

**Understanding Structure and Selectivity in Nanostructured  
Lyotropic Liquid Crystal Membranes using Molecular  
Simulations**

by

**Benjamin Joseph Coscia**

B.A., University of Connecticut, 2014

M.S., University of Colorado Boulder, 2017

A thesis submitted to the  
Faculty of the Graduate School of the  
University of Colorado in partial fulfillment  
of the requirements for the degree of  
Doctor of Philosophy  
Department of Chemical and Biological Engineering

2020

This thesis entitled:  
Understanding Structure and Selectivity in Nanostructured Lyotropic Liquid Crystal Membranes  
using Molecular Simulations  
written by Benjamin Joseph Coscia  
has been approved for the Department of Chemical and Biological Engineering

---

Prof. Michael Shirts

---

Prof. Richard Noble

---

Prof. Douglas Gin

---

Prof. Matthew Glaser

---

Prof. Robert Davis

Date \_\_\_\_\_

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

Coscia, Benjamin Joseph (Ph.D., Chemical Engineering)

## Understanding Structure and Selectivity in Nanostructured Lyotropic Liquid Crystal Membranes using Molecular Simulations

Thesis directed by Prof. Michael Shirts

The ability to perform highly selective aqueous separations at low cost is beneficial to a variety of chemical industries

Periodic, nanostructured porous polymer membranes made from the cross-linked inverted hexagonal phase of self-assembled lyotropic liquid crystals (LLCs) are a promising class of materials for selective separations.

The uniform size and complex chemical topology of the pores formed by self-assembled amphiphilic molecules such as liquid crystals make them promising candidates for selective separations.

In this work, we investigate an experimentally characterized LLC polymer membrane using atomistic molecular modeling. We

First, we gained a deep understanding of nanoscopic pore structure in order to make sure we got the chemical environment in the pores correct.

In particular, we compare simulated X-ray diffraction (XRD) patterns with experimental XRD data to quantify and understand the differences between simulation and experiment.

Finally, we explore the composition and structure of the nanopores and reveal that there exists a composition gradient rather than an abrupt partition between the hydrophilic and hydrophobic regions. A caveat is that the time scales of the dynamics are extremely long for this system, resulting in simulated structures that appear too ordered, thus requiring careful examination of the metastable states observed in order to draw any conclusions.

We observe transport of water, sodium ions and 20 small polar solutes within the pores of a lyotropic liquid crystal (LLC) membrane using atomistic molecular simulations. We find that the transport of a species is dependent not only on molecular size, but on chemical functionality as

well. We observe that all solutes perform intermittent hops between lengthy periods of entrapment. Three different trapping mechanisms are responsible for this behavior. First, solutes that drift out of the pore can become entangled among the dense monomer tails. Second, solutes can donate hydrogen bonds to the monomer head groups. Third, solutes can coordinate with sodium counterions. The degree to which a solute is affected by each mechanism is dependent on the chemical functionality of the solute.

Mathematically modeling complex transport phenomena at the molecular level can be a powerful tool for identifying transport mechanisms and predicting macroscopic properties. We use two different stochastic time series models, parameterized from long molecular dynamics (MD) simulation trajectories of a cross-linked  $H_{II}$  phase lyotropic liquid crystal (LLC) membrane, in order to predict solute mean squared displacements (MSDs) and solute flux, and thus solute selectivity, in macroscopic length pores.

First, using anomalous diffusion theory, we show how solute dynamics can be modeled as a fractional diffusion process subordinate to a continuous time random walk. From the MD simulations, we parameterize the distribution of dwell times, hop lengths between dwells and correlation between hops. We explore two variations of the anomalous diffusion modeling approach. The first variation applies a single set of parameters to the solute displacements and the second applies two sets of parameters based on the solute’s radial distance from the closest pore center.

Next, we generalize Markov state models, treating the configurational states of the system as a Markov process where each state has distinct transport properties. For each state and transition between states, we parameterize the distribution and temporal correlation structure of positional fluctuations as a means of characterization and to allow us to predict solute MSDs. We show that both models reasonably reproduce the MSDs calculated from MD simulations. However, qualitative differences between MD and Markov state dependent model-generated trajectories may limit its usefulness.

Finally, we demonstrate how one can use these models to estimate flux of a solute across a macroscopic-length pore and, based on those quantities, the membrane’s selectivity towards each

solute. This work helps to connect microscopic chemically-dependent solute motions that do not follow simple diffusive behavior with macroscopic membrane performance.

## Dedication

To all of the fluffy kitties.

## Acknowledgements

I would like to acknowledge and thank a number of people whose support and guidance has not gone unnoticed. First, I thank my advisor, Michael Shirts, who has been instrumental to my growth as a competent and confident researcher, pushing me to do high quality science. I thank the entire Shirts group for their feedback and encouragement as well as for making our lab an enjoyable to work. I thank Richard Noble and Douglas Gin for their guidance on past and present experimental research on LLC membranes. I also thank Michael McGrath, Gregory Dwulet and Sarah Dischinger, members of the Gin and Noble groups, for providing invaluable experimental perspective. I thank Matthew Glaser for his contributions to my understanding of liquid crystal systems. Our first paper would not have been complete without his insight. I thank Joseph Yelk for his effort creating the X-ray diffraction code on which our first paper relied. I thank Christopher Calderon for his guidance on applying Bayesian non-parametric techniques to solute time series.

I would like to acknowledge my financial support: The ACS Petroleum Research Fund grant #59814-ND7 and the Graduate Assistance in Areas of National Need (GAANN) fellowship which is funded by the U.S. Department of Education.

Finally, I would like to acknowledge my high performance computing resources: Molecular simulations were performed using the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number ACI-1548562. Specifically, it used the Bridges system, which is supported by NSF award number ACI-1445606, at the Pittsburgh Supercomputing Center (PSC). This work also utilized the RMACC Summit supercomputer, which is supported by the National Science Foundation (awards ACI-1532235 and

ACI-1532236), the University of Colorado Boulder, and Colorado State University. The Summit supercomputer is a joint effort of the University of Colorado Boulder and Colorado State University.



## Contents

### Chapter

<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	Membranes for Aqueous Separations . . . . .	1
1.1.1	Applications of Selective Membranes . . . . .	2
1.2	Competing Membrane Technologies . . . . .	5
1.2.1	Reverse Osmosis Membranes . . . . .	5
1.2.2	Nanofiltration Membranes . . . . .	6
1.2.3	Nanostructured Membranes . . . . .	7
1.3	Cross-linked Self Assembled Liquid Crystal Membranes for Selective Aqueous Separations . . . . .	10
1.3.1	The $H_{II}$ Phase . . . . .	11
1.3.2	The $Q_I$ Phase . . . . .	12
1.4	Modeling Membrane Separations . . . . .	13
1.4.1	Macroscopic Treatments . . . . .	14
1.4.2	Atomistic Molecular Simulation of LLC Membranes . . . . .	16

<b>Bibliography</b>	<b>22</b>
---------------------	-----------

### Appendix

## Tables

### Table

## Figures

### Figure

1.1	.....	3
1.2	(a) Previous understanding of the LLC pores are essentially speculations based on limited chemical and experimental data. (b) We use detailed molecular modeling in this paper in order to appropriately model the pore's complex architecture, which is crucial to understanding the mechanism of solute transport. In both pictures, the head group region is colored blue and the tail region is colored cyan. ....	18

## Chapter 1

### Introduction

#### 1.1 Membranes for Aqueous Separations

Pressure driven membrane processes have become an increasingly useful tool for performing aqueous separations.

- Untreated water can be a very complex solution with particles ranging in size from microns down to nanometers
- Sediment, bacteria, algae, proteins, small organic molecules, and ions are all common components of aqueous streams.
- The diversity in size and chemical topology of contaminants makes the design of membrane processes meant to separate these components complex.
- To deal with complex aqueous streams, and to prevent excessive membrane fouling, multiple types of membranes are often used in series, removing larger particles first. [5]

Modern membrane design is completely dependent on the target particle separation.

