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

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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 counter ions. 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.

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Contents

Chapter

Appendix

Tables

Table

Figures

Figure

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. [1]

- Sediment, bacteria, algae, proteins, small organic molecules, and ions are all common components of aqueous streams. [2]

- 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. [3]

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. [4]

- Ultrafiltration (UF) membranes have pore diameters of about 5-500 nm and are useful for the separation of sugars, proteins, viruses and colloidal materials. [5]

- 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. [6]

- 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. [7]

- 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. [8]

- 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. [2]

- Increasing permeabilities beyond those already achieved may have only a small effect on energy requirements and capital costs.

- Cohen-Tanugi *et al.* calculated that a theoretical tripling of membrane permeability would only reduce energy consumption by up to 15% in a seawater RO plant. [9]
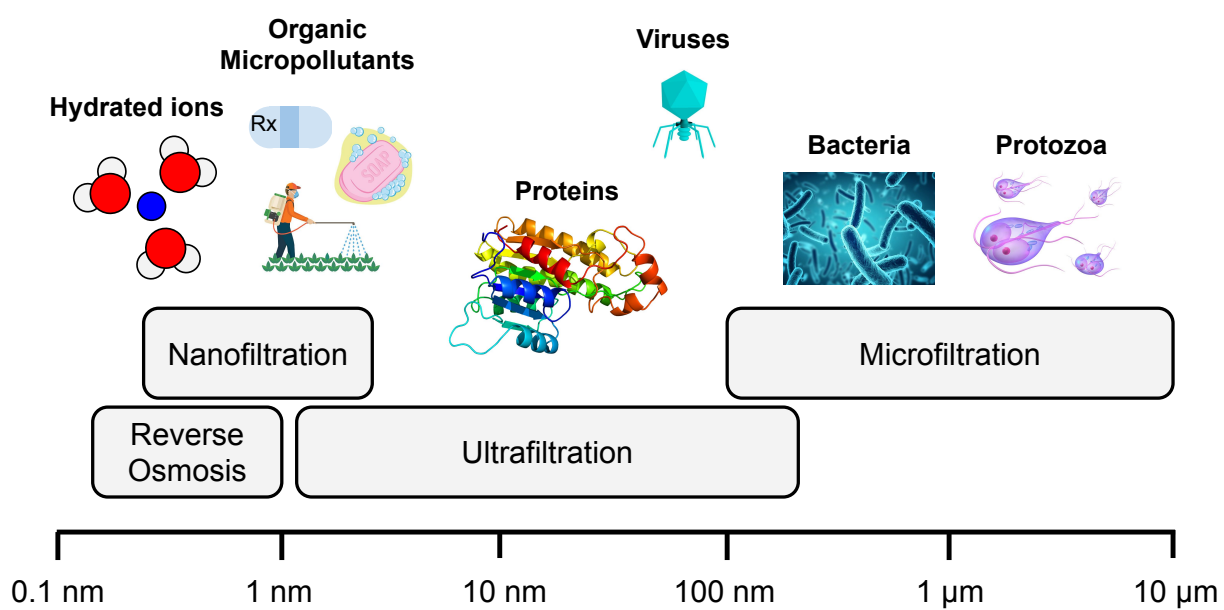
Figure 1.1: Caption of the future

- Perhaps the biggest detriment to energy consumption is the practical need for multiple membrane passes in order to achieve a desired purity. [10]

- Additionally, many membranes are not suited for high purity separations of small neutral species which necessitates chemical and capital costs for post-treatment. [11, 12]

- Addressing these problems with highly selective separations may lead to more gains. [13]

1.1.1   Applications of Selective Membranes

Selective separations are useful in a wide range of applications. They can be used to separate components in both gaseous and aqueous phases. [14]. We will focus this section on aqueous separations since they are the target process for the following studies.

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

- It is estimated that by 2025, 1.8 billion people may live in water-stressed regions. [15]

- Membrane deslination via RO and thermal muli-stage flash distillation are both widely used processes for creating potable water in these regions. [12]

- Compared with thermal distillation techniques, RO has been shown to be more environmentally friendly and economical due to its lower energy requirements.[16]

- However, thermal techniques are still preferred where excess waste heat or cheap thermal energy is available, such as cogeneration plants.[17]

Organic Micropollutants: Municipal and industrial wastewaters are contaminated by harmful micropollutants, which can have adverse effects on human health even at low concentrations.[18]

- Micropollutants include pharmaceuticals, personal care products, hormones, pesticides and industrial chemicals which find their way into our drinking water supply. [19]

- Sources of micropollutants incude industrial wastewater, agricultural runoff, landfill leachates and domestic effluents. [20]

- Unfortunately, most waste water treatment plants are not designed for complete removal of these contaminants. [21]

- There is a need for a new generation of membranes that can better target specific molecules.

