the pressure profile across the Knudsen layer.

Figure 6.5. Radial average kinetic and potential energy of the water molecules at 343 K. Though the total energy of the system is conserved as NVE ensemble was used, there is a clear shift in the slope of the radial distribution.

6.3.4 Knudsen Layer characteristics

Estimating the thickness and location of the Knudsen layer directly from the density profile is challenging because these two properties are independent of the changes in bulk vapour pressure. Instead, they can be more accurately determined by examining the critical points of the radial pressure profile. In this study, the transient behaviour of radial pressure distribution during non-equilibrium conditions is calculated using the proposed discretized shell method highlighted in Figure 6.1 earlier. By

determining the local partial pressure at every sub-shell, the dynamical behaviour of the Knudsen layer can be visualized

Fig. 6.6 shows the evolution of the radial pressure profile during the simulation time. The Knudsen layer is defined as the region where the partial pressure witnesses a dramatic drop (Aoki *et al.* 2003). From the figure, the Knudsen layer can be approximated to be located between 85 to 95 Å away from the centre of mass at 500 ps. Previously, Gusarov *et al.* (2002) proposed the thickness of the Knudsen layer to be the length value whereby the heat flux decreased by a factor of ten. In Fig. 6.5a, the average kinetic energy appears to be around 0.035 kcal mol⁻¹ at 85 Å and approaching one-tenth of that value at approximately 10 Å away. This agreement validates the accuracy of this method for estimating the Knudsen layer thickness. The relative location of the Knudsen layer can also be observed from Fig. 6.6, from initially around 80 Å at 50 ps and subsequently shifting to ~87 Å when approaching equilibrium. This shift is also reflected in the change in gradient of Fig. 6.5a.

As the system reaches saturation, the peak partial pressure shows a relaxation from 160 atm to around 65 atm. The large initial pressure potential is clearly due to the vacuum ambient environment (Lu *et al.* 2019). while the subsequent relaxation in pressure corresponds to the saturation in bulk vapour. However, despite the relaxation, the radial pressure gradient at the Knudsen layer does not converge to zero. Instead, it displays a nonlinear deterministic behaviour even as the bulk system approaches the equilibrium state. Given that a significant pressure potential still occurs at saturation ($t > 500$ ps), it can be stipulated that a purely diffusive and expansion mechanism would not be adequate to describe the entire evaporation process. Instead, this phenomenon can be explained through a transition in the interfacial transport mechanisms. Initially, the evolution of vapour pressure is driven by the diffusive and expansion forces due to the large density gradient. As the system approaches saturation, the non-equilibrium kinetics across the Knudsen layer begin to dominate, whereby the evaporation is now governed by a kinetically limited transport mechanism which was reported previously in the literature (Lu *et al.* 2019).

Figure 6.6. Basis spline radial pressure profile of various timesteps at 343.15 K. Significant shifting in the pressure distribution occurs between 50 to 500 ps.

6.3.5 Evaporation coefficient

Another line of inquiry in this study is whether the dynamical processes in the quasi-equilibrium can be represented in a general manner quantitatively. Here, the computed flux $J(t)$ and vapour pressure $P_v(t)$ in Equations (6.5) and (6.6) are used to verify the Hertz-Knudsen and Schrage equations. The resulting evaporation coefficients calculated using these two equations are found to change significantly during nonequilibrium evaporation. By combining the Hertz-Knudsen and Schrage equations as well as Equation (6.7), a time-dependent relationship of the evaporation coefficient σ_e using both the Hertz-Knudsen formula and Schrage theory can be developed as follows:

$$\sigma_{e-HK} = \frac{J_0 \sqrt{2\pi m k_B T}}{\Delta h_{lv} P_{sat}} e^{-(\kappa - \kappa_p)t} \quad (6.8)$$

$$\sigma_{e-Schrage} = \frac{\frac{2J_0 \sqrt{2\pi m k_B T}}{\Delta h_{lv} P_{sat}} e^{-(\kappa - \kappa_p)t}}{2 + \frac{2J_0 \sqrt{2\pi m k_B T}}{\Delta h_{lv} P_{sat}} e^{-(\kappa - \kappa_p)t}} \quad (6.9)$$

The enthalpy change can be calculated by measuring the averaged difference of total energy ($E_k + E_p$) between the bulk vapour and liquid region. By substituting ΔP with our regression model, the resulting function of the evaporation coefficient for the Schrage and Hertz-Knudsen equations is plotted in Fig. 6.7.

From the figure, an order of magnitude difference can be observed between the estimation from the two models. Since a universally accepted value of σ_e (Persad *et al.* 2016) does not exist in the literature, studying the dynamical behaviour of the coefficient is also a main focus of this study. Given that both equations assume quasi-equilibrium conditions at the interface (Barrett *et al.* 1992), the coefficient values are artificially large initially. This is because the system does not follow a Maxwell-Boltzmann distribution (Frezzotti *et al.* 2011) in the beginning due to the homogenous starting condition after the deletion of the vapour molecules.

