Nanoporous graphene as a reverse osmosis membrane: Recent insights from theory and simulation

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HIGHLIGHTS

- We review recent progress in the computational study of graphene as an RO membrane.
- We introduce graphene and current knowledge about its mass transport properties.
- We examine six key mechanisms that govern salt rejection in graphene.
- Molecular dynamics have played a dominant role in the study of graphene membranes.
- We suggest a greater role for quantum-level simulations and macroscale computation.

GRAPHICAL ABSTRACT
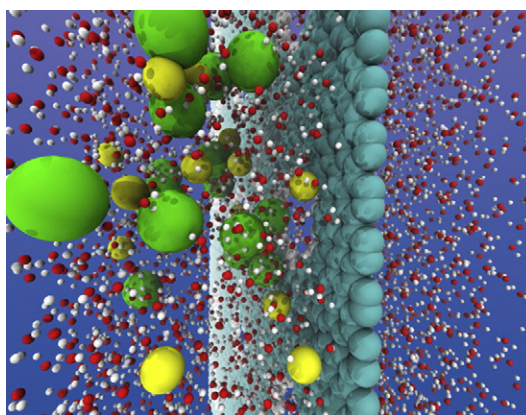
ABSTRACT

In this review, we examine the potential and the challenges of designing an ultrathin reverse osmosis (RO) membrane from graphene, focusing on the role of computational methods in designing, understanding, and optimizing the relationship between atomic structure and RO performance. In recent years, graphene has emerged as a promising material for improving the performance of RO. Beginning at the atomic scale and extending to the RO plant scale, we review applications of computational research that have explored the structure, properties and potential performance of nanoporous graphene in the context of RO desalination.

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1. Introduction

Desalination has seen important improvements in energy efficiency, reliability and economics since the 1960s thanks to numerous advances in reverse osmosis (RO) technology [1,2]. However, the semipermeable membranes that lie at the core of the RO process still rely on the same polyamide thin-film composite (TFC) design as three decades ago. As a result, the main improvements in RO membrane technology in recent decades (including the development of fully-crossed linked aromatic TFC membranes in the 1970s, of enhanced morphological control in the 1990s and more recently of nanostructured additives) have largely

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been incremental rather than revolutionary. Thus, RO membranes leave tremendous room for improvement. The best TFC membranes today are only 1.5–2× more permeable than 20 years ago, and they still degrade in the presence of chlorine, making disinfection difficult and leaving them vulnerable to fouling [3]. In order for desalination to live up to the water challenges of the 21st century [4], a step-change is needed in RO membrane technology.

Graphene holds promise as an 'ultimate' RO membrane. It is stronger, thinner and more chemically robust than the polyamide active layers in TFC RO membranes, and researchers across disciplines have begun to explore this material's potential as a next-generation RO membrane [5–9]. At the same time, a number of physical and chemical phenomena involved in graphene-based desalination must be better understood in order to leverage the full potential of graphene for RO.

Thanks to significant advances in the field of computational materials science and simulation-based research in the past decades, it is becoming possible to answer some of the outstanding questions in the development of graphene-based RO membranes. Atomic-level simulations are helping to guide the development of functional graphene membranes in the laboratory through predictive materials design, and modeling techniques at the mesoscale and the macroscale are enabling a better understanding of the performance benefits and challenges that are likely to come in the development of graphene RO membranes.

In this review, we examine the role of computational methods in exploring the potential of graphene as an RO membrane. We begin with a brief introduction to graphene and its material properties, followed by an overview of the key computational methods that have been employed to date in the study of graphene for desalination. We then highlight work by our group and by others that has offered a computational proof-of-concept that nanoporous graphene could act as a water desalination membrane and that has explored the effect of graphene structure (in particular nanopore size and graphene chemistry) on RO performance. We then turn to the mechanical resilience of graphene and discuss the knowledge to date about the ability of graphene to withstand the hydraulic pressures required for RO without ripping. Finally, we discuss how computational methods can help predict the long-term economic and engineering benefits of graphene membranes at the plant-scale. While there are many reviews on graphene, and more recently reviews on the specific application of graphene and graphene oxide to mass separation [10] and desalination [11,12], in this paper we provide an in-depth look at the role of computational methods in developing single-layer graphene for RO.

2. What is graphene?

Graphene is a two-dimensional material that consists of a hexagonal (i.e., honeycomb) lattice of covalently bonded carbon atoms (see Fig. 1). Although it is the basic building block of graphite, and even though it had been studied since the mid-20th century [13,14], graphene has only been isolated in its freestanding, two-dimensional form in the past decade [15]. It has continued to fascinate researchers ever since, earning the researchers who pioneered its development a Nobel Prize in 2010 and becoming the subject of over 45 000 peer-reviewed research articles at the time of writing.

Much of the original interest in graphene arose out of the material's unique electronic properties, especially the fact that electric charge is carried throughout the material by so-called massless Dirac fermions [16] and that these Dirac fermions behave as a two-dimensional electron gas with ballistic transport behavior on the micrometer scale [17]. As a result of these properties, graphene is being investigated as a successor to silicon in mainstream electronics [18] and as a potential enabler of quantum computing [19], to name only a few examples.

However, it has come to light in recent years that graphene also holds significant promise for mass separation applications. In 2008, Bunch et al. demonstrated for the first time that pristine, defect-free monolayer graphene is impermeable to helium gas, and that the layer could form a membrane with a stiffness as high as ~1 TPa [20]. Jiang
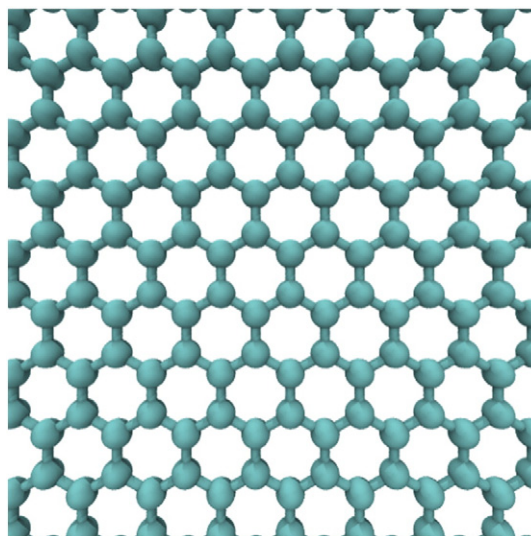

Fig. 1. Crystal lattice of graphene.

et al. subsequently added to the understanding of the promising mass separation behavior of graphene by predicting computationally that graphene with rectangular nanopores on the order of 0.34 nm could separate H_2 from CH_4 with a selectivity as high as 10^8, meaning that it is 10^8 times more permeable to H2 than to CH4 [21]. Meanwhile, it was also shown that nanoporous graphene (NPG) has potential for genetic sequencing applications by translocating individual DNA molecules through a nanopore [22–24]. The mass separation behavior of NPG suggests that it might also hold promise as an RO membrane for water desalination. In contrast with TFC membranes in which the precise mechanisms of salt rejection and water permeation are still not fully understood due to the amorphous nature of the polyamide active layer [3,25,26], the atomic thinness of graphene presents a more elegant and – in principle – simpler desalination process. However, the specific physical and chemical properties of ions in a hydrated environment and the complex hydrogen-bonding behavior of water at the nanoscale mean that NPG's ability to act as an effective RO membrane is far from obvious. Moreover, graphene remains a highly challenging material to characterize at the atomic scale experimentally. Therefore, computational methods, spanning from the atomic scale all the way to macroscopic modeling, are ideally suited to study these mechanisms and how they can be harnessed to design a radically new kind of RO membrane.