- Separation membranes are most broadly classified based on the size of the particle they reject.
- Microfiltration (MF) membranes contain pores with diameters ranging from 100-10000 nm. They can separate large particles like bacteria and protozoa. [1]

- Ultrafiltration (UF) membranes have pore diameters of about 5-500 nm and are useful for the separation of sugars, proteins, viruses and colloidal materials. [2]
- Nanofiltration (NF) membranes have pores on the order of 1 nm in diameter and can be used for the separation of small organic molecules and charged species. [3]
- Reverse osmosis (RO) membranes are dense amorphous polymers with tortuous pathways formed by collapsed polymer networks. Their dense polymer architecture rejects all solutes to a high degree except for water making them useful for separating hydrated ions from water. [4]
- We have summarized the uses of the different classes of membrane technologies in Figure 1.1.

Membranes are generally designed to maximize two key performance metrics: permeability and selectivity.

- Permeability is used to quantify the rate at which solvent and solutes pass through the membrane.
- Selectivity quantifies the relative rates of passage of two substances.
- A related quantity to selectivity, rejection, quantifies the fraction of undesired solute that does not pass through the membrane.

Although there has been considerable focus on creating membranes with high permeabilities, there is a case to be made that shifting the focus to membrane selectivity may offer a more effective route towards lowering the cost of membrane separations. [12]

- Increasing permeabilities beyond those already achieved may have only a small effect on energy requirements and capital costs.
- Cohen-Tanugi et al. calculated that tripling membrane permeability could reduce energy consumption up to 15% in a seawater reverse osmosis plant. [6]

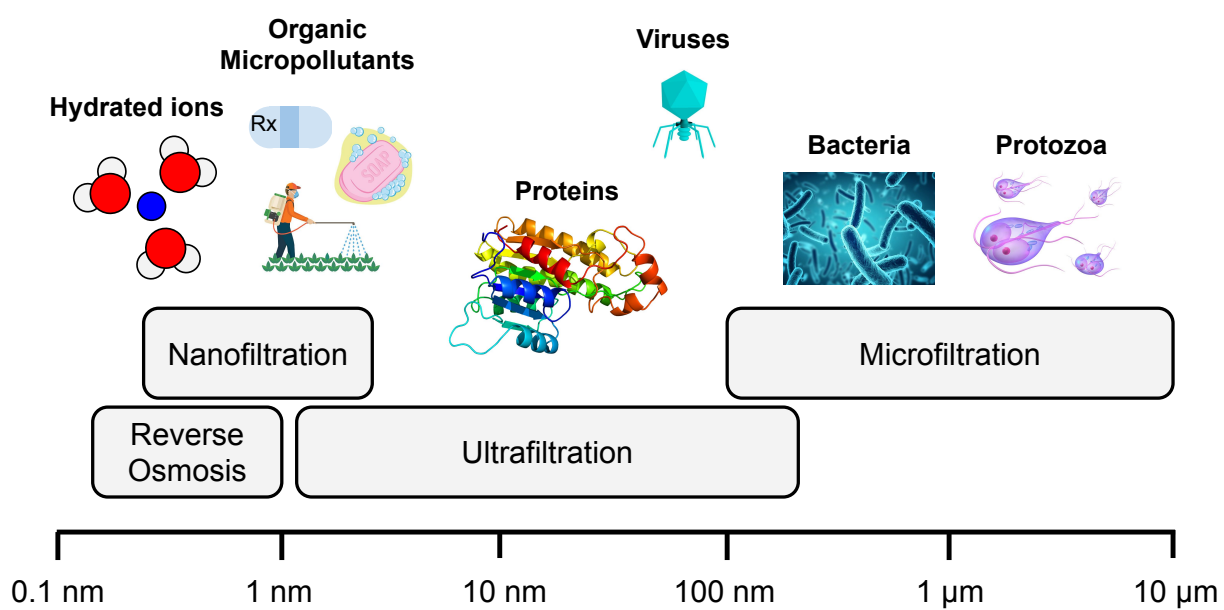


Figure 1.1

- Perhaps the biggest detriment to energy consumption is the practical need for multiple membrane passes in order to achieve a desired purity.
- Additionally, many membranes are not suited for high purity separations of small neutral species which necessitates chemical and capital costs for post-treatment
- Addressing these problems with highly selective separations may lead to more gains.

### 1.1.1 Applications of Selective Membranes

Selective separations are useful in a wide range of applications.

*Desalination:* Creating potable water from seawater or brackish water is of paramount importance in water-scarce areas.

- Compared with thermal distillation techniques, reverse osmosis has been shown to be more environmentally friendly and economical due to its lower energy requirements.[7]
- Thermal techniques are still preferred where excess waste heat or cheap thermal energy is available, such as cogeneration plants.[8]
- RO has smaller footprint

*Organic Micropollutants:* Municipal and industrial wastewaters are contaminated by harmful micropollutants, which have adverse effects on human health even at low concentrations[9]

- Micropollutants include pharmaceuticals, personal care products, hormones, pesticides and industrial chemicals which find their way into our drinking water supply
- Is there any infrastructure built to combat this?

*Recovery of Valuable Dissolved Species:* We can use highly selective membranes in order to recover potentially valuable dissolved species from complex waste streams.

Municipal waste-waters are rich in carbon, nitrogen and phosphorus-containing compounds.

- The recovery of such products, which can be achieved using a selective membrane, has numerous potential uses.[10]
- For example, nitrogen and phosphorus recovery can help sustain fertilizer production which will help meet global food demand as population continues to increase.[11]

Industrial waste-waters are often quite complex with up to six times more total dissolved solids than seawater[12].

- For example, flowback water, produced during hydraulic fracturing of shale formations consists of relatively high concentrations of salts, metals, and soluble organic compounds.
- The majority of this water is disposed through deep well injection, however there is a growing public concern about its management which has prompted the use of separation technologies such as RO and NF in order to reduce the volume of contaminated water [13].
- Some of the dissolved organic compounds in flowback water, such as acetate, are potentially valuable and can be recovered with highly selective membranes [14].

*Breathable barriers:* Finally, there is a great deal of military interest in creating breathable barriers which selectively allow the passage of water in both directions but blocks out harmful contaminants.

- Need to allow sweating
- Can even put catalytic groups in the pores to break down contaminants

## 1.2 Competing Membrane Technologies

### 1.2.1 Reverse Osmosis Membranes

The first aqueous separations membranes were developed in the 1960s and were made of the amorphous polymer cellulose acetate (CA). [15]



- Reid and Spencer were among the first to show the ability of these membranes to reject NaCl to high degrees ( $\sim 99\%$ ) with high applied pressures (270 atm). [16]
- The most limiting drawback to CA membranes is their chemical instability, undergoing severe hydrolysis at pH values outside the range 4–6. [17]

Amorphous thin film composite (TFC) polyamide membranes are the current industry standard for high purity separations.

- Developed in the 1980s, polyamide membranes are capable of rejecting salt to a higher degree and can operate at a wider pH range and higher feed pressure than CA membranes. [18]
- TFC polyamide membranes are typically formed by the interfacial synthesis of a polyamide selective layer on the surface of a microporous polysulfone support layer.
- The support layer gives the membrane mechanical strength without hindering the flow of water thereby permitting a very thin selective layer where molecular separations occur. [19]
- These membranes are typically used for RO membrane processes. [20]

The dense polymer selective layers of TFC membranes require high feed pressures, in the range of 5 – 120 bar, in order to achieve a useful permeate flux. [3]

- While the energy requirements to attain these pressures are still less than the energy requirements of thermal distillation[7], it is often desirable to create membranes that can operate at lower feed pressures.
- A target separation may not require the high pu
- It is not always necessary to achieve the high purity permeate streams resulting from RO
- It is also possible that a target separation may be possible with less restrictive pathways for water to follow.
- This has driven research into nanofiltration.

