

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

by

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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.

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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 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.

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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.

Membrane design is completely dependent on the target particle separation.

- Membranes are classified based on the size of the particle they reject.
- Microfiltration membranes contain pores with diameters ranging from 100-10000 nm. They can separate large particles like bacteria and protozoa. [1]
- Ultrafiltration membranes have pore diameters of about 5-500 nm and are useful for the separation of sugars, proteins, viruses and colloidal materials. [2]
- Nanofiltration 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 membranes are dense amorphous polymers with no explicit pores. 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 different classes of membrane technologies in Figure 1.1.
- To deal with complex aqueous streams, and to prevent excessive membrane fouling, these technologies are often used in series, removing larger particles first. [5]

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. [6]

- 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, ΔP 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:

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

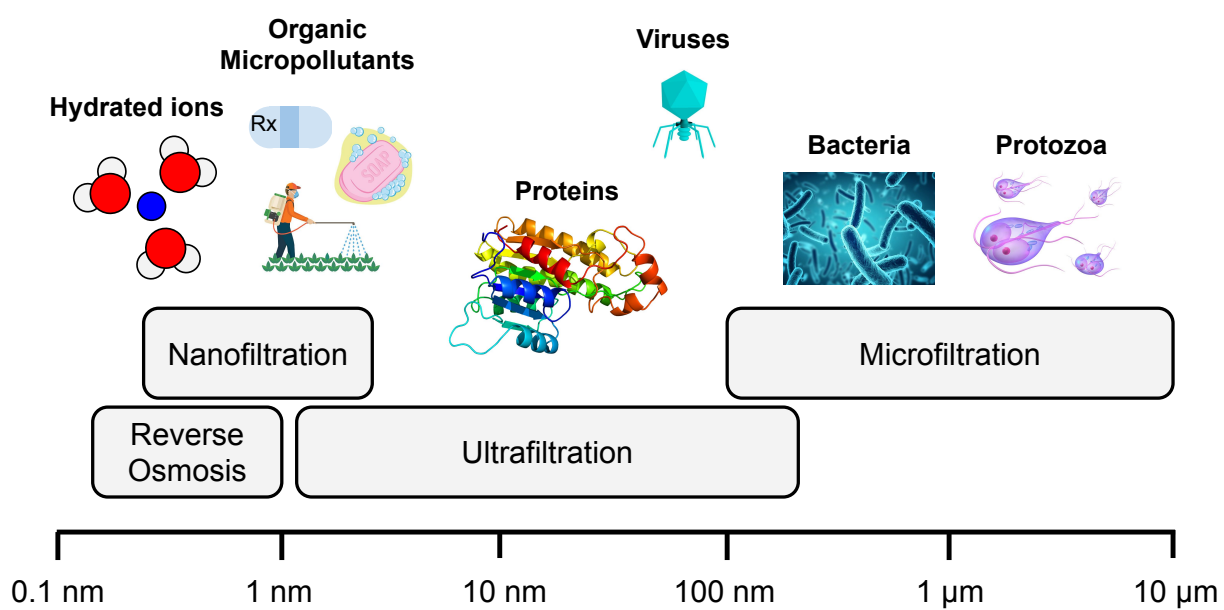


Figure 1.1

where ε is the surface porosity, r_p the pore radius, δ_m the membrane thickness, and μ 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 . [6]
- P is an intrinsic material property and is thus independent of membrane thickness.
- The water permeability coefficient *is* dependent on thickness, δ_m , and can be formulated in terms of the pure water permeability, P_w .
-

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

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 Δc_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.

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.

- 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. [7]
- 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.[?]

- Thermal techniques are still preferred where excess waste heat or cheap thermal energy is available, such as cogeneration plants.[?]
- 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[8]

- 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.[9]
- For example, nitrogen and phosphorus recovery can help sustain fertilizer production which will help meet global food demand as population continues to increase.[10]

Industrial waste-waters are often quite complex with up to six times more total dissolved solids than seawater[11].

- 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 [12].
- Some of the dissolved organic compounds in flowback water, such as acetate, are potentially valuable and can be recovered with highly selective membranes [13].

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 Amorphous Membranes

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

- Desalination, concentration
- Typically you have a porous support layer for mechanical strength and very thin active layer where the separations occur.
- Usually only let water through. Usually have to remineralize the water to make it drinkable.