3. The role of computation

Computational materials science is rapidly becoming an essential component of research in energy technology, biomedical research, semiconductors and countless other fields. Ranging from macroscopic modeling all the way to atomistic simulations, computational methods have played an enabling role in the design and enhancement of solar cells [27–29], batteries [30,31], fuel cells [32], chemical sensors [33] and actuators [34,35], to cite only a few examples. Computational materials research can be employed to advance several types of objectives. Computation is especially helpful when the objective is *prediction*, e.g., for predicting a stable material structure or the relationship between material structure and properties. It is often successfully used for *understanding*, i.e., when the objective is to uncover the causal mechanism underlying a phenomenon, or to explain a surprising experimental observation. Finally, it can *provide guidelines* in the scientific process, e.g., by identifying the optimal regions of a material phase-space for a given application, or determining the most promising approaches towards experimentally making a material.

3.1. Types of computational methods

A graphical overview of computational methods relevant to NPG membranes is shown in Fig. 2. Quantum mechanical methods are well suited for the study of systems in which bonding, chemical reactions or electronic properties are at play. The most popular quantum method, Density Functional Theory (DFT), employs functionals to approximate the electron correlation and exchange energies in order to predict the ground-state electron density of atomic systems. Thanks to relatively high accuracy and high parallelizability over hundreds of processors, DFT has become a popular method for computing the electronic properties of materials and molecules. DFT is also a valuable tool when estimating the interactions between molecules in which quantum effects (e.g., hybridization of electron orbitals) play a non-negligible role. DFT has been used, for example, in the study of ion beam induced defects in graphene [36] and ion-graphene binding [37]. In addition to DFT, Quantum Monte Carlo and GW calculations provide higher accuracy in the simulation of electronic structure, at the expense of greatly increased computational time [121,122]. These high-order methods have yet to be applied to the study of NPG for desalination.

The most popular method to date for computationally studying NPG has been Molecular Dynamics (MD). MD simulations compute the evolution of a system of atoms from an original configuration and under a set of constraints [38,39]. These simulations work by calculating the forces between atoms at each time step, and updating the positions of all the atoms at the following timestep using Newton's equations of motion. MD simulations rely on several inputs: an initial configuration of the system (including the positions, atomic elements, and possibly the bonding states and partial charges of all atoms depending on the forcefields used); a set of forcefields that describe the force on an atom as a function of the atoms around it; and a set of constraints (including geometric boundary conditions, a thermodynamic ensemble, and a thermostat or barostat method if applicable). A key advantage of MD is that depending on the choice of forcefield, the behavior of relatively large molecular systems (up to 10^9 atoms) can be investigated over physically meaningful timescales (typically between 1 ns and 1 μs). The potentials that are used to compute the force between atoms are typically classical in nature, in that they do not explicitly calculate the behavior of the electrons in the system but instead represent the force between two atoms using analytical expressions. In the study of NPG as an RO membrane, MD simulations generally include two water reservoirs separated by an NPG layer, and water and ions are subjected to a driving force across the membrane (e.g., pressure or an electric field).[1] The resulting trajectories yield information about the water and solute fluxes, which can be used to estimate the water permeability and salt rejection of the membrane. The trajectories also contain information about the underlying physics of the system, including the dynamical properties of the fluid, the behavior of the membrane, and the physical mechanism for salt permeation.

MD simulations have also been successfully paired with quantum-mechanical calculations, called *ab initio* MD, in order to model the behavior of systems in which classical potentials cannot properly account for the physics at play [40,41]. This approach has yielded insights into the dynamics of water on graphene [42,43] as well as the potential of carbon nanotubes (CNTs) for desalination [44], and will continue to play an important role in the study of NPG, e.g., to identify promising synthesis approaches or to understand the interaction of graphene with chlorine, as discussed below.

One approach for reducing the computational burden of simulating chemical systems has involved treating the majority of the system classically and only certain atoms quantum-mechanically in so-called hybrid quantum-mechanics/molecular-mechanical (QM/MM) simulations [45]. The QM/MM approach has been applied to problems as diverse as

biomolecular systems [46], catalytic reactions [47] and fracture mechanics [48], but to date has not been employed extensively in the study of NPG. The QM/MM approach offers a useful tradeoff between computational speed and physical accuracy when chemical reactions occur in only a subset of the system. As a result, this approach could be used, for example, to explore how surface chemistry might help reduce the incidence of mineral scaling onto an NPG membrane surface, or to investigate catalytic activity.

Coarse-grained MD simulations can also reduce the computational burden compared with fully atomistic MD simulations [49,50]. This approach, which reduces the number of degrees of freedom by grouping atoms into units, has been used successfully to study CNT/detergent interactions [51], the interphase thickness in polyamide [52], and biological membranes [49].

The Monte Carlo (MC) method is well-suited for studying time-independent thermodynamic behavior (e.g., adsorption properties or material phase transitions) [53,54]. MC simulations sample the phase-space of a molecular system by randomly modifying the system configuration at each iteration and conditionally selecting the new configuration based on its computed energy. Because MC simulates the configurational phase-space of the system rather than the time-evolution of a particular system configuration, this method is well-suited to research questions that focus on equilibrium properties. For example, MC simulations could be employed to investigate the adsorption properties of NPG.

Alternatively, MC simulations are also used to simulate the evolution of a system whose dynamics would be computationally prohibitive for MD due to the presence of multiple local energy minima. This approach, known as kinetic Monte Carlo (KMC), has been used broadly to study a wide range of dynamical properties, e.g., the growth of graphene on copper [55] or the kinetics of gas transport across membranes [56,57]. An advantage of all the molecular-scale simulation methods outlined above is that they can be applied to systems whose behavior is not known a priori. This has allowed many studies to elucidate the underlying dynamics behind phenomena that had been observed experimentally but whose explanation had not been fully understood, as well as to design new materials.

Beyond atomistic simulations, recent progress in the development of multiscale and macroscale methods has enabled a more rigorous approach to studying the relationship between molecular-scale structure, material properties and ultimately system performance [58]. In the context of NPG membranes, MD simulations have been coupled with Finite Element Method (FEM) calculations and continuum modeling to study the mechanical strength of an NPG membrane from the atomic scale to the macroscale [7,59], and DFT calculations have been coupled with MD simulations and macroscopic descriptions of membrane-substrate interactions to investigate the interfacial adhesion of graphene [60].

Ultimately, the real-world impacts of NPG will occur at the macroscale, whether in the form of more affordable clean water, more compact RO plants or new applications. Thus, system-level simulations have an essential role to play in furthering our understanding of how NPG might fit into future RO-based technologies. Macroscopic simulations that draw from mechanical, chemical and systems engineering as well as economics have already been successfully applied in the field of desalination [61–63]. Simulations at this scale can help study the inputs and outputs of an RO membrane module containing NPG, the effect of feed water properties on system performance, the or economics of more permeable or chlorine-resistant membranes.