### 1.2.2 Nanofiltration Membranes

NF membranes have pores on the order of 1 nm in size. Larger pore sizes allow lower feed pressures (3 - 20 bar) [3] An ideal NF membrane should have densely packed, uniform-sized and non-tortuous pores. This combination has been practically difficult to realize.

The most widely used methods of NF membrane fabrication are interfacial polymerization and phase inversion.

- By modifying the monomer materials, one can control the structural morphology produced by interfacial polymerization to create pores larger than those in RO membranes. [21]
- During phase inversion, one submerges a polymer, dissolved in a solvent, in a non-solvent. A solid, porous polymer membrane is all that remains once all solvent has been removed by non-solvent exchange. [22]
- Although commercially dominant, both of these techniques suffer from tortuous and polydisperse in size pores which results in far from ideal selectivities.

Track-etching is another technique which attempts to eliminate polydispersity and tortuosity. During track-etching, a polymer film is bombarded with charged particles, then chemically etched to create pores. [23]

- Although the pores are uniform and non-tortuous, benefitting selectivity, the membranes have an extremely low pore density subsequently low permeability.

### 1.2.3 Nanostructured Membranes

Nanostructured membrane materials have the potential to achieve the high selectivity of RO with the low feed pressure requirements of NF. Nanostructured materials of interest typically have explicit nm-size pores that are uniform in size, eliminating issues with polydispersity. There have been a number explorations into different kinds of technologies for this application.

Ultrathin-film graphene and graphene oxide membranes are an active area of research because they are atomically thick materials and therefore offer potential for extremely high permeability membranes. [24]

- The tightly packed aromatic network of  $sp^2$  hybridized carbon atoms that make up graphene sheets precludes the passage of even the smallest monoatomic species, helium. [25]
- Controllably-sized pores have been created in pristine graphene by plasma etching and by charged particle bombardment. [26, 27]
- Graphene oxide (GO), a highly oxidized modification of graphene, consist of epoxy, hydroxyl and carboxylate functional groups. [28]
- Many groups study GO membranes because they have improved antibacterial properties over graphene, leading to less membrane fouling, and because their functionality can be modified in order to achieve solute-specific separations. [29, 30]
- Despite their promise, scalable synthesis of monolayer graphene and GO membranes without introducing microscopic, performance degrading defects has not yet been achieved. [31, 32]
- Multilayered GO membranes have shown considerably more progress since their synthesis procedures are low cost and scalable. [33]
- GO sheets are particularly easy to make into multilayered membranes since they stack on top of each other, held together by hydrogen bonds. [34]
- The potential of graphene and GO membrane certainly merits their continued exploration. Many groups are still working in order to work on better control and standardization of their synthesis, improving their designability for specific separations, and further improving their scalability. [32]

Carbon nanotubes (CNTs) have shown promise as aqueous separations membranes due to unprecedentedly fast water transport.[24]

- CNTs are an allotrope of carbon consisting of tubular graphitic layers. [35]
- One can control CNT diameters down to 0.5 nm in size which has inspired the creation of CNT membranes for reverse osmosis applications. [36]
- Molecular dynamics simulations have predicted and experiments have confirmed that CNTs are extremely fast transporters of water. [37, 38]
- MD simulations by Kalra et al. predicted water transport at rates comparable to the transmembrane protein aquaporin-1. [39]
- Experiments have exhibited water transport rates orders of magnitude higher than predictions by continuum modeling. [40]
- This enhancement has been explained as a result of nearly friction-less single-file water flow through the hydrophobic CNT interiors. [39]
- Functionalization of the CNT pore entrances can potentially lead to highly selective separations. [41]
- Practically, dispersing and aligning CNTs into a polymer matrix is extremely difficult because they tend to agglomerate due to van der Waals forces. [42]
- Some work has been to functionalize the carbon nanotubes in order to better incorporate them, however facile incorporation at scale remains a challenge yet to be overcome. [43]

Zeolite membranes offer the potential for permeabilities comparable to ultrafiltration, with selectivities as good as NF and RO. [44]

- Zeolites have highly uniform nm-sized crystalline structures with cage-like cavities that allow movement and trapping of small solutes.

- The crystalline frameworks are typically formed by networks of silicon and aluminum each attached to 4 oxygen atoms in a tetrahedral arrangement. [45]
- One can replace the silicon and aluminum atoms via ion exchange in order to control the size of the cavities and hence its molecular-sieving properties. [46]
- Zeolite-coated ceramic membranes have shown the most promise for RO applications because of their mechanical stability under high applied pressure and chemical stability for withstanding disinfectants. [47]
- A number of studies have tested the permeability and sodium salt rejection of various zeolite membranes, however their high permeabilities typically come at the cost of low selectivities and vice versa. [48, 49]
- Zeolites are also prone to defects in the crystalline structure which would require substantial modification to the traditional synthesis procedures in order to fix. [50]

Finally, metal organic frameworks (MOFs) have been recently introduced to the field of aqueous separations.

- MOFs are highly porous and flexible crystalline structures made of metal clusters coordinated to organic ligands. [51]
- There is a much wider breadth of research into MOFs as gas separation membranes because they tend to be unstable in water. [52]
- But a new generation of water-stable MOFs is making it possible to use them in aqueous separations. [53]
- Purification of both aqueous and gaseous streams using MOFs are typically achieved by selective adsorption or catalytic degradation. [54]
- MOFs have been applied towards the removal of a number of common water contaminants including dyes, pesticides, endocrine disruptors, and pharmaceuticals. [55, 56, 57, 58]

- Although aqueous MOF separations are theorized to surpass the performance of conventional membrane separations, it is still a budding field. The stability and reusability of the material must be guaranteed before they can be implemented at scale. [59]

### 1.3 Cross-linked Self Assembled Liquid Crystal Membranes for Selective Aqueous Separations

Amphiphilic molecules that form ordered nanostructures have shown potential to as nanoporous membranes...

Under the right conditions, the shape and amphiphilic character of the monomers in Figure TBD drives their self assembly into ordered nanostructures.

- Monomer 1 can form the inverted hexagonal phase ( $H_{II}$ )
- Monomer 2 will form the bicontinuous cubic phase ( $Q_I$ )
- The tails have vinyl groups which can be cross-linked for mechanical strength.

In this work we attempt to understand how one can design LLC membranes as alternative nanostructured materials for highly selective aqueous separations.

#### 1.3.1 The $H_{II}$ Phase

The  $H_{II}$  phase is characterized by hexagonally packed, uniform-sized and straight pores.

- The hydrophilic head groups aggregate in the pore centers to create cylindrical aqueous channels.
- These pore channels are lined with the chemical functionality of the LLC monomers and have the potential to interact with solutes in a chemically-dependent manner.
- In theory, this pore topology and geometry is ideal for high flux and highly selective separations.

Unfortunately, it is a difficult task to align the self-assembled hexagonal mesophases into continuous pores that traverse the thickness of the membrane.

- Although the membranes have shown high experimental selectivity, their flux has been very low due to misalignment of the hexagonal mesophases.

Considerable recent efforts have made progress towards the macroscopic alignment of the hexagonal mesophases.

- Feng et al. leverage the magnetic anisotropy of the columnar mesophases in order to control their alignment with a magnetic field. [60]
- Feng et al. also used an approach called soft confinement which takes advantage of the hexagonal columns preference towards anchoring perpendicular to either a PDMS or glass substrate. [61]
- Finally, Feng et al. designed a third technique which uses a structure directing molecule in order to template the assembly of a fatty acid molecule into ordered columnar phases. [62]

### 1.3.2 The $Q_I$ Phase

The bicontinuous cubic, or  $Q_I$  phase, is a class of nanostructured phases characterized by 3D interconnected pores.