Figure 6.7. Evaporation Coefficient as a function of time calculated from both the Hertz-Knudsen and Schrage equations at 343, 333, 323 and 313 K. The Schrage equation provides an estimation close to an order of magnitude different from the Hertz Knudsen equation.

It has been commonly suggested that the HK equation often underestimates the vapour flux while the Schrage equation tends to overestimate instead (Yttrhus *et al.* 1996). Here, our results show clearly that σ_e is in fact time-sensitive during the non-equilibrium state (*i.e.*, the first nanosecond of the simulation) in a closed system, and both equations tend to underestimate the vapour flux particularly the HK equation. Therefore, we conclude that both evaporation models are not reliable to predict the

transient evaporation flux in a closed system, which is often the more realistic configuration in engineering applications.

Since P_{sat} and Δh_{lv} can be easily obtained experimentally, we propose here an improved model to predict the instantaneous flux values in a closed system more accurately. From Fig. 6.6a, the difference between our measured bulk evaporation flux and Maxwell-Boltzmann distribution prediction follows a clear exponential growth pattern. Therefore, a modification can be made to the Hertz-Knudsen formula as follow:

$$J(t) = \frac{\Delta h_{lv}}{\sqrt{2\pi m k_B T}} P_{sat} e^{-\sigma_e t} \quad (6.10)$$

where $\sigma_e = \kappa - \kappa_p$. In other words, we propose to represent the transient behavior of the vapor flux of a closed system using an exponential form. Table 6.2 summarizes the value of κ , κ_p and σ_e calculated from the simulations at the 4 temperature values based on Eq. (6.9). The coefficient value ranges from 0.001 ps⁻¹ to 0.0018 ps⁻¹ with σ_e generally decreasing with the rise in temperature, which is consistent with the physical expectation that a closed system reaches the dynamical equilibrium faster at lower temperatures.

Table 6.2. Calculated values of κ , κ_p and σ_e at 4 different temperatures

Temperature	313K	323K	333K	343K
κ (ps ⁻¹)	0.01302	0.00951	0.00741	0.00835
κ_p (ps ⁻¹)	0.0113	0.00772	0.00619	0.00719
σ_e (ps ⁻¹)	0.00172	0.00179	0.00122	0.00116

6.4 Summary

In this study, the ELBA coarse-grained water model is utilized to overcome the limitations in system scales and computation costs, to accurately study the non-

equilibrium evaporation of a water droplet in a closed system using MD simulations. We first demonstrate the validity of the ELBA model as a computationally efficient coarse-grained model for multi-phase kinetic studies, and that the properties observed are based on physical phenomenon and not artefacts from force field interactions. The verification is further proven by realistic bulk vapour pressure values and agreement in the Knudsen layer length from the radial pressure and kinetic energy profiles. Subsequently, the spatial distribution of thermodynamics properties and their time evolution during non-equilibrium simulation are captured. The results illustrate the dynamic changes in the transport mechanism from diffusive-dominant to kinetically limited. They also show the reason why the Kelvin equation still applies at nanometre scale systems, which can be attributed to the fact that the density profiles are independent of the dynamical changes in pressure gradients. The theoretical flux predictions from both the classical Hertz-Knudsen and Schrage equations fail to capture the evaporation flux in this closed system. Instead, we propose an improved model with a transient correction term, which can better determine the evaporation fluxes of water molecules at nano-scale interfaces. We note that various other parameters that affect the evaporation flux, such as interface geometry, surface tension, etc, are not considered in this study. Thus, additional work in the direction of closed system evaporation kinetics should be explored in the future both experimentally and computationally, with better analytical models developed to capture such behaviours.

Finally, we remark that the results from this study challenge the outcomes of many classical evaporation MD studies, which typically define a ‘deleting region’ where all molecules entering this spatial domain are removed. Such non-equilibrium conditions are intended to mimic the constant evaporation conditions. However, due to the sensitivity of the system, the distance of the deleting region from the interface becomes very critical because it can affect the surface kinetics if not sufficiently far. For example, our previous works utilising this classical approach predicted flux values as higher than 7.5 molecules/ps at room temperatures (Kieu *et al.* 2019). In comparison, the highest recorded flux value in this study was only less than 4 molecules ps⁻¹ at 343 K given the more realistic assessment. Furthermore, we also

remark that the initial evaporation flux can be quite high due to the large concentration gradient with the vacuum space, and therefore not all values extracted represent the long-term behaviour. In this study, the closed system reaches saturation within 500 ps, highlighting the relatively short period when dynamical behaviours occur. Therefore, a closed system approach might in fact be preferred for general evaporative MD studies in the future, since it might not be necessary for the simulations to run for an extended period of time to capture the true evaporation behaviour.