As will be discussed below, such state-of-the-art calculations are playing an increasingly significant role in advancing our understanding of the potential of graphene as an RO membrane. The aim of this review is to highlight how computational materials science methods have enabled insights into NPG as an RO membrane. It should be noted, however, that existing computational methods also have their own shortcomings, and that further methodological development, while beyond the scope of this paper, is of critical importance. For example, it has

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[1] See Supplementary Information for more 'hands-on' methodological details about how to perform MD simulations of NPG membranes.
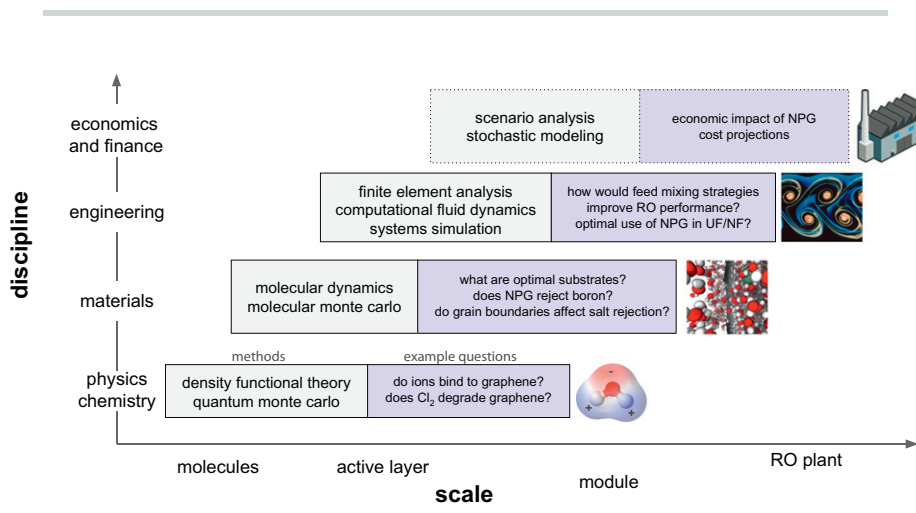
Fig. 2. Schematic of key computational methods available for the development of NPG for desalination. Economic simulations in the top-right corner are represented in dotted lines because they represent a qualitatively different type of research than the science and engineering methods covered in this paper.

been pointed out that there is no universally accepted intermolecular potential for water, and water–carbon interactions depend highly on the choice of potential [64]. Moreover, the fluid–fluid and cross parameters derived in MD for bulk systems must be applied with care to nanoconfined spaces. In this regard, it has been argued that density functional theory with the addition of a semi-empirical dispersion potential is a promising simulation approach to model water–carbon interactions [64]. Another methodological concern in MD simulations is the effect of thermostat choice on the observed rate of water passage across nanopores [65]. Fortunately, rapid advances in methodologies and computing platforms are encouraging a greater role for computation in designing novel materials [66–68]. With an appropriate understanding of the benefits and limitations of computational methods, such approaches are helping to catalyze the development of new materials in fields that have historically relied primarily on experimental research, including water desalination technology.

4. Proof of concept

The fundamental hypothesis behind the development of graphene for water desalination is that NPG could act as an RO membrane by rejecting salt ions and other molecular species while allowing water to pass through its nanopores, and that its performance in RO would exceed that of the TFC membranes in use today. We now turn to MD results that validate this hypothesis.

Prior computational work lent credence to the hypothesis that NPG could act as an effective RO membrane. Previous computational research had shown that CNTs and other cylindrical nanopores could desalinate water [69–72]. In 2008, Sint et al. showed computationally that graphene was selectively permeable to certain solvated ions and impermeable to others when nanopores existed in the material [73]. The authors discovered that the chemical functional groups at the edge of the nanopores played a critical role in determining which ions were rejected. Moreover, Suk and Aluru demonstrated in 2010 that nanopores as small as 0.75 nm could allow water molecules to pass through [74]. These graphene nanopores exhibited even higher water permeability than CNTs for radii larger than 0.8 nm, due to the higher water velocity in the center of the nanopores.

Several inherent properties of graphene also suggested that graphene might outperform TFC membranes. In particular, the water flux across a membrane theoretically scales inversely with the membrane's thickness, suggesting that graphene's atomic thinness ($d = 0.34$ nm) might enable far greater water permeability than the polyamide active layers in TFC membranes ($d \sim 100$ nm). Whereas

TFC membranes are degraded by chlorine due to extensive amide bond cleavage under N-chlorination and chlorination-promoted hydrolysis [75], graphene is not known to degrade by this mechanism. If graphene does exhibit greater tolerance to chlorine than polyamide, this would represent a significant advantage in preventing membrane fouling without degradation.

In 2012, we demonstrated for the first time that NPG could act as an RO membrane by simultaneously allowing for water permeation and rejecting salt ions [5]. Using classical MD simulations to model periodic sheets of NPG with varying nanopore sizes and chemistries, and applying pressure to a feed of saltwater using a rigid piston, we calculated the water permeability and estimated the salt rejection for each NPG system (see Fig. 3a). Consistent with Suk and Aluru, we found that nanoporous graphene exhibits ultrahigh water permeability per nanopore.[2] Assuming a nanopore density on the order of $\rho \sim 1 \times 10^{13}$ cm^{-2}, we estimated that the water permeability of NPG could be as high as $A_m \sim 10^3$ L/(m^2-h-bar), which is 2–3 orders of magnitude greater than in TFC membranes ($A_m \sim 1$ L/(m^2-h-bar)) (see Fig. 3b).[3]

We found that this performance is highly dependent on graphene's atomic-scale structure, including the size of the nanopores and the chemistry of the functional groups at the nanopore edges. Two simple hydrophobic and hydrophilic chemistries were compared: H (hydrogen) and OH (hydroxyl). It was shown that hydrogenated nanopores exhibit lower water permeability but higher salt rejection than hydroxylated ones (see Fig. 4a). We attributed this difference to the fact that both water molecules and solvated salt ions need to break more hydrogen bonds while passing through the hydrogenated nanopores, due to their hydrophobic character.

This work also showed that the salt rejection of NPG is highly sensitive to the nanopore radius, a. While NPG exhibited full salt rejection for small enough nanopores ($a \leq 0.27$ nm), the rejection dropped to 84% for $a = 0.40$ nm in hydrogenated nanopores and to 52% for $a = 0.44$ nm in

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[2] Although initial publications by our group and others referred to the permeability of NPG in units of water flow per area of membrane per net driving applied pressure (L/(m^2-h-bar)), it can be argued that the permeability of nanoporous membranes is best expressed in m^3/h/bar/pore, since the achievable pore density of such membranes has yet to be determined experimentally.