- Aside from its tortuous pore architecture, it shares the uniform size and complex topological features of the  $H_{II}$  phase which lends itself to highly selective separations.
- Although water and solutes must follow a longer path in order to pass through  $Q_I$  membranes, they are more practical to synthesize because the mesophases do not require alignment.

The space group of the  $Q_I$  phase configuration formed by monomer 1 is uncertain and thought to be either  $Pn3m$  or  $Ia3d$ .

- 6 Q phase architectures have been identified in small molecule amphiphile systems. [63]
- Of these, only 4 are consistent with diffraction data generated by the gemini surfactant used here. [64]
- $Q^{230}$  (Ia3d),  $Q^{224}$  (Pn3m),  $Q^{229}$  (Im3m) or  $Q^{212}$  (P4<sub>3</sub>32) phase of type I configuration
- The presence of  $1/\sqrt{6}$  and  $1/\sqrt{8}$  peaks rules out the  $Q^{227}$  (Fd3m) and  $Q^{223}$  (Pm3n) configurations.
- The Pn3m and Ia3d architectures are the most common [63, 65]
- The most likely phase is the type I  $Q^{230}$  (Ia3d) because it is the most common phase observed between lamellar and hexagonal phases and the monomeric alkyltrimethylammonium salts used to synthesize the gemini LCs exhibit clear Ia3d symmetry.

Due to its more facile synthesis, there has been significantly more development of  $Q_I$  phase membranes.

- The first generation of  $Q_I$  membranes was made by the self-assembly of a gemini phosphonium monomer in water. [64]
- Hatakeyama et al. improved the industrial viability of  $Q_I$  phase membranes by using a gemini ammonium monomer which is both easier and cheaper to synthesize. [66]
- Free standing films of both first and second generation  $Q_I$  phase membranes cannot withstand high pressure. Because solution casting was ineffective, Zhou et. al used a hot-pressing method to make mechanically strong membranes which involves heating the initial monomer mixture to 70°C and pressing it with 12 tons of force into a thick microporous, hydrophilic polymer support. [67]
- The most recent generation of  $Q_I$  membranes uses an imidazolium-based gemini LLC monomer which is capable of being solution cast into defect-free thin films on porous sup-



ports. This improvement resulted in a ten-fold increase in flux while retaining selectivities similar to earlier generations. [68]

State of the art  $Q_I$  membranes offer selectivities that are competitive with existing commercial technologies.

- When separating organic solutes from NaCl,  $Q_I$ -phase membrane filtration experiments have shown selectivity 2–3 times higher than commercial RO and 6–12 times higher than commercial NF membranes [14].
- Water permeability is higher than commercial RO membranes but less than commercial NF. There is work being done to reduce the thickness of the selective layer in order to increase permeability.

## 1.4 Modeling Membrane Separations

Mathematical descriptions of transport in complex separations membranes are a powerful way to understand mechanisms and formulate design principles. [69, 70, 71] The complexity of a well-fit model generally parallels the complexity of the transport mechanism being studied, as well as the transport information the model conveys. In dense homogeneous membranes, the solution-diffusion model can extract diffusion and partition coefficients and has successfully predicted solute transport rates. [72] Analogously, pore-flow models yield predictions of diffusion coefficients and solute transport rates in nanoporous membranes. [73] Modern single particle tracking approaches have taken researchers beyond continuum modeling allowing them to characterize complex diffusive behavior. [74] At the molecular level, one can use molecular dynamics (MD) simulations to study both single particle dynamics and bulk transport properties with atomic-level insight. [75, 76] All of these approaches facilitate generation of hypotheses about the molecular origins of separations by attempting to give a more intuitive understanding of how solutes move as a function of their environment, in turn suggesting experiments that could be performed.

### 1.4.1 Macroscopic Treatments

The most widely used approaches to modeling transport in membranes of all types are based on macroscopic theory. In this section we will discuss the two prevailing theories: the pore flow model and the solution-diffusion model.

Membrane permeation is the result of a chemical potential gradient,  $\frac{d\mu_i}{dx}$ .

- The flux of component  $i$  is proportional to this gradient:

$$J_i = -L_i \frac{d\mu_i}{dx} \quad (1.1)$$

where  $L_i$  is a coefficient of proportionality. [72]

- Chemical potential gradients can be induced by concentration, pressure, temperature and electromotive forces.
- We will limit our discussion to concentration and pressure gradients.

For pressure driven membrane processes, water flux through both porous and amorphous membranes can be described by

$$J_w = A(\Delta P - \Delta\pi_m) \quad (1.2)$$

where  $J_w$  is volumetric water flux,  $A$  is the water permeability coefficient,  $\Delta P$  is the applied hydraulic pressure and  $\Delta\pi_m$  is the trans-membrane osmotic pressure difference. The water permeability coefficient is dependent on how one models flow through the membrane.

In porous membrane architectures, water flux is modeled as laminar flow through cylindrical pores.

- The derivation follows Hagen-Poiseuille flow with inclusion of morphological characteristics:

$$A = \frac{\varepsilon r_p^2}{8\mu\delta_m} \quad (1.3)$$

where  $\varepsilon$  is the surface porosity,  $r_p$  the pore radius,  $\delta_m$  the membrane thickness, and  $\mu$  the solution viscosity.

- Separation is typically characterized in terms of solute rejection,  $R$ .

$$R = 1 - \frac{c_p}{c_f} \quad (1.4)$$

where  $c_p$  and  $c_f$  are the concentrations of the rejected species in the permeate and feed respectively.

- Solutes with radii smaller than the pore will be rejected. A distribution of pore sizes prevents perfect rejection.

In amorphous membranes, water and solute flux are modeled using the solution-diffusion model.

- It is hypothesized that water and solute molecules partition into the membrane and diffuse across the polymer matrix due to a chemical potential gradient and then desorb into the permeate.
- The product of a component's solubility and diffusivity is commonly referred to as its permeability,  $P$ . [72]
- $P$  is an intrinsic material property and is thus independent of membrane thickness.
- The water permeability coefficient *is* dependent on thickness,  $\delta_m$ , and can be formulated in terms of the pure water permeability,  $P_w$ .

- 

$$A = \frac{P_w V_w}{\delta_m R_g T} \quad (1.5)$$

where  $V_w$  is molar volume of water,  $R_g$  is the gas constant and  $T$  is absolute temperature.

- Solute flux is modeled as:

$$J_s = \frac{P_s}{\delta_m} \Delta c_m = B \Delta c_m \quad (1.6)$$

where  $B$  is a solute permeability coefficient and  $\Delta c_m$  is the concentration difference across the selective membrane layer.

- Under these assumptions, rejection can be reformulated as

$$R = \frac{A}{A + B} \quad (1.7)$$

which approaches unity as the solute flux tends towards zero.

#### 1.4.2 Atomistic Molecular Simulation of LLC Membranes

Our current understanding of the molecular details of LLC polymer membranes' nanostructure is not sufficient to be able to precisely design them for specific separations. Dischinger et al. attempted to use an empirical model that correlates the physiochemical properties of the counterion used in a Q<sub>I</sub>-phase LLC membrane to solute rejection[77]. Although their model showed some qualitative agreement with experiment, the quality of fit of their model was limited due to complex solute-membrane interactions that could not easily be modeled. Additionally, they observed an unexpected discrepancy in the relationship between uncharged solute rejection and water permeability, which will require a more in-depth knowledge of the difference between solute and solvent transport.

Over the past 20 years, H<sub>II</sub>-phase LLC polymer membrane studies have been limited primarily to the Na-GA3C11 monomer with some characterization done after minor structural modifications. For example, Resel et al. varied the length of the monomer tails and the counterion used and observed its effect on pore spacing [78]. In a later study of rejection performance, it was shown that membranes formed by cross-linked Na-GA3C11 in the H<sub>II</sub> phase cannot separate solutes less than 1.2 nm in diameter because the pores are too large [79]. We do not yet understand how to controllably reduce the effective pore size or how to tune the chemical environment in the nanopores of this or related materials for small molecule separations. The only source of predictive modeling for LLC systems have been macroscopic models that likely do not adequately describe transport at these length scales [80]. Modeling with molecular detail could provide sufficient information about the mechanisms and chemical features to better inform experimental design of similar nanostructured membranes.