Recovery of Valuable Dissolved Species: In addition to removing contaminants to clean waste water, we can also use highly selective membranes in order to recover potentially valuable dissolved species from complex municipal and industrial waste streams. [22, 23]

Municipal waste-waters are rich in carbon, nitrogen and phosphorus-containing compounds. [24]

- The recovery of such products, which can be achieved using a selective membrane, has numerous potential uses.[25]

- For example, nitrogen and phosphorus recovery can help sustain fertilizer production which will help meet global food demand as population continues to increase.[26]

Industrial waste-waters are often quite complex with up to six times more total dissolved solids than seawater.[2]

- For example, flowback water, produced during hydraulic fracturing of shale formations consists of relatively high concentrations of salts, metals, and soluble organic compounds. [27]

- 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. [28]

- Some of the dissolved organic compounds in flowback water, such as acetate, are potentially valuable and can be recovered with highly selective membranes [29].

1.2   Historical Development of Membrane Technology

Membranes for separations are a relatively young technology. Over the past 60 years, the field has grown into a commercially viable technology and the focus has shifted primarily towards incremental improvements in performance and most importantly, targeted separations. This section will briefly cover a subset of the most relevant membrane technologies which have ultimately inspired this thesis.

1.2.1   Reverse Osmosis Membranes

The first aqueous separations membranes were developed for RO applications in the 1960s and were made of the amorphous polymer cellulose acetate (CA). [30]

- Reid and Spencer were among the first to show the ability of these membranes to reject NaCl to high degrees ($\sim$ 99 %) while subject to high applied pressures (270 atm). [31]

- The most limiting drawback to CA membranes is their chemical instability, undergoing severe hydrolysis at pH values outside the range 4–6. [32]

Amorphous thin film composite (TFC) polyamide membranes are the current industry standard for high purity RO separations. [33]

- Developed in the 1980s, polyamide membranes are capable of rejecting salt to a higher degree and can operate at wider pH ranges and higher feed pressures than CA membranes. [34]

- TFC polyamide membranes are typically formed by the interfacial polymerization 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. [35]

The dense polyamide selective layers of TFC membranes require high feed pressures, in the range of 5 – 120 bar, in order to achieve a useful permeate flux. [6]

- While the energy requirements to attain these pressures are still less than the energy requirements of thermal distillation[16], it is often desirable to create membranes that can operate at lower feed pressures.

- 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 membranes containing larger pores.

- This has driven research into nanofiltration.

1.2.2   Nanofiltration Membranes

Since their introduction in the late 1980s, NF membranes have been applied towards an increasing number of separations since they bridge the gap in capabilities between reverse osmosis and ultrafiltration. [36]

- Nanofiltration membranes have pores on the order of 1 nm in size.

- Larger pore sizes allow lower operating pressures (3 – 20 bar) which lowers energy consumption. [6]

- An ideal NF membrane should have densely packed, uniform-sized and non-tortuous pores. [37] This combination has been practically difficult to realize.

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

- NF membranes created by interfacial polymerization are made similarly to RO membranes. By modifying the monomer materials, one can control the structural morphology in order to create pores larger than those in RO membranes. [38]

- 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. [39]

- Although commercially dominant, both of these techniques suffer from tortuous pores and polydisperse pore sizes which results in far from ideal selectivities.

Track-etching is another NF fabrication 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. [40]

- Although the pores are uniform and non-tortuous, benefiting selectivity, the membranes have an extremely low pore density and 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 of explorations into different kinds of technologies for this application.

Graphene and graphene oxide 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. [41]

- 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. [42]

- Controllably-sized pores have been created in pristine graphene by plasma etching and by charged particle bombardment. [43, 44]

- Graphene oxide (GO), a highly oxidized modification of graphene, consist of epoxy, hydroxyl and carboxylate functional groups. [45]

- 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. [46, 47]

- Despite their promise, scalable synthesis of monolayer graphene and GO membranes without introducing microscopic, performance degrading defects has not yet been achieved. [48, 49]

- Multilayered GO membranes have shown considerably more progress since their synthesis procedures are low cost and scalable. [50]

- GO sheets are particularly easy to make into multilayered membranes since they stack on top of each other, held together by hydrogen bonds. [51]

- 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. [49]

Carbon nanotubes: Carbon nanotubes (CNTs) have shown promise as aqueous separations membranes due to unprecedentedly fast water transport.[41]

- CNTs are an allotrope of carbon consisting of tubular graphitic layers. [52]

- One can control CNT diameters down to 0.5 nm in size which has inspired the creation of CNT membranes for reverse osmosis applications. [53]