[3] There exists some confusion between the terms 'permeability' and 'permeance', in part due to differing conventions between research fields. In certain research fields (e.g., gas separation membranes), the flux per unit pressure is called the permeance, while the term permeability denotes the permeance multiplied by the membrane thickness. In the RO membrane community, it is the former quantity (flux per unit pressure) that is referred to as 'permeability'. This is the definition we use in this article.
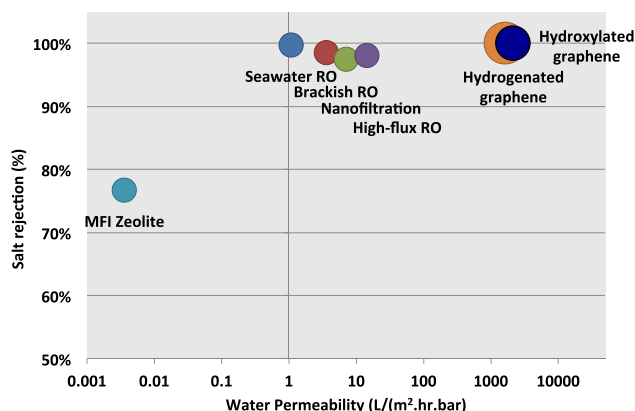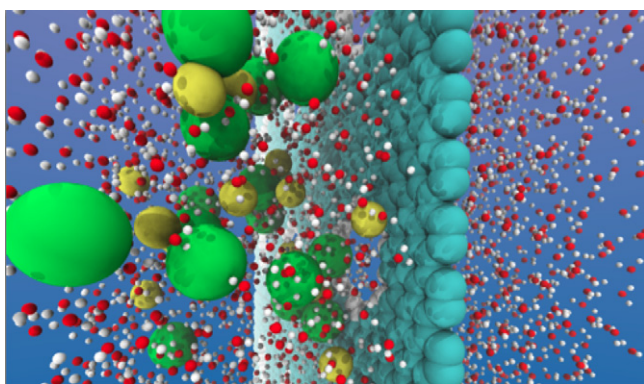
Fig. 3. (a) Schematic of nanoporous graphene rejecting NaCl while allowing for water passage. (b) Performance plot of salt rejection and water permeability for NPG compared with conventional RO membrane technologies.
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hydroxylated nanopores.[4] An important consequence of this finding is that it will be critical to achieve precise – and highly uniform – nanopore size in large-scale NPG membranes in order to make viable RO membranes. This requirement will inform the various approaches under consideration for introducing nanopores into graphene, for example by bombarding a graphene sheet with energetic C_{180} fullerenes [77].

One limitation of the initial proof-of-concept of NPG's desalination performance was that the simulations were performed under very high pressures (1000 bar to 3000 bar) in order to obtain the best possible statistics of water flux in a finite simulation time. In a follow-on study, we confirmed that NPG retains its ultrahigh water permeability under the realistic pressures employed in RO (10 bar to 100 bar) by showing that the water flux across NPG continues to scale linearly with applied pressure down to this lower pressure range [76]. To this end, we examined the desalination process across NPG under feed pressures as low as 29 bar using much longer MD simulations (see Fig. 4d), and we also allowed the graphene atoms to deform under the effect of applied pressure.

5. Effect of graphene structure on RO performance

5.1. Water transport

5.1.1. How do water molecules pass through NPG?

In order to understand why NPG exhibits such high water permeability, it is essential to identify the mechanisms by which water transports across the membrane, and how the specific size and chemistry of the nanopores affects this transport. MD simulations are well suited to this problem and have provided in recent years some important answers to this end. At the nanoscale, water molecules form a complex hydrogen-bonding network. Thus, the water flux across NPG is governed by the ability of molecules to enter the nanopores in a favorable geometric orientation and hydrogen-bonding configuration. The water transport across NPG does not proceed strictly in a single file. Instead, water molecules rapidly diffuse away from the nanopore after passing through the membrane, meaning that entrance/exit effects dominate the transport behavior, unlike in CNTs [78]. The angular orientation of water permeating through graphene also exhibits a distinct ordering effect [79]. The degree to which water molecules reorient and order themselves as they pass through nanopores depends on the pore chemistry. For example, water

is more highly ordered in the vicinity of a hydrogenated pore than hydroxylated pores, because the H (hydrophobic) passivation restricts the number of hydrogen-bonding configurations available to water molecules traversing the membrane. This ordering effect influences the free energy landscape of water molecules in the nanopore vicinity, which determines, in turn, the water flux across the membrane [5].

Two-dimensional potential energy maps and density maps can also yield valuable insights about the dynamics of water transport across NPG. For example, in a classical MD simulation, potential energy maps are calculated using the sum of LJ and Coulomb interactions at each position, while density maps result from tracking and averaging the occupation of an atomic species in one-, two-, or three-dimensional bins. Looking at square nanopores in graphene, Zhu et al. used 2D potential and density maps to reveal discrete density distributions for oxygen near the edge of the nanopore, and to identify the nanopore size threshold from discrete to continuum water flow to be about 1.5 nm [79].

5.1.2. How does water flowrate depend on pore size?

MD simulations have also been employed to quantitatively estimate the flowrate of water across pores in NPG. In a follow-up to their 2010 study [80], Suk and Aluru investigated water transport mechanisms and hydrodynamic properties such as water flux, pressure variation, velocity, viscosity and slip length. The flowrate per pore per unit pressure (p_Q) for a graphene pore follows:

$$p_Q(a) = \frac{\pi\left(a^4 + 4a^3\delta\right)}{8\mu}\frac{1}{L_h} \tag{1}$$

where L_h is the hydrodynamic membrane length, a is the pore radius, μ is the water viscosity, and δ is the slip length. The calculations of p_Q by Suk and Aluru provide a useful estimate of the water permeability of the membrane, which can be approximated as ρp_Q, where ρ is the number density of nanopores available for water transport per m^2 of membrane.

Consequently, the overall water permeability of an NPG membrane will depend directly on the density of nanopores per unit area. Several studies, including our own, have hypothesized that the nanopore density in NPG could be in the range of $10^{11} - 10^{13}$ cm^{-2} based on a relatively close spacing of nanopores. Ignoring the role of pore chemistry for simplicity, the authors found that water viscosity and slip length actually increase for smaller nanopore radii. The authors also found empirically that $L_h(a) = 0.27a + 0.95$, $\mu(a) = (0.000847\ Pa\ s\ nm)/a + 0.00085$ Pa s and $\delta(a) = (0.1517\ nm^2)/a + 0.205$ nm. Collectively, these results indicate that the water flux across NPG depends on the chemistry, size and geometry of the nanopores.

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[4] It should be noted that there exist several definitions for the radius of a nanopore at the atomic scale. In our work [5], we calculated a based on the open pore area, effectively taking into account the pore functional groups and the van der Waals radius of the atoms. Other studies measure a based on the center-to-center distance between opposite carbon atoms, which yields a nominally larger nanopore radius.
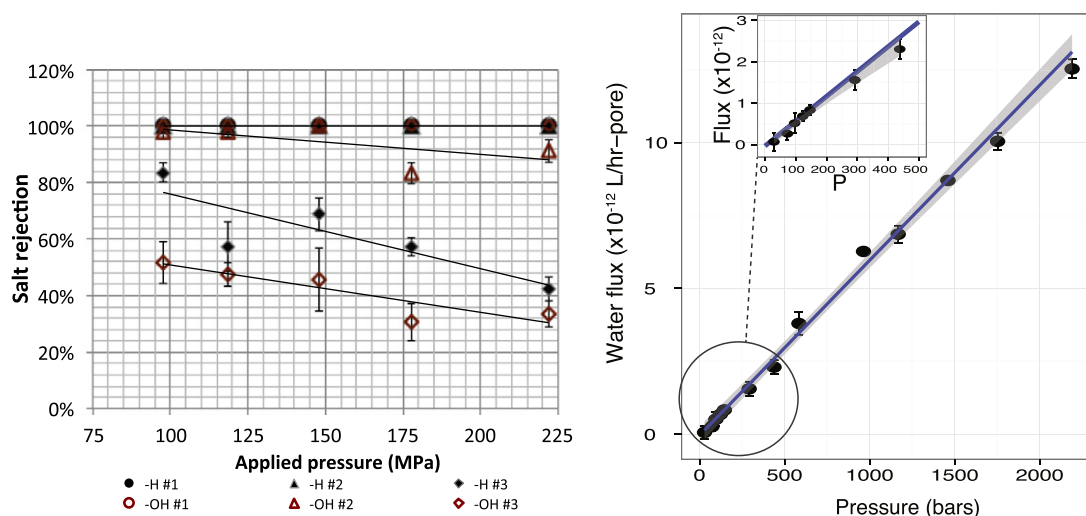
Fig. 4. a) Salt rejection across NPG vs. feed pressure from MD simulations for different nanopore sizes and pore edge chemistries, reprinted with permission from [5]. Copyright 2012 American Chemical Society. b) Water flux across hydrogenated NPG vs feed pressure, reprinted with permission from [76].