A molecular-level understanding of the relationship between monomer structure and solute transport can help provide guidelines to reduce the large chemical space available to design monomers for creation of separation-specific membranes.

- Atomistic MD simulations can provide the required level of detail (Figure 1.2b), assuming the force fields are sufficiently accurate.
- With such an atomistic model, we can directly observe molecular-level solute transport and suggest governing mechanisms.
- We can also observe how the choice of head group interacts with solutes of interest.
- In addition, we can interchange counterions which may influence both the pore size and the strength of the Donnan potential.

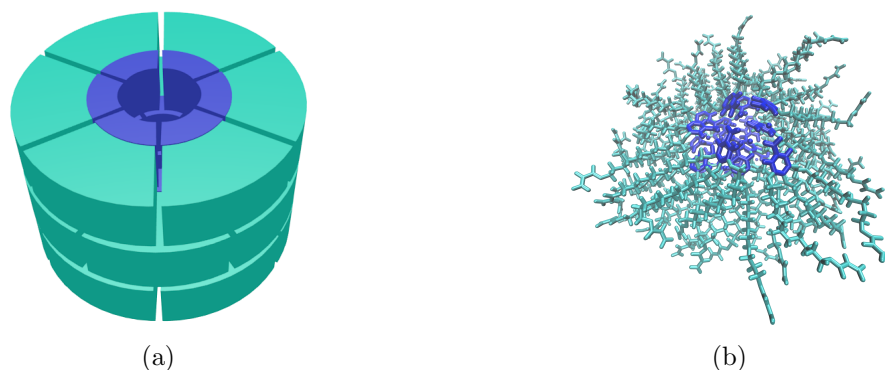


Figure 1.2: (a) Previous understanding of the LLC pores are essentially speculations based on limited chemical and experimental data. (b) We use detailed molecular modeling in this paper in order to appropriately model the pore's complex architecture, which is crucial to understanding the mechanism of solute transport. In both pictures, the head group region is colored blue and the tail region is colored cyan.

Although the  $Q_{II}$  phase shows the most promise for practical applications, the focus of this work will be on the  $H_{II}$  phase.

- The  $H_{II}$  phase is an easier to geometry to model and analyze.

- We also have detailed structural data which is necessary for validating our model.
- All of the analysis techniques we use can be equally adapted to the more complicated  $Q_I$  phase geometry.

There are few molecular simulation studies which study structure and transport in LLC systems.

- Mondal et al. used MD simulations to study the self assembly of gemini surfactants and observed the formation of  $H_{II}$  and  $Q_I$  phases depending on water content.[81]
- Mantha and Yethiraj as well as Roy et al. studied the dynamics of confined water in these systems and showed orders of magnitude differences in their motion dependent on system geometry. [82, 83]
- Jackson et al. as well as Mantha et al. have combined experiment with simulation in order to show how the choice of monomer head group counterion regulate water dynamics. [84, 85]
- Sakamoto et al. and Nada et al. observed the dynamics of water molecules and ions and hypothesized transport mechanisms in a simplified model of an LLC nanopore. [86, 87]

Because there is relatively sparse coverage of these types of simulation systems in the literature, we have built a detailed molecular model from the ground up. There are four primary research questions that we will address in this work.

(1) What is the nanoscopic structure?

- Before we can try to understand the molecular mechanisms of solute transport, we need to ensure that we model the chemical environment within the nanopores in a way that is consistent with experiment.
- We use experimental structural data in order to validate our model.

(2) Which solute-membrane interactions have the greatest influence on transport rates?

- After gaining a detailed picture of the nanopore structure, we can feel confident that solutes in this system will experience the same interactions which are present in a real system.
  - We create independent systems for each of 20 small polar solutes and observe transport mechanisms whose dominance is dependent on solute chemical functionality.
  - We characterize three different trapping mechanisms which lead to subdiffusive transport behavior.
- (3) Can we formulate mechanistic models whose dynamical properties are consistent with our molecular simulations and can be used to extrapolate macroscopic behavior which MD simulations cannot.
- Using our qualitative understanding of the dominant trapping mechanisms, we develop stochastic time series models which we can use to mimic solute dynamic behavior on time scales orders of magnitude longer than our simulations.
  - We attempt to reproduce both quantitative and qualitative solute trajectory behavior on MD simulation-length timescales.
  - We then show how we can use our most promising model in order to connect microscopic transport to macroscopic flux and selectivity.
- (4) How can time series data directly inform us about transport mechanisms?
- Although our stochastic models show great promise, their development require some qualitative and quantitative understanding of dominant transport mechanisms.
  - In the final chapter, we use the infinite hidden Markov model in order to automatically detect and parameterize a unknown number of hidden dynamical modes exhibited by solute time series.
  - This more flexible approach allows us to both infer mechanisms based on differences in dynamical behavior and generate stochastic trajectory realizations which we can

use to predict flux and selectivity.

The next four chapters offer answers to each of the above questions and are adapted from various first author manuscripts at various stages in the publication process as described below. The introduction to each adaptation is condensed in order to avoid redundancy and all other sections are left intact. The supporting information documents for each manuscript are given in the appendices.

*Chapter 2:* adapted from manuscript entitled “Understanding the Nanoscale Structure of Inverted Hexagonal Phase Lyotropic Liquid Crystal Polymer Membranes.” published in the Journal of Physical Chemistry B. [88]

*Chapter 3:* adapted from manuscript entitled “Chemically Selective Transport in a Cross-Linked H<sub>II</sub> Phase Lyotropic Liquid Crystal Membrane.” published in the Journal of Physical Chemistry B. [75]

*Chapter 4:* adapted from a manuscript in review with Physical Review E, entitled “Capturing Subdiffusive Solute Dynamics and Predicting Selectivity in Nanoscale Pores with Time Series Modeling”. The final manuscript may change based on reviewer feedback.

*Chapter 5:* adapted from the draft of a manuscript in preparation with the working title “Statistical Inference of Transport Mechanisms and Long Time Scale Behavior from Time Series of Solute Trajectories in Nanostructured Membranes.” The content will change as the draft is finalized and after reviewer feedback.