Chapter 7 Conclusion and recommendations

This chapter summarizes the major conclusion of the works and presents the outlooks for future work.

7.1 Conclusion

This research study utilized the computational method of MD simulations to investigate the surface and structural design of nanocompounds for desalination and water treatment processes. The performance of the compounds with effects from surface properties are evaluated. The insight into the molecular mechanism behind the behaviors of the system at the nanoscale is also provided. The study thus illustrates that the modelling approach exhibits promising potential in accelerating the development of nanocompounds for desalination processes.

The reliability of the approach is also verified. By using the force fields which have been thoroughly developed in the literature, the models can represent the interaction between the atoms and molecules at the nanoscale and reproduce all the phenomenon's observed from experiments. Furthermore, all the modifications made to the examined structures are based on practical characterization techniques in experimental condition. Therefore, the examined structures and their modifications are able to be synthesized or characterized.

The key results are summarized in the following:

7.1.1 Pressure-driven water transport through graphene multilayer

i) The water flux inside the multi-layer graphene depends linearly on the applied pressure. To optimize the performance of the membrane in terms of both permeation and selectivity, the number of graphene layers of the membrane need to be carefully considered.

ii) The permeation rate is insensitive to the size distribution of gaps in the graphene layer as long as these gaps are large enough to allow water transport. Thus, controlling the uniformity of the gaps plays a critical role in maintaining the selectivity of the membrane.

iii) The interlayer distance has a great impact on the layered structure of water molecules inside the membrane, and the functionalization of the gap-edge can further contribute to enhancing the flux by lowering the free energy barrier.

7.1.2 Water evaporation through a capillary graphene bilayer with tunable hydrophilicity

i) The evaporation flux increases as the surface is tuned from hydrophobic to hydrophilic. However, too hydrophilic surface increases the attractive interaction towards the water molecules and impedes evaporation. Therefore, adequate hydrophilicity is recommended to benefit the evaporation.

ii) In a concave meniscus interface, water molecules at the intermediate regions between the surface and the centre point are the most mobilized, and evaporation occurs mainly from these regions.

iii) A high temperature can further amplify the capillary effect by encouraging the diffusion of water molecules on the surface, leading to an augmented increase in the evaporation enhancement.

iv) The capillary distance also plays an important role in the expansion of the liquid-vapor interface. The results show there exists an optimal distance between 10 and 14 nm.

7.1.3 Evaporation of water on graphene oxide with the effect of surface morphology

- i) The surface roughness impedes the natural spreading of the water molecules, thus diminishing the hydrophilicity of the GO surface. However, the evaporation flux shows a monotonical increase with the surface roughness.
- ii) The valley areas on the corrugated surface have a critical role in gathering the water molecules inside their concave space and modifying their density distribution. Water molecules inside the valleys have a higher tendency of collision, leading to a higher probability of evaporation at this area.
- iii) When the evaporating water layer becomes thinner, the corrugation GO surface still maintains its advantage over the flat surface since the evaporation flux is not affected by the shrink of the vapor-liquid interface.
- iv) Since the wrinkles on the GO surface can be controlled during the fabrication and characterization, it is advantageous to capture the patterning effect of oxidized valleys and pristine peaks pattern in the future design of the compounds to optimize their performance.

7.1.4. Evaporation kinetics of Nano Water Droplet

- i) ELBA water model is shown a computationally efficient coarse-grained model for multi-phase kinetic studies as the properties observed is in agreement with the physical phenomenon.
- ii) The classical Hertz-Knudsen and Schrage equations fail to capture the evaporation flux of a closed system. Thus, future works with better analytical models developed to capture such behaviors are necessary.
- iii) In constant evaporation studies, due to the sensitivity of the nanoscale system, the distance of the deleting/accelerating regions from the evaporative interface is quite critical as it must be far enough to not affect the surface kinetics.

7.2 Recommendations

The current study focuses mainly on investigating the performance of carbon-based materials. Recently, various new structures derived from zeolites, metal organic framework (MOF) and other composite compounds have been brought into examination. In order to accurately model the performance of such novel structures in MD simulations, the force field parameters need to be correctly determined. Coupling method of MD and density functional theory (DFT) calculation would be a necessary step to accelerate the searching progress.

Due to the computational limits, the system size could not exceed several hundreds of nanometres, and the simulation time could not be longer than nanosecond scale. In evaporation simulations, these limitations significantly affect the accuracy of the obtained data since the level of averaging is not sufficient, which causes big fluctuation in the data analysis. Thus, the coarse-graining method is a vital solution and highly recommended in large-scale evaporation systems.

Evaporation systems are multi-phase systems which consist of difference density regions. Compared to homogenous system, the speed up of computing due to parallelization is not as effective since the method is to partition the simulation box into even spatial chunks and then assign the particles in one chunk to one processor. Hence, novel computing architecture should be developed to tackle the issue.

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