5.2. Salt rejection

The salt rejection of existing TFC membranes is typically extremely high — upwards of 99% in most cases. Since salt rejection is a non-negotiable performance criterion in most RO applications, it is imperative to understand the mechanisms by which salt is rejected across graphene nanopores in order to ensure the highest possible salt rejection. In this section, we review key results from computational studies that explore the mechanisms for salt rejection across NPG. We note that the finite system sizes and limited simulation times accessible in MD simulations (typically on the order of ~10,000 atoms and several nanoseconds, respectively) make it difficult to distinguish between 95% and 100% salt rejection. Therefore, precise estimates of the salt rejection of NPG remain limited at the time of writing. Nevertheless, molecular simulations have provided useful guidelines for understanding the effect of pore chemistry and pore size on the salt rejection capability of NPG.

In a useful review of the mechanisms of water transport and salt rejection across nanoporous membranes (including NPG but also CNTs, silicon nitride membranes and boron nitride nanopores), Thomas et al. propose six mechanisms to explain salt rejection in nanoporous membranes [81]:

1. size exclusion (bare ion);
2. dehydration effects (steric exclusion of the hydration shell);
3. charge repulsion;
4. subtler effects involving specific interactions with the pore as observed in biological channels;
5. interactions of solutes with specific chemical structures of the pore;
6. and entropic differences.

These six mechanisms represent a useful framework for understanding salt rejection across NPG.

The first and second mechanisms (steric exclusion of bare ions or their hydration shells) are the most straightforward mechanisms for salt rejection. Because the hydrated radius of ions in water is larger than the effective size of an H_2O molecule, MD simulations indicate that NPG with small enough nanopores exhibits full salt rejection within the precision of the simulations [5]. Based on this effect, the critical nanopore diameter for rejecting NaCl appears to be between 0.6 and 0.8 nm, which is consistent with the hydration radius of the ions and with prior results for ion rejection from CNTs [71].

The third mechanism is charge repulsion: nanopore chemistry is known to affect the rejection of ions by adding a fixed electrical charge to the nanopore edge. Donnan exclusion theory, which describes the rejection mechanism across charged membranes, predicts that negative fixed charge in a membrane will enhance its salt rejection by impeding the flux of negative ions. Zhao et al. have shown using MD simulations that the Donnan exclusion principle applies to NPG, and that negatively charged nanopore edges impede the passage of Cl^- while enhancing the transport of K^+ under an applied electric field [82]. In particular, it was found that the membrane's electrical resistance would increase by an order of magnitude if the negative charge per nanopore hypothetically increased from 0 to $-30e$ for large pores with $a = 10$ Å.

The fourth mechanism mentioned by Thomas et al. (subtler pore/solute interactions) refers to effects that occur as a result of the overall nanopore morphology. These mechanisms have not been comprehensively studied in the context of NPG membranes, but they play an important role in biological membranes. Studies of biological membranes have shown that pore/solute effects such as overcoordination and undercoordination play an important role in the ion selectivity of biological water channels. For example, MD simulations have shown that potassium channels enhance sodium rejection by geometrically requiring an eight-fold coordination inside the nanopore, which is energetically unfavorable for sodium ions [83]. Such interactions may arise from electrostatic or van der Waals interactions, geometric effects or requirements for the number of species that can coordinate the solute. Given that pore/solute effects have not been extensively adapted to graphene membranes, such mechanisms represent an important opportunity for further research.

The fifth mechanism involves the action of specific chemical structures within the nanopore. Along these lines, He et al. have explored the potential of bioinspired functionalizations in NPG [84]. The authors found using classical MD simulations that a graphene nanopore containing four carbonyl groups preferentially conducts K^+ over Na^+, while a nanopore functionalized by four negatively charged carboxylate groups selectively binds Na^+ but transports K^+ over Na^+. In comparing the ion rejection behavior of these functionalized nanopores to the activity of biological protein channels, the authors showed that the ion conduction in a nanopore with three carboxylate groups takes place via a knock-on mechanism (see Fig. 5). This study showed that collective effects between ions can influence the salt rejection of NPG, and that the chemistry and shape of the nanopores plays an important role in determining whether these effects are present or not. However, it remains to be determined whether collective mechanisms like the knock-on process highlighted in this study would also apply in RO, where the ion concentration near the membrane is much lower than in conductance experiments and where the electric fields do not play a significant role in driving the passage of ions.
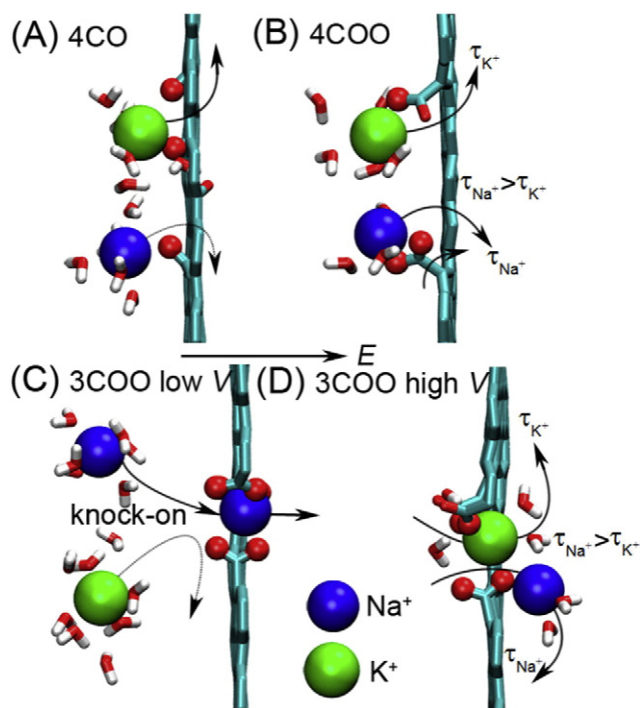
Fig. 5. Mechanisms of ion selectivity of nanopores with (A) 4 carboxyl groups, (B) 4 carboxylate groups, and (C,D) 3 carboxylate groups under low and high transmembrane voltages. Reprinted with permission from [84]. Copyright 2013 American Chemical Society.

The final mechanism involves entropic differences. Because salt rejection is governed by the free energy barrier through each nanopore, an NPG membrane can also reject salt by restricting the number of physical configurations (e.g., geometric orientation) in which salt ions can successfully enter the nanopore. For example, we found in our original study of NPG membranes that hydrogenated nanopores exhibit higher salt rejection than hydroxylated ones by restricting the number of allowed geometric orientations and hydrogen-bonding configurations for hydrated ions attempting to enter the nanopore (see Fig. 4a) [5].