## Bibliography

- [1] H. Ma, B. S. Hsiao, and B. Chu, "Functionalized electrospun nanofibrous microfiltration membranes for removal of bacteria and viruses," Journal of Membrane Science, vol. 452, pp. 446–452, Feb. 2014.
- [2] J. Davey and A. I. Schäfer, "Ultrafiltration to Supply Drinking Water in International Development: A Review of Opportunities," in Appropriate Technologies for Environmental Protection in the Developing World (E. K. Yanful, ed.), pp. 151–168, Dordrecht: Springer Netherlands, 2009.
- [3] B. Van Der Bruggen, C. Vandecasteele, T. Van Gestel, W. Doyen, and R. Leysen, "A Review of Pressure-Driven Membrane Processes in Wastewater Treatment and Drinking Water Production," Environ. Prog., vol. 22, pp. 46–56, Apr. 2003.
- [4] D. M. Warsinger, S. Chakraborty, E. W. Tow, M. H. Plumlee, C. Bellona, S. Loutatidou, L. Karimi, A. M. Mikelonis, A. Achilli, A. Ghassemi, L. P. Padhye, S. A. Snyder, S. Curcio, C. D. Vecitis, H. A. Arafat, and J. H. Lienhard, "A Review of Polymeric Membranes and Processes for Potable Water Reuse," Prog. Polym. Sci., vol. 81, pp. 209–237, June 2018.
- [5] M. F. A. Goosen, S. S. Sablani, H. Al-Hinai, S. Al-Obeidani, R. Al-Belushi, and D. Jackson, "Fouling of Reverse Osmosis and Ultrafiltration Membranes: A Critical Review," Separation Science and Technology, vol. 39, pp. 2261–2297, Jan. 2005.
- [6] D. Cohen-Tanugi, R. K. McGovern, S. H. Dave, J. H. Lienhard, and J. C. Grossman, "Quantifying the Potential of Ultra-Permeable Membranes for Water Desalination," Energy Environ. Sci., vol. 7, no. 3, pp. 1134–1141, 2014.
- [7] A. J. Morton, I. K. Callister, and N. M. Wade, "Environmental Impacts of Seawater Distillation and Reverse Osmosis Processes," Desalination, vol. 108, pp. 1–10, Feb. 1997.
- [8] S. Bhojwani, K. Topolski, R. Mukherjee, D. Sengupta, and M. M. El-Halwagi, "Technology review and data analysis for cost assessment of water treatment systems," Science of The Total Environment, vol. 651, pp. 2749–2761, Feb. 2019.
- [9] R. P. Schwarzenbach, B. I. Escher, K. Fenner, T. B. Hofstetter, C. A. Johnson, U. v. Gunten, and B. Wehrli, "The Challenge of Micropollutants in Aquatic Systems," Science, vol. 313, pp. 1072–1077, Aug. 2006.
- [10] C. M. Sales and P. K. Lee, "Resource Recovery from Wastewater: Application of Meta-Omics to Phosphorus and Carbon Management," Curr. Opin. Biotechnol., vol. 33, pp. 260–267, June 2015.

- [11] M. Xie, H. K. Shon, S. R. Gray, and M. Elimelech, "Membrane-Based Processes for Wastewater Nutrient Recovery: Technology, Challenges, and Future Direction," Water Res., vol. 89, pp. 210–221, Feb. 2016.
- [12] J. R. Werber, C. O. Osuji, and M. Elimelech, "Materials for Next-Generation Desalination and Water Purification Membranes," Nat. Rev. Mater., vol. 1, p. 16018, May 2016.
- [13] K. B. Gregory, R. D. Vidic, and D. A. Dzombak, "Water Management Challenges Associated with the Production of Shale Gas by Hydraulic Fracturing," Elements, vol. 7, pp. 181–186, June 2011.
- [14] S. M. Dischinger, J. Rosenblum, R. D. Noble, D. L. Gin, and K. G. Linden, "Application of a Lyotropic Liquid Crystal Nanofiltration Membrane for Hydraulic Fracturing Flowback Water: Selectivity and Implications for Treatment," J. Membr. Sci., vol. 543, pp. 319–327, Dec. 2017.
- [15] R. E. Kesting, "Semipermeable membranes of cellulose acetate for desalination in the process of reverse osmosis. I. Lyotropic swelling of secondary cellulose acetate," Journal of Applied Polymer Science, vol. 9, no. 2, pp. 663–688, 1965.
- [16] C. E. Reid and H. G. Spencer, "Ultrafiltration of Salt Solutions at High Pressures," J. Phys. Chem., vol. 64, pp. 1587–1588, Oct. 1960.
- [17] K. D. Vos, F. O. Burris, and R. L. Riley, "Kinetic study of the hydrolysis of cellulose acetate in the pH range of 2–10," Journal of Applied Polymer Science, vol. 10, no. 5, pp. 825–832, 1966.
- [18] J. E. Cadotte, R. S. King, R. J. Majerle, and R. J. Petersen, "Interfacial Synthesis in the Preparation of Reverse Osmosis Membranes," Journal of Macromolecular Science: Part A - Chemistry, vol. 15, pp. 727–755, Apr. 1981.
- [19] J. Kucera, "Biofouling of Polyamide Membranes: Fouling Mechanisms, Current Mitigation and Cleaning Strategies, and Future Prospects," Membranes, vol. 9, p. 111, Sept. 2019.
- [20] R. W. Baker, Membrane Technology and Applications. John Wiley & Sons, July 2012. Google-Books-ID: FhtBKUq4rL8C.
- [21] M. N. A. Seman, M. Khayet, and N. Hilal, "Nanofiltration thin-film composite polyester polyethersulfone-based membranes prepared by interfacial polymerization," Journal of Membrane Science, vol. 348, pp. 109–116, Feb. 2010.
- [22] C. A. Smolders, A. J. Reuvers, R. M. Boom, and I. M. Wienk, "Microstructures in Phase-Inversion Membranes. Part 1. Formation of Macrovoids," J. Membr. Sci., vol. 73, pp. 259–275, Oct. 1992.
- [23] P. Apel, "Track Etching Technique in Membrane Technology," Radiat. Meas., vol. 34, pp. 559–566, June 2001.
- [24] T. Humplik, J. Lee, S. C. O'Hern, B. A. Fellman, M. A. Baig, S. F. Hassan, M. A. Atieh, F. Rahman, T. Laoui, R. Karnik, and E. N. Wang, "Nanostructured Materials for Water Desalination," Nanotechnology, vol. 22, no. 29, p. 292001, 2011.

- [25] J. S. Bunch, S. S. Verbridge, J. S. Alden, A. M. van der Zande, J. M. Parpia, H. G. Craighead, and P. L. McEuen, “Impermeable atomic membranes from graphene sheets,” Nano Lett., vol. 8, pp. 2458–2462, Aug. 2008.
- [26] S. P. Surwade, S. N. Smirnov, I. V. Vlassiouk, R. R. Unocic, G. M. Veith, S. Dai, and S. M. Mahurin, “Water desalination using nanoporous single-layer graphene,” Nature Nanotech., vol. 10, pp. 459–464, May 2015.
- [27] C. J. Russo and J. A. Golovchenko, “Atom-by-atom nucleation and growth of graphene nanopores,” PNAS, vol. 109, pp. 5953–5957, Apr. 2012.
- [28] H. M. Hegab and L. Zou, “Graphene oxide-assisted membranes: Fabrication and potential applications in desalination and water purification,” Journal of Membrane Science, vol. 484, pp. 95–106, June 2015.
- [29] S. Liu, T. H. Zeng, M. Hofmann, E. Burcombe, J. Wei, R. Jiang, J. Kong, and Y. Chen, “Antibacterial Activity of Graphite, Graphite Oxide, Graphene Oxide, and Reduced Graphene Oxide: Membrane and Oxidative Stress,” ACS Nano, vol. 5, pp. 6971–6980, Sept. 2011.
- [30] Z. He, J. Zhou, X. Lu, and B. Corry, “Bioinspired Graphene Nanopores with Voltage-Tunable Ion Selectivity for Na<sup>+</sup> and K<sup>+</sup>,” ACS Nano, vol. 7, pp. 10148–10157, Nov. 2013.
- [31] D. Cohen-Tanugi, L.-C. Lin, and J. Grossman, “Multilayer Nanoporous Graphene Membranes for Water Desalination,” Nano Lett., vol. 16, pp. 1027–1033, Jan. 2016.
- [32] Y. Wei, Y. Zhang, X. Gao, Z. Ma, X. Wang, and C. Gao, “Multilayered graphene oxide membranes for water treatment: A review,” Carbon, vol. 139, pp. 964–981, Nov. 2018.
- [33] L. Zhang, J. Liang, Y. Huang, Y. Ma, Y. Wang, and Y. Chen, “Size-controlled synthesis of graphene oxide sheets on a large scale using chemical exfoliation,” Carbon, vol. 47, pp. 3365–3368, Nov. 2009.
- [34] S. Homaigohar and M. Elbahri, “Graphene membranes for water desalination,” NPG Asia Mater., vol. 9, pp. e427–e427, Aug. 2017.
- [35] S. Iijima, “Helical microtubules of graphitic carbon,” Nature, vol. 354, pp. 56–58, Nov. 1991.
- [36] L. F. Sun, S. S. Xie, W. Liu, W. Y. Zhou, Z. Q. Liu, D. S. Tang, G. Wang, and L. X. Qian, “Creating the narrowest carbon nanotubes,” Nature, vol. 403, pp. 384–384, Jan. 2000.
- [37] G. Hummer, J. C. Rasaiah, and J. P. Noworyta, “Water conduction through the hydrophobic channel of a carbon nanotube,” Nature, vol. 414, no. 6860, pp. 188–190, 2001.
- [38] S. Joseph and N. R. Aluru, “Why are carbon nanotubes fast transporters of water?,” Nano letters, vol. 8, no. 2, pp. 452–8, 2008.
- [39] A. Kalra, S. Garde, and G. Hummer, “Osmotic water transport through carbon nanotube membranes,” Proc Natl Acad Sci U S A, vol. 100, pp. 10175–10180, Sept. 2003.
- [40] J. K. Holt, H. G. Park, Y. Wang, M. Stadermann, A. B. Artyukhin, C. P. Grigoropoulos, A. Noy, and O. Bakajin, “Fast Mass Transport Through Sub-2-Nanometer Carbon Nanotubes,” Science, vol. 312, pp. 1034–1037, May 2006.