- Molecular dynamics simulations have predicted and experiments have confirmed that CNTs are extremely fast transporters of water. [54, 55]

- MD simulations by Kalra *et al.* predicted water transport at rates comparable to the transmembrane protein aquaporin-1. [56]

- Experiments have exhibited water transport rates orders of magnitude higher than predictions by continuum modeling. [57]

- This enhancement has been explained as a result of nearly friction-less single-file water flow through the hydrophobic CNT interiors. [56]

- Functionalization of the CNT pore entrances can potentially lead to highly selective separations. [58]

- Practically, dispersing and aligning CNTs into a polymer matrix is extremely difficult because they tend to agglomerate due to van der Waals forces. [59]

- 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. [60]

Zeolites: Zeolite membranes offer the potential for permeabilities comparable to ultrafiltration, with selectivities as good as NF and RO. [61]

- 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. [62]

- One can replace the silicon and aluminum atoms via ion exchange in order to control the size of the cavities and hence its molecular-seiving properties. [63]

- 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. [64]

- A number of studies have tested the permeability and sodium salt rejection of various zeolite membranes, however their high permeabilities typcially come at the cost of low selectivities and vice versa. [65, 66]

- Zeolites are also prone to defects in the crystalline structure which would require substantial modification to the traditional synthesis procedures in order to fix. [67]

Metal organic frameworks: 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. [68]

- There is a much wider breadth of research into MOFs as gas separation membranes because they tend to be unstable in water. [69]

- But a new generation of water-stable MOFs is making it possible to use them in aqueous separations. [70]

- Purification of both aqueous and gaseous streams using MOFs are typically achieved by selective adsorption or catalytic degradation. [71]

- MOFs have been applied towards the removal of a number of common water contaminants including dyes, pesticides, endocrine disruptors, and pharmaceuticals. [72, 73, 74, 75]

- 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. [76]

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

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

- People are particularly interested in self-assembled materials because they offer the potential of uniform-sized pores and tunable chemical and physical properties. [2]

- There are two major classes of self-assembled amphiphilic materials: block copolymers and liquid crystals.

Block copolymers contain more than one distinct repeating unit which facilitates the formation of self-assembled structures based on differences in the subunit amphiphilicity. [37]

- Block copolymer membranes typically have pores on the order of 5-50 nm which makes them useful for UF applications, however there is progress being made towards smaller pores in the NF regime. [77]

Under the right conditions, the shape and amphiphilic character of liquid crystal monomers drives their self-assembling into ordered nanostructures with uniform-sized pores on the order of 1 nm in size. [78]

- They have been used as membranes before. [79]

- As shown in Figure TBD, monomer 1 will form the inverted hexagonal phase (H_{II}) [80] while monomer 2 will form the bicontinuous cubic phase (Q_I) [81]

- 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.

- We chose to study liquid crystals because they are already suitable as NF membranes and there has been sufficient experimental characterization. [79, 82, 83]

1.3.1 The H_{II} Phase

The H_{II} phase is characterized by hexagonally packed, uniform-sized and straight pores. [80]

- 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.

- The inhomogeneity of the pores suggests that the effective pore size may depend on the solute. Both the size, shape and chemical functionality will influence how a solute partitions within the membrane.

- 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. [84]

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

- Feng *et al.* leveraged the magnetic anisotropy of the columnar mesophases in order to control their alignment with a magnetic field. [82]

- This study showed an 85-fold increase in ionic conductivity in the aligned versus unaligned state, demonstrating a huge increase in feasibility as an industrial membrane.

- 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. [83]

- 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. [85]

- Aligned hexagonal phase membranes exhibited an 85 fold increase in ionic conductivity. [82]

1.3.2 The Q_I Phase

The bicontinuous cubic, or Q_I phase, is a class of nanostructured phases characterized by a network of 3 dimensionally interconnected pores. [86]

- 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. [87]

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. [88]

- Of these, only 4 are consistent with diffraction data generated by the gemini surfactant used here. [89]

- Q^{230} (Ia3d), Q^{224} (Pn3m), Q^{229} (Im3m) or Q^{212} (P4$_3$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 [88, 90]

- 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. [89]

- 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. [91]

- 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 hotpressing 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. [87]

- 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 supports. This improvement resulted in a ten-fold increase in flux while retaining selectivities similar to earlier generations. [81]

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 [29].

- 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. [92, 93, 94] 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. [95] Analogously, pore-flow models yield predictions of diffusion coefficients and

solute transport rates in nanoporous membranes. [96] Modern single particle tracking approaches have taken researchers beyond continuum modeling allowing them to characterize complex diffusive behavior. [97] 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. [98, 99] 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:

$$J_i = -L_i \frac{d\mu_i}{dx} \tag{1.1}$$

  where L_i is a coefficient of proportionality. [95]

- L_i is an intrinsic materials property dependent on ...