Potential of mean force (PMF) calculations from MD can shed further light on the energetics of salt rejection across NPG. In PMF calculations, a molecule is steered along a reaction coordinate (e.g., a geometrical path) using umbrella sampling, and its energy is tracked at each coordinate over several ns [38]. These calculations often employ the weighted histogram analysis method in order to obtain a one-dimensional free energy profile for the mechanism of interest [85]. Konatham et al. used this approach to compute the free energy landscape for Na^+, Cl^- and H_2O passing across NPG for several nanopore diameters and functionalizations [6]. Their calculations revealed that hydroxylated NPG with 0.75 nm pores exhibits promising desalination performance thanks to a high energy barrier for Cl^- passage (19 kcal/mol in the limit of low feed concentration). These PMF calculations also indicated that the energy barrier for Cl^- passage decreases to 10 kcal/mol as the feed concentration increases to 0.25 M, due to increased electrostatic interactions between the Cl^- ion and Na^+ ions near the nanopore. Although one might worry that increased feed concentrations could reduce the salt rejection of NPG, especially given the importance of concentration polarization in RO operations [86], the authors also found that the energy barrier for Cl^- passage remains large at even higher salt concentrations, indicating that steric exclusion will remain a dominant mechanism for salt rejection even in the presence of concentration polarization.

PMFs should not be confused with 'effective' free-energy profiles, which have also been used to characterize the dynamics of transport across graphene-based membranes [87–89] and which calculate an energy map from a single MD simulation using the average occupation density: $E = -k_B T \log(P)$, where k_B is Boltzmann's constant and P is the average occupancy of the species at the given location. Effective free-energy profiles also provide some information about the relative rejections of different NPG membranes, but their relevance is limited by the fact that a single simulation may not allow for adequate sampling of the system phase-space.

Looking at idealized graphene oxide (GO) framework membranes – which differ from NPG in that their building blocks are GO sheets connected by linkers – Nicolai et al. have examined the dynamics of desalination by plotting the potential energy map experienced by both Na^+ and Cl^- in the plane of the membrane [89]. These potential maps indicate the regions where the potential is lowest (in this case, close to the boronic acid groups in the linkers) and they also highlight the relative energetics of cations and anions.

In addition, numerous studies have looked at NPG's ionic conductance in solution. In these studies, an electric field is applied across a graphene membrane immersed in an ionic solution, and the relationship between ionic current across the membrane and voltage provides insights into the conductance of the membrane. Garaj et al. used ionic conductance experiments to show experimentally that single- and double-layer NPG membranes act as ionic insulators [23]. In their 2010 study, Suk and Aluru highlighted the critical role of nanopore chemistry in determining the ion rejection performance of NPG by showing using MD that nanopores functionalized with nitrogen and fluorine rejected all ions except lithium, sodium and potassium ions while hydrogenated nanopores allowed only chloride and bromine to cross [74]. The same authors later showed that unlike in thicker nanoporous membranes, solvated ions passing through a graphene pore conserve the majority of their hydration shell: even for the smallest nanopore considered, the coordination number for K^+ and Cl^- only decreased slightly from 7 to 6.6 [78]. A key result of this study was that steric hindrance plays a much greater role in the physical mechanism for ion rejection across NPG than in conventional TFC membranes, although the authors only considered bare (unfunctionalized) graphene nanopores, which are not fully realistic since unpassivated carbons are highly reactive in reality, and would rapidly become passivated by functional groups under experimental conditions.

By furthering our understanding of the physical mechanisms by which certain ions can (or cannot) pass through graphene nanopores, these ionic conductance studies have helped establish important design principles for high-rejection and ion-selective NPG membranes. However, the fact that most results were obtained under an applied electric field rather than a hydrostatic pressure gradient suggests that these design rules are more readily applied to ion-exchange applications; the relevance of these results to RO is still an active area for future research.[5]

6. Beyond molecular-scale simulations: the role of multiscale and macroscale computation

Designing the next generation of RO membranes will require collaborative efforts that span from fundamental nanoscale physics to applied engineering. Ultimately, the molecular-level desalination properties that were highlighted above will need to be integrated into macroscopic products and subsequently into large-scale engineering systems. In the following paragraphs, we review studies taken from our work that leverage computational methods in order to bring molecular scale

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[5] In particular, we note that the correspondence between ionic conductance and salt rejection is not a systematic one. While low ionic conductance is generally an indication of high salt rejection, it should be recognized that a membrane with low ionic conductance may also exhibit poor salt rejection if its water permeability is also low. Similarly, a membrane with high fixed charge density may exhibit high co-ion conductance under an applied electric field but high salt rejection thanks to the Donnan exclusion principle [3]. This principle states that co-ion passage becomes hindered due to the counter-ions that are repelled by the free charge in the membrane and the requirement of maintaining overall charge neutrality. As a result, the studies cited here provide some useful insights into the physical interactions between graphene nanopores and salt ions, but the conclusions cannot be directly translated into quantitative estimates of salt rejection.

insights to the engineering scale. First, we will discuss how multiscale computational research can help investigate the complex mechanical behavior of an NPG membrane. Similar to TFC membranes, in which the polyamide active layer is supported mechanically by a polysulfone substrate with pores on the order of 0.1 μm to 1 μm, NPG will have to sit atop a support layer (see Fig. 6a). Polysulfone may be a promising candidate for NPG because it is more mechanically flexible and more economical than the anodic aluminium oxide or polycarbonate track-etch that have been used in bench-scale experimental studies of graphene membranes [90,91,8]. Thus, it is critical to understand the properties of graphene on the micrometer lengthscale. Moreover, the graphene-support assembly will most likely be rolled between channel spacers into spiral-wound membrane modules, which will themselves be placed in series within each pressure vessel, and these pressure vessels will be operated in parallel in a RO plant. Second, we will highlight how systems and module-level modeling can help explore how NPG might translate into real-world benefits (e.g., lower energy consumption or higher permeate recovery). To this end, it is necessary to account for the complex relationship between water flux, concentration polarization, fluid mixing in the feed channel, viscous losses, RO plant design, and performance.

6.1. Mechanical strength: will graphene rip?

Graphene is sometimes referred to as the strongest known material, by which it is meant that graphene in its monocrystalline form holds the record for the highest breaking strength at (σ_{max}~ 1 GPa) and a Young's modulus of about 1 TPa [92]. However, the ultimate thinness of graphene also represents a potential weakness: since the thickness of graphene is only $d = 0.34$ nm, and since the stress in a membrane under pressure scales as $d^{-2/3}$, a simple calculation suggests that graphene might experience 45 times greater stress for a given pressure and support geometry than a much thicker polyamide active layer with $d \sim 100$ nm [93]. While studies have looked at the adhesion properties of graphene on polymer substrates [94] and the mechanical properties of

suspended graphene under mechanical loading [20,92], it is also critical to understand the physical regime in which NPG can withstand mechanical pressures in the specific context of RO. Several studies have contributed a critical understanding to this problem. Song et al. recognized that substrate pores play an important role in the mechanical resilience of graphene [59]. Using classical MD simulations, they modeled graphene clamped over small hexagonal pores (3 nm to 20 nm) and subjected the graphene to pressure using argon gas. By looking at the principal virial atomic stresses in the membrane, the authors found that in-plane stretching dominates the deformation and elastic energy of graphene under pressure, and that the mechanical loading of the membrane can be modeled as biaxial in-plane strain. They also found that graphene could withstand applied pressures in the GPa range, and that introducing a nanopore in previously pristine graphene reduced ΔP_{max} in half while also shifting the fracture location from the clamped graphene edges to the nanopore edges.