- [41] F. Fornasiero, H. G. Park, J. K. Holt, M. Stadermann, C. P. Grigoropoulos, A. Noy, and O. Bakajin, "Ion exclusion by sub-2-nm carbon nanotube pores.," Proceedings of the National Academy of Sciences of the United States of America, vol. 105, no. 45, pp. 17250–17255, 2008.
- [42] N. G. Sahoo, S. Rana, J. W. Cho, L. Li, and S. H. Chan, "Polymer nanocomposites based on functionalized carbon nanotubes," Progress in Polymer Science, vol. 35, pp. 837–867, July 2010.
- [43] S. Kim, L. Chen, J. K. Johnson, and E. Marand, "Polysulfone and functionalized carbon nanotube mixed matrix membranes for gas separation: Theory and experiment," Journal of Membrane Science, vol. 294, pp. 147–158, May 2007.
- [44] E. M. V. Hoek, M. T. M. Pendergast, and A. K. Ghosh, "Nanotechnology-Based Membranes for Water Purification," in Nanotechnology Applications for Clean Water (Second Edition) (A. Street, R. Sustich, J. Duncan, and N. Savage, eds.), Micro and Nano Technologies, pp. 133–154, Oxford: William Andrew Publishing, Jan. 2014.
- [45] S. M. Auerbach, K. A. Carrado, and P. K. Dutta, eds., Handbook of zeolite science and technology. New York: M. Dekker, 2003. OCLC: ocm52850544.
- [46] Y. Li, T.-S. Chung, and S. Kulprathipanja, "Novel Ag+-zeolite/polymer mixed matrix membranes with a high CO<sub>2</sub>/CH<sub>4</sub> selectivity," AIChE Journal, vol. 53, no. 3, pp. 610–616, 2007.
- [47] M. Pendergast and E. M.V. Hoek, "A review of water treatment membrane nanotechnologies," Energy & Environmental Science, vol. 4, no. 6, pp. 1946–1971, 2011.
- [48] L. Li, J. Dong, T. M. Nenoff, and R. Lee, "Desalination by Reverse Osmosis Using MFI Zeolite Membranes," J. Membr. Sci., vol. 243, pp. 401–404, Nov. 2004.
- [49] M. C. Duke, J. O'Brien-Abraham, N. Milne, B. Zhu, J. Y. S. Lin, and J. C. Diniz da Costa, "Seawater desalination performance of MFI type membranes made by secondary growth," Separation and Purification Technology, vol. 68, pp. 343–350, Aug. 2009.
- [50] I. Kumakiri, T. Yamaguchi, and S.-i. Nakao, "Application of a Zeolite A Membrane to Reverse Osmosis Process," Journal of Chemical Engineering of Japan, vol. 33, no. 2, pp. 333–336, 2000.
- [51] H. Furukawa, K. E. Cordova, M. O'Keeffe, and O. M. Yaghi, "The Chemistry and Applications of Metal-Organic Frameworks," Science, vol. 341, Aug. 2013.
- [52] D. Feng, W.-C. Chung, Z. Wei, Z.-Y. Gu, H.-L. Jiang, Y.-P. Chen, D. J. Darensbourg, and H.-C. Zhou, "Construction of Ultrastable Porphyrin Zr Metal–Organic Frameworks through Linker Elimination," J. Am. Chem. Soc., vol. 135, pp. 17105–17110, Nov. 2013.
- [53] K. Wang, H. Huang, W. Xue, D. Liu, X. Zhao, Y. Xiao, Z. Li, Q. Yang, L. Wang, and C. Zhong, "An ultrastable Zr metal–organic framework with a thiophene-type ligand containing methyl groups," CrystEngComm, vol. 17, no. 19, pp. 3586–3590, 2015.
- [54] J.-R. Li, J. Sculley, and H.-C. Zhou, "Metal–Organic Frameworks for Separations," Chem. Rev., vol. 112, pp. 869–932, Feb. 2012.
- [55] X. Zhang, Y. Gao, H. Liu, and Z. Liu, "Fabrication of porous metal–organic frameworks via a mixed-ligand strategy for highly selective and efficient dye adsorption in aqueous solution," CrystEngComm, vol. 17, no. 31, pp. 6037–6043, 2015.

- [56] Y. S. Seo, N. A. Khan, and S. H. Jhung, "Adsorptive removal of methylchlorophenoxypropionic acid from water with a metal-organic framework," Chemical Engineering Journal, vol. 270, pp. 22–27, June 2015.
- [57] Z. Li, Y.-n. Wu, J. Li, Y. Zhang, X. Zou, and F. Li, "The Metal–Organic Framework MIL-53(Al) Constructed from Multiple Metal Sources: Alumina, Aluminum Hydroxide, and Boehmite," Chemistry – A European Journal, vol. 21, no. 18, pp. 6913–6920, 2015.
- [58] Z. Hasan, J. Jeon, and S. H. Jhung, "Adsorptive removal of naproxen and clofibric acid from water using metal-organic frameworks," Journal of Hazardous Materials, vol. 209–210, pp. 151–157, Mar. 2012.
- [59] E. M. Dias and C. Petit, "Towards the Use of Metal–Organic Frameworks for Water Reuse: A Review of the Recent Advances in the Field of Organic Pollutants Removal and Degradation and the Next Steps in the Field," J. Mater. Chem. A., vol. 3, no. 45, pp. 22484–22506, 2015.
- [60] X. Feng, M. E. Tousley, M. G. Cowan, B. R. Wiesenauer, S. Nejati, Y. Choo, R. D. Noble, M. Elimelech, D. L. Gin, and C. O. Osuji, "Scalable Fabrication of Polymer Membranes with Vertically Aligned 1 nm Pores by Magnetic Field Directed Self-Assembly," ACS Nano, vol. 8, pp. 11977–11986, Dec. 2014.
- [61] X. Feng, S. Nejati, M. G. Cowan, M. E. Tousley, B. R. Wiesenauer, R. D. Noble, M. Elimelech, D. L. Gin, and C. O. Osuji, "Thin Polymer Films with Continuous Vertically Aligned 1 nm Pores Fabricated by Soft Confinement," ACS Nano, vol. 10, pp. 150–158, Jan. 2016.
- [62] X. Feng, K. Kawabata, G. Kaufman, M. Elimelech, and C. O. Osuji, "Highly Selective Vertically Aligned Nanopores in Sustainably Derived Polymer Membranes by Molecular Templating," ACS Nano, vol. 11, pp. 3911–3921, Apr. 2017.
- [63] P. Mariani, V. Luzzati, and H. Delacroix, "Cubic phases of lipid-containing systems: Structure analysis and biological implications," Journal of Molecular Biology, vol. 204, pp. 165–189, Nov. 1988.
- [64] B. A. Pindzola, J. Jin, and D. L. Gin, "Cross-Linked Normal Hexagonal and Bicontinuous Cubic Assemblies via Polymerizable Gemini Amphiphiles," J. Am. Chem. Soc., vol. 125, pp. 2940–2949, Mar. 2003.
- [65] B. R. Wiesenauer and D. L. Gin, "Nanoporous polymer materials based on self-organized, bicontinuous cubic lyotropic liquid crystal assemblies and their applications," Polym J, vol. 44, pp. 461–468, June 2012.
- [66] E. S. Hatakeyama, B. R. Wiesenauer, C. J. Gabriel, R. D. Noble, and D. L. Gin, "Nanoporous, Bicontinuous Cubic Lyotropic Liquid Crystal Networks via Polymerizable Gemini Ammonium Surfactants," Chem. Mater., vol. 22, pp. 4525–4527, Aug. 2010.
- [67] M. Zhou, P. R. Nemade, X. Lu, X. Zeng, E. S. Hatakeyama, R. D. Noble, and D. L. Gin, "New Type of Membrane Material for Water Desalination Based on a Cross-Linked Bicontinuous Cubic Lyotropic Liquid Crystal Assembly," J. Am. Chem. Soc., vol. 129, pp. 9574–9575, Aug. 2007.