- Chemical potential gradients can be induced by concentration, pressure, temperature and electromotive forces.

- We will limit our discussion to concentration and pressure gradients because these are primarily forces used for separations with the types of membranes we will be studying.

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

$$J_w = A(\Delta P - \Delta \pi_m) \tag{1.2}$$

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

In porous membrane architectures, water and solute flux are modeled as laminar flow through cylindrical pores.

- The derivation follows Hagen-Poiseuille flow with inclusion of morphological characteristics: [33]

$$A = \frac{\varepsilon r_p^2}{8\mu\delta_m} \tag{1.3}$$

  where ε is the surface porosity, r_p the pore radius, δ_m the membrane thickness, and μ the solution viscosity.

- Solute flux, J_s is related to J_w but scaled by the empirically measured permeate concentration:

$$J_s = c_p J_w \tag{1.4}$$

- Analytical expressions for solute flux, such as the Donnan Steric Pore Model (DSPM), are typically quite complicated because they attempt to incorporate more system features leading to less assumptions. [100]

Solute rejection is the quantity typically used to characterize the performance of a filtration membrane.

- Under the pore flow model, solutes with radii smaller than the pore will not pass through the membrane.

- A membrane with uniform-sized pores smaller than the solute being targeted for separation should have a solute flux of 0. However, in practice, most membranes have a distribution of pore sizes, some large enough to allow solutes to pass.

- Therefore, separation performance is typically characterized in terms of solute rejection, R.

$$R = 1 - \frac{c_p}{c_f} \tag{1.5}$$

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

- The DSPM has been used to directly predict rejection. [101, 100]

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. [95]

- P is an intrinsic material property and is thus independent of membrane thickness.

- The water permeability coefficient, A, *is* dependent on thickness, δ_m, and can be formulated in terms of the pure water permeability, P_w.

-

$$A = \frac{P_w V_w}{\delta_m R_g T} \tag{1.6}$$

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

- Solute flux is modeled as:

$$J_s = \frac{P_s}{\delta_m} \Delta c_m = B \Delta c_m \tag{1.7}$$

where B is a solute permeability coefficient and Δc_m is the concentration difference across the selective membrane layer. [102]

- Under these assumptions, rejection can be reformulated as

$$R = \frac{A}{A + B} \tag{1.8}$$

which approaches unity as the solute flux tends towards zero. [6]

These equations provide a somewhat limited perspective on the molecular details of transport.

- The pore flow model neglects molecular level interactions with the membrane and assumes all transport occurs within the cylindrical pore region. In this work, we will show that solutes are not confined to the "pore region" and that motion is heavily influenced by interactions with membrane.

- The solution-diffusion model assumes that solutes undergo Brownian motion. As will be discussed, solutes appear to undergo subdiffusive behavior on short timescales.

- Therefore, we may need a more descriptive theory in order to appropriately address questions of membrane design.

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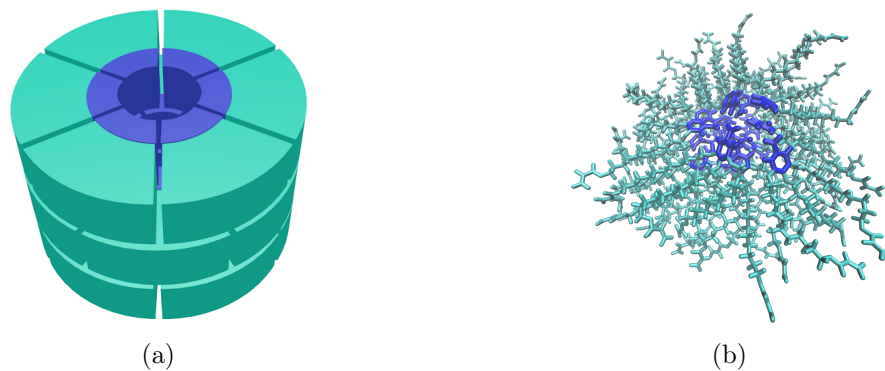
Figure 1.2: (a) Previous understanding of the LLC pores are essentially speculations based on limited chemical and experimental data. (b) We use detailed molecular modeling in this paper in order to appropriately model the pore's complex architecture, which is crucial to understanding the mechanism of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

Although the Q_I 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.[103]

- 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. [104, 105]

- 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. [106, 107]

- 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. [108, 109]

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 promsiing 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 my 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. [110]

Chapter 3: adapted from manuscript entitled "Chemically Selective Transport in a Cross-Linked H_{II} Phase Lyotropic Liquid Crystal Membrane." published in the Journal of Physical Chemistry B. [98]

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.

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