Liu et al. added to this understanding by realizing that the mechanical properties of graphene would vary as a function of porosity p: they found that the tensile modulus of NPG scales roughly as $-p^{0.64}$, and that its fracture stress σ_f depends on porosity as well as nanopore size and shape [9]. For a given nanopore geometry, they found that σ_f scales with porosity as $\Delta \sigma_f \sim -p$. The authors also recognized that the mechanical loading of graphene over larger support pores could be modeled using a continuum description that would relate the stress in the membrane, σ, to its elastic properties and to the applied pressure. Using this, the authors predicted that NPG would be able to withstand 5.5 MPa as long as the support pores were smaller than 0.6 μm.

Refining their model to account for the fact that σ_f is not a single function of porosity but instead depends on both nanopore radius and nanopore separation, we recently found that NPG should be able to withstand nearly ten times greater pressures ($\Delta P_{max} \approx 57$ MPa) than typically used in RO as long as the pores in the support material are smaller than 1 μm [7]. By determining the mechanical properties (fracture stress σ_{max}, Young's modulus E_M and Poisson's ratio ν) of NPG as a function of nanopore radius and porosity using MD simulations, and by
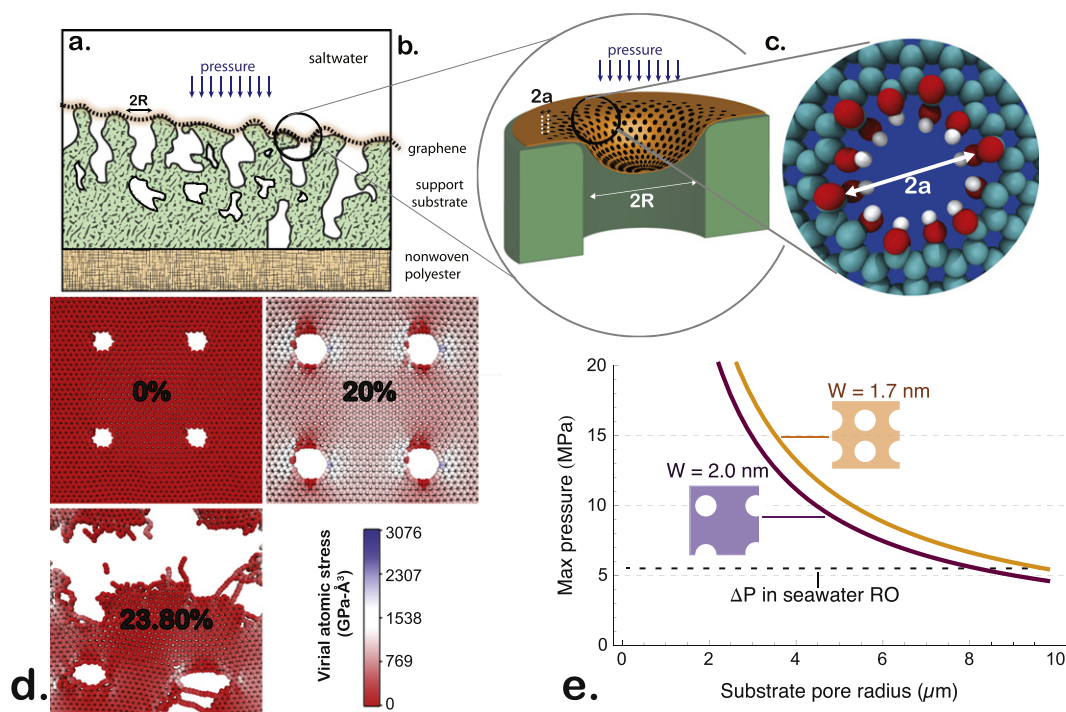

Fig. 6. (a) Schematic diagram of NPG over a porous polysulfone support layer. (b) Mechanical loading on a patch of NPG due to applied pressure in an RO system. (c) Atomic-scale visualization of carboxylated NPG with nanopore radius a. (d) Stress distribution in an NPG sheet under increasing biaxial strain. (e) Maximum hydraulic pressure at membrane failure calculated as a function of support pore radius for two different nanopore separations.
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integrating these properties into a continuum mechanical model for a thin membrane clamped over circular pores, we determined ΔP_{max} as a function of support pore size and graphene porosity (see Fig. 6). We found that the choice of support material is essential for the mechanical integrity of an NPG membrane in RO, since support layers with pores larger than ≈ 8 μm may allow the membrane to fracture under trans-membrane pressures as low as 5 MPa (Fig. 6e). Surprisingly, we also found that ΔP_{max} can in some cases *increase* as a function of graphene porosity, and we attributed this behavior to a competition between de-creasing E_M and decreasing σ_{max} as a function of increasing porosity. Further studies are still needed in order to fully understand how graphene adheres to a polymer support, how the deflection of graphene occurs near the edges of support pores, and how nanopores and graphene grain boundaries impact the mechanical resilience of NPG. Thus, the combined application of computational techniques at the at-omistic and continuum scales will continue to provide important in-sights into the most promising pathways to producing a NPG membrane that is able to withstand the pressures required for RO.

6.2. Predicted benefits at the plant scale

As was discussed above, the permeability of NPG could be as a high as ~1000 L/m²-h-bar or take on lower values depending on its porosity. Therefore, another promising area of research is in the design of systems that would benefit most from the ultrahigh permeability of NPG.

Because the water permeability of polymer-based RO membranes has only improved by a factor of 1.5–2 in the last two decades [3], a systematic understanding of the relationship between greater water permeability and potential performance enhancements is lacking in the field. For example, should a more permeable membrane ideally be used to reduce the inlet pressure in an existing RO system, or to increase the flux at the same pressure?

Building upon an existing body of knowledge about concentration polarization [96,86,97], energy consumption in RO [98] and plant economics [99,100], we have shed light on this question by modeling the key performance metrics in an RO system as a function of mem-brane permeability and operational conditions [95]. This modeling re-quired a proper description of the relationship between applied inlet pressure, feed salinity and flowrate, concentration polarization at the membrane surface, mass transfer coefficient inside the feed channel, membrane permeability and several other key parameters, many of which vary as a function of distance along the membrane axis in a cross-flow assembly (see Fig. 7a). Omitting the effects of fouling as a first step, we modeled the key performance parameters of an RO system (permeate recovery ratio and flowrate, required inlet pressure, etc.) as a function of membrane permeability and inputs into the RO system (water salinity, membrane module length, etc.). We found that a $3\times$ more permeable membrane could reduce the required pressure for sea-water RO by 15% for the same permeation production and recovery ratio, or that it could alternatively reduce the number of pressure ves-sels required for a given total permeate production by 44% for the same energy consumption and recovery ratio (see Fig. 7). We also found that the benefits would be significantly greater for brackish water (46% percent lower pressure or 63% fewer pressure vessels). Fi-nally, we demonstrated that the performance improvements from ultrapermeable membranes exhibit a sharp law of diminishing returns, at least for the existing RO system architecture: in other words, an NPG membrane with permeability 3 L/(m²-h-bar) would save nearly as much energy and capital costs as a much higher porosity NPG mem-brane with 1000 L/(m²-h-bar).

7. Discussion and outlook

In this review, we have highlighted how computational approaches can be employed to understand, predict and ultimately design a future generation of RO membranes based on graphene. NPG represents a promising material for the future of RO membranes for water desalina-tion, and computational material science methods are playing an essen-tial role in the development of this new technology area.