- [68] B. M. Carter, B. R. Wiesenauer, E. S. Hatakeyama, J. L. Barton, R. D. Noble, and D. L. Gin, "Glycerol-Based Bicontinuous Cubic Lyotropic Liquid Crystal Monomer System for the Fabrication of Thin-Film Membranes with Uniform Nanopores," Chem. Mater., vol. 24, pp. 4005–4007, Nov. 2012.
- [69] H. Vinh-Thang and S. Kaliaguine, "Predictive Models for Mixed-Matrix Membrane Performance: A Review," Chem. Rev., vol. 113, pp. 4980–5028, July 2013.
- [70] J. Geens, B. Van der Bruggen, and C. Vandecasteele, "Transport Model for Solvent Permeation Through Nanofiltration Membranes," Sep. Purif. Technol., vol. 48, pp. 255–263, Mar. 2006.
- [71] S. Darvishmanesh and B. Van der Bruggen, "Mass Transport through Nanostructured Membranes: Towards a Predictive Tool," Membranes, vol. 6, Dec. 2016.
- [72] J. G. Wijmans and R. W. Baker, "The solution-diffusion model: a review," Journal of Membrane Science, vol. 107, pp. 1–21, Nov. 1995.
- [73] D. R. Paul, "Diffusive Transport in Swollen Polymer Membranes," in Permeability of Plastic Films and Coatings: To Gases, Vapors, and Liquids (H. B. Hopfenberg, ed.), Polymer Science and Technology, pp. 35–48, Boston, MA: Springer US, 1974.
- [74] C. Manzo and M. F. Garcia-Parajo, "A Review of Progress in Single Particle Tracking: From Methods to Biophysical Insights," Rep. Prog. Phys., vol. 78, p. 124601, Oct. 2015.
- [75] B. J. Coscia and M. R. Shirts, "Chemically Selective Transport in a Cross-Linked HII Phase Lyotropic Liquid Crystal Membrane," J. Phys. Chem. B, June 2019.
- [76] E. J. Maginn, R. A. Messerly, D. J. Carlson, D. R. Roe, and J. R. Elliott, "Best Practices for Computing Transport Properties 1. Self-Diffusivity and Viscosity from Equilibrium Molecular Dynamics [Article v1.0]," LiveCoMS, vol. 1, no. 1, pp. 6324–, 2018.
- [77] S. M. Dischinger, M. J. McGrath, K. R. Bourland, R. D. Noble, and D. L. Gin, "Effect of Post-Polymerization Anion-Exchange on the Rejection of Uncharged Aqueous Solutes in Nanoporous, Ionic, Lyotropic Liquid Crystal Polymer Membranes," J. Membr. Sci., vol. 529, pp. 72–79, May 2017.
- [78] R. Resel, G. Leising, P. Markart, M. Kriechbaum, R. Smith, and D. Gin, "Structural properties of polymerised lyotropic liquid crystals phases of 3,4,5-tris( $\omega$ -acryloxyalkoxy)benzoate salts," Macromol. Chem. Phys., vol. 201, pp. 1128–1133, July 2000.
- [79] M. Zhou, T. J. Kidd, R. D. Noble, and D. L. Gin, "Supported Lyotropic Liquid-Crystal Polymer Membranes: Promising Materials for Molecular-Size-Selective Aqueous Nanofiltration," Adv. Mater., vol. 17, pp. 1850–1853, Aug. 2005.
- [80] E. S. Hatakeyama, C. J. Gabriel, B. R. Wiesenauer, J. L. Lohr, M. Zhou, R. D. Noble, and D. L. Gin, "Water Filtration Performance of a Lyotropic Liquid Crystal Polymer Membrane with Uniform, Sub-1-Nm Pores," J. Membr. Sci., vol. 366, no. 1-2, pp. 62–72, 2011.
- [81] J. Mondal, M. Mahanthappa, and A. Yethiraj, "Self-Assembly of Gemini Surfactants: A Computer Simulation Study," J. Phys. Chem. B, vol. 117, pp. 4254–4262, Apr. 2013.

- [82] S. Mantha and A. Yethiraj, “Dynamics of Water Confined in Lyotropic Liquid Crystals: Molecular Dynamics Simulations of the Dynamic Structure Factor,” J. Chem. Phys., vol. 144, p. 084504, Feb. 2016.
- [83] S. Roy, D. Skoff, D. V. Perroni, J. Mondal, A. Yethiraj, M. K. Mahanthappa, M. T. Zanni, and J. L. Skinner, “Water Dynamics in Gyroid Phases of Self-Assembled Gemini Surfactants,” J. Am. Chem. Soc., vol. 138, pp. 2472–2475, Mar. 2016.
- [84] G. L. Jackson, S. Mantha, S. A. Kim, S. O. Diallo, K. W. Herwig, A. Yethiraj, and M. K. Mahanthappa, “Ion-Specific Confined Water Dynamics in Convex Nanopores of Gemini Surfactant Lyotropic Liquid Crystals,” J. Phys. Chem. B, vol. 122, pp. 10031–10043, Nov. 2018.
- [85] S. Mantha, G. L. Jackson, M. K. Mahanthappa, and A. Yethiraj, “Counterion-Regulated Dynamics of Water Confined in Lyotropic Liquid Crystalline Morphologies,” J. Phys. Chem. B, vol. 122, pp. 2408–2413, Mar. 2018.
- [86] T. Sakamoto, T. Ogawa, H. Nada, K. Nakatsuji, M. Mitani, B. Soberats, K. Kawata, M. Yoshio, H. Tomioka, T. Sasaki, M. Kimura, M. Henmi, and T. Kato, “Development of Nanostructured Water Treatment Membranes Based on Thermotropic Liquid Crystals: Molecular Design of Sub-Nanoporous Materials,” Advanced Science, vol. 5, no. 1, p. 1700405, 2018.
- [87] H. Nada, T. Sakamoto, M. Henmi, T. Ogawa, M. Kimura, and T. Kato, “Transport mechanisms of water molecules and ions in sub-nano channels of nanostructured water treatment liquid-crystalline membranes: a molecular dynamics simulation study,” Environmental Science: Water Research & Technology, 2020.
- [88] B. J. Coscia, J. Yelk, M. A. Glaser, D. L. Gin, X. Feng, and M. R. Shirts, “Understanding the Nanoscale Structure of Inverted Hexagonal Phase Lyotropic Liquid Crystal Polymer Membranes,” J. Phys. Chem. B, vol. 123, pp. 289–309, Jan. 2019.