Operation requires high feed pressures. (5 - 120 bar) [3]

1.2.2 Standard Nanofiltration Membranes

Unlike RO membranes, NF membranes have explicitly defined pores. An ideal NF membrane should have densely packed, uniform-sized and non-tortuous pores. This combination has been very difficult to realize.

NF membranes are typically made by a phase-inversion process. The most widely used phase-inversion process is immersion precipitation.

- During which 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 [14].
- The resultant pores are polydisperse in size, which hurts membrane selectivity.

A second technique used to create NF membranes is called track-etching in which a polymer film is bombarded with charged particles, then chemically etched to create pores [15]. The pores are uniform, which benefits selectivity; however, the membranes have a low porosity and subsequently low permeability.

Explicitly defined pores allow lower feed pressures (3 - 20 bar), [3] however, polydispersity in pore size lowers their selectivity relative to RO.

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.

Ultrathin-film graphene and graphene oxide membranes are an active area of research because they are atomically thick and therefore offer potential for extremely high permeability membranes. [16]

- However, scalable synthesis without introducing microscopic, performance degrading defects has not yet been achieved. [17, 18]

Carbon nanotubes (CNTs) have shown promise as aqueous separations membranes due to unprecedentedly fast water transport.[16, 19]

- Practically, dispersing and aligning CNTs into a polymer matrix is extremely difficult because they tend to agglomerate due to Van der Waals forces. [20]

- Some work has been to functionalize the carbon nanotubes in order to better incorporate them.

Zeolite-coated ceramic membranes offer the potential for permeabilities comparable to ultra-filtration, with selectivities as good as NF and RO.

- A number of studies have tested the permeability and sodium salt rejection of various zeolite membranes, however none have fully overcome the permeability-selectivity tradeoff. [21, 22, 23]

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

- They were originally used for gas separations

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

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 study LLC membranes as an alternative nanostructured material 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. [24]
- 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. [25]
- 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. [26]

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. [27]
- Of these, only 4 are consistent with diffraction data generated by the gemini surfactant used here. [28]
- Q^{230} ($Ia3d$), Q^{224} ($Pn3m$), Q^{229} ($Im3m$) or Q^{212} ($P4_332$) 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 [27, 29]
- 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-forming monomers.

- The first generation of Q_I membranes was made by the self-assembly of a gemini phosphonium monomer in water. [28]
- 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. [30]
- 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. [31]

- 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. [32]

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 [13].
- 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 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_I -phase LLC membrane to solute rejection[33]. 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_{II} -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 [34]. In a later study of rejection performance, it was shown that membranes formed by cross-linked Na-GA3C11 in the H_{II} phase cannot separate solutes less than 1.2 nm in diameter because the pores are too large [35]. 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 [36]. 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.

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.

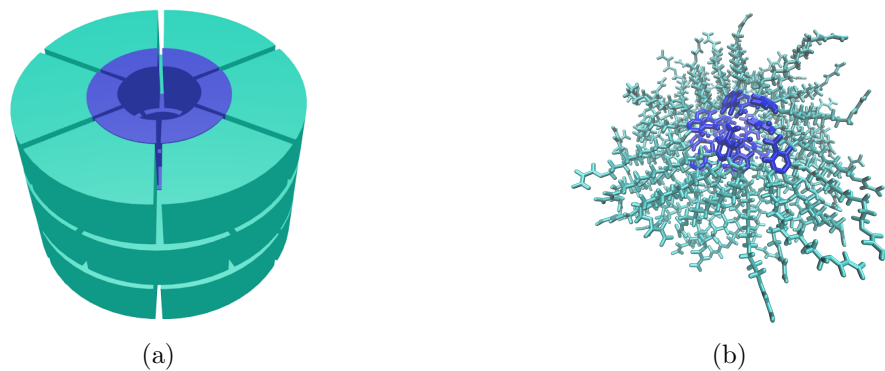


Figure 1.2: (a) Previous understanding of the LLC pores are essentially speculations based on limited chemical and experimental data. (b) We use detailed molecular modeling in this paper in order to appropriately model the pore’s complex architecture, which is crucial to understanding the mechanism of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

- 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.[37]
- 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. [38, 39]
- 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. [40, 41]
- 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. [42, 43]

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 estimate experimentally-relevant macroscopic properties?

- 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 we learn mechanisms with minimal human intervention?

- 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.

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