Ultimately, the success of NPG technology will be determined by the field's ability to synthesize this material, first in the laboratory and eventually in a scalable and economical manufacturing process. The experimental synthesis of nanoporous graphene has become a subject of tremendous interest [101–103]. Achieving highly uniform, sub-nanometer pores in large-scale sheets of graphene is arguably the most important outstanding goal for the field of NPG membranes, and
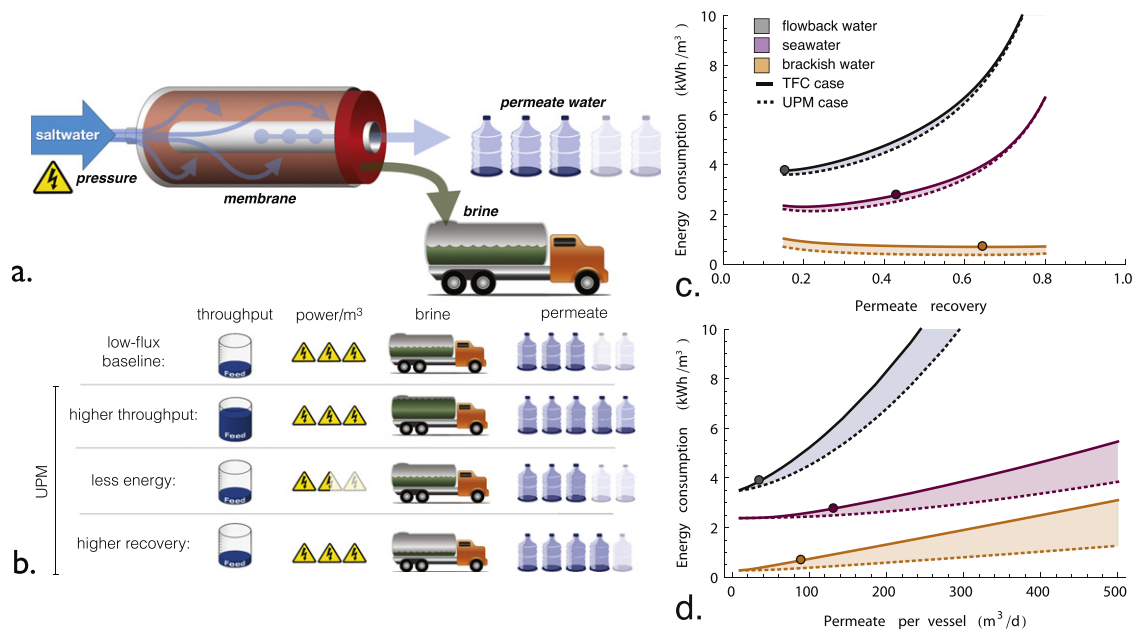

Fig. 7. (a) Schematic representation of cross-flow RO. (b) Comparison of RO performance with low-flux (baseline) membranes and ultra-permeable membranes (UPMs). (c) Specific en-ergy consumption of RO as a function of recovery ratio. (d) Specific energy consumption of RO as a function of permeate production per vessel. In (c) and (d), solid lines depict conventional TFC membranes and dashed lines represent UPMs with $A_m = 3$ L/(m²-h-bar). Circles depict a reference case with TFCs.
Adapted from Ref. [95] — Published by The Royal Society of Chemistry.

O'Hern et al. have recently produced pores with diameters of (0.40 ± 0.24) nm and densities exceeding 1×10^{12} cm^{-2}, while retaining structural integrity of the graphene [8]. Computational methods can help guide this experimental process. For example, MD simulations have been already employed to identify the optimal parameters in the creation of nanopores using irradiation by heavy ions or fullerenes [104, 77]. Approaches for creating nanopores using self-assembly, doping, chemical etching and so forth will likely benefit from computational insights. In particular, experimental efforts at producing full-coverage sheets of graphene by chemical vapor deposition (CVD) often yield sheets with overlapping flakes and multilayer regions in addition to patches of monolayer graphene. If the individual graphene layers within a multilayer region can be made nanoporous, an outstanding question is whether the multilayer region can also exhibit RO performance. Future MD simulations should be aimed at shedding light on this question.

Another experimental research direction has focused on the production of composite membranes that feature graphene oxide (GO) thin-films [105–110]. Although these thin-films of GO are thicker than graphene and may not feature atomically precise nanopores, they still hold significant promise for desalination due to the tunable chemistry and morphology of the layers [12]. Computational methods at the nanoscale and mesoscale could play a guiding role in the production of GO-based RO membranes, for instance by studying the effect of processing parameters (chemical environment, annealing time and temperature) on the morphology, chemistry and RO performance of GO layers.

If NPG represents a new era of materials development in the field of water technology, we believe that many important research directions remain to be explored. One such area is the interaction between ions in solution and graphene, since classical MD simulations only capture this interaction very roughly. Preliminarily work on this topic suggests that Na$^+$ ions are more strongly attracted to graphene surfaces than classical MD simulations would suggest [111] and that bare (unsolvated) anions can either physisorb or covalently bind to a graphene surface [37]. The implications of these ion-graphene interactions for RO performance remain to be explored. The chlorine resistance of NPG will likewise need to be examined using quantum-level calculations in order to supplement insights from existing work [112,113]. Further work should also look at the effect of grain boundaries (GBs) in graphene on salt rejection. The role of GBs in the mechanical properties of graphene has been studied [114–117], but the dynamics of water and ions near graphene GBs remains an area ripe for new research.

As we highlighted above, the benefits of ultrapermeable membranes exhibit a law of diminishing returns beyond 3 L/(m^2-h-bar), at least in existing RO systems. Thus, future work should also focus on identifying new desalination systems that can leverage the full potential of NPG. Because the benefits of UPMs are largely governed by concentration polarization effects, one promising step in this direction has been the study of unsteady-state shear strategies for increasing mass transfer and ultimately enhancing the performance of UPMs [118].

Finally, we believe that computational efforts will also play an important role in exploring the use of NPG for applications beyond RO desalination. For example, it is plausible that NPG could perform better in removing boron than TFC membranes, since boron permeates through TFC membranes in its uncharged boric acid form but might be rejected by steric exclusion. Classical MD simulations could help to validate or invalidate this hypothesis. Another emerging application for NPG membranes is in Forward Osmosis (FO), another desalination method whose performance is arguably even more limited by membrane permeability than RO [119] and where recent work based on MD simulations suggests that such membranes could offer benefits over existing FO membranes [120]. Computational research at the engineering-scale could also help design new approaches for ultrafiltration/nanofiltration (UF/NF) using graphene with larger pores (>1 nm) than for RO.

This review has highlighted some of the key approaches by which computational methods have been instrumental in the design, understanding and optimization of NPG as an RO membrane. We believe that future work will prove essential in bridging the gap between computational understanding and experimental progress, and will represent an important step in helping address the future of water in the 21st century.

Acronyms and symbols

E_M: elastic modulus; σ: membrane stress; σ_f: fracture stress; A_m: water permeability; p: porosity; d: membrane thickness; a: nanopore radius; ρ: nanopore density; p_Q: flowrate per pore per unit pressure; L_h: hydrodynamic pore length; CNT: carbon nanotube; RO: reverse osmosis; FO: forward osmosis; NPG: nanoporous graphene; GO: graphene oxide: TFC: thin-film composite; MD: molecular dynamics; DFT: density functional theory; UF: ultrafiltration; NF: nanofiltration; LJ: Lennard–Jones; UPM: ultra-permeable membrane.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.desal.2014.12.046.

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