PhD Research Proposal: Molecular Level Design of Nanoporous Lyotropic Liquid Crystal Membranes for Aqueous Separations

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1 State of the Art

Commercial Membranes for Small Molecule Separations

More highly selective nanoporous membranes would be extremely useful in performing complex aqueous separations with seawater and various types of wastewater.

- For example, Sodium chloride and boron in seawater [1] and organic micropollutants found in municipal and industrial wastewaters [2] represent just a few of the diverse contaminants of water sources.

- By efficiently separating contaminants from feed solutions with highly selective membranes, it is possible to reduce the number of required membrane passes and post-treatment steps needed for a given filtration process [3], thus lowering energy requirements.

- Additionally, one can also extract valuable resources from the feed streams. For example, flowback water produced during hydraulic fracturing of shale formations contains dissolved species such as acetate whose extraction has economic value [4].

Reverse osmosis (RO) and nanofiltration (NF) are two prevailing membrane filtration processes that can be used to separate solutes on the order of 1 nm in size and smaller, including ions.

- Both apply hydraulic pressure to the feed solution in order to overcome osmotic pressure and force water and unfiltered components through the membrane.

- RO membranes are typically thin film composite with a porous mechanical support layer and a thin but dense polymer matrix active layer where separations occur.[5]

- RO separates solutes based on the solute's ability to dissolve into and diffuse through the tortuous pathways available in dense active layer.

- RO offers high selectivity at the cost of relatively high energy requirements since one must apply a large hydraulic pressure in order to achieve an economical flux.

- In contrast to RO membranes, NF membranes have explicit pores on the order of 1 nm in size.

- Typically, separations are achieved based on size exclusion and charge exclusion if the membrane surface is charged.

- NF membranes require significantly less applied pressure in order to achieve solute flux comparable to RO.

- Unfortunately, conventional synthesis processes, such as phase-inversion[6] are stochastic in nature which yields pores that are polydisperse in size.[3]

- Pore size polydispersity is detrimental to membrane selectivity

The downfall of RO and NF membranes can be summarized by the well-known permeability-selectivity tradeoff. Namely, it is difficult to increase the permeability of a desired molecular or atomic species, while maintaining the same retention of an undesired species.[3]

Nanostructured Membranes

Nanostructured membranes attempt to overcome the permeability-selectivity tradeoff through molecular level design.

- Graphene sheets, carbon nanotubes (CNTs) and zeolites are three highly studied nanostructured technologies.

Graphene membranes are an extremely active are of research because they offer potential for extremely high permeability membranes.

- 2D materials

- Functionalization?

- Easy to introduce defects

- Multi-layered

Carbon nanotubes have shown promise due to unprecedentedly fast water transport.

- Functionalization of nanotubes

- Aligned nanotubes difficult to synthesize

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

- 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.

- 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.

- 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.

- Most are prone to defects in the crystalline structure.

Lyotropic Liquid Crystal Membranes

Preliminary evidence has shown that cross-linked lyotropic liquid crystal (LLC) membranes can be produced at moderate scale and may be capable of performing highly selective separations.

- LLCs are amphiphilic molecules that have the ability to self-assemble into porous nanostructures [7] and can be cross-linked to create mechanically strong membrane films with periodic pores on the order of 1 nm in diameter [8].

- LLC membrane pores are uniform in size because they are formed by self-assembly.

- Since LLC polymer membranes lack an appreciable pore size distribution, they inherently exhibit high selectivity due to their strict molecular weight cut-off (MWCO) [8].

- Additionally, LLC monomers can be salts, and therefore lead to Donnan exclusion of ions in solution.[9]

The feasibility of nanostructured LLC polymer membranes for selective separations has been demonstrated using LLC monomers that form the type 1 bicontinuous cubic (Q_I)[10, 11, 12] and the inverted hexagonal (H_{II}) [8] phases.

- 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.[4]

- When separating a series of various sized dyes, the H_{II}-phase membrane showed complete rejection of dyes bigger than 1.2 nm in size [8].

The H_{II}-phase pore geometry (Figure **??**) has a higher theoretical capacity for transport than the Q_I phase.

- The H_{II} phase forms at room temperature in the presence of ca. 10 wt% water and consists of hexagonally packed, hydrophilic pore columns[7].

- In the absence of water, neat monomer will form the same hexagonal columnar structure which, in the literature, has been referred to as the Col_h thermotropic phase[13].

Q_I-phase membranes consist of a tortuous network of three dimensionally interconnected pores that prevent optimal through-plane transport.

- In contrast, the densely packed, non-tortuous and uniform sized pores of H_{II}-phase membranes represent the ideal geometry for achieving high solute flux[14].

- However, the hexagonally packed LC domains of the H_{II}-phase generally form mutually unaligned domains, which hurts membrane permeability.

- This domain scale misalignment had inhibited further development of this technology, and research efforts were focused on the Q_I phase, whose geometry does not require alignment [15].

Recently, researchers have learned how to macroscopically align the hexagonal domains which has revived research into H_{II}-phase LLC polymer membranes.

- In 2014, Feng et al. showed that one can align Col_h domains, created by the "dry" monomer Na-GA3C11, using a magnetic field with subsequent cross-linking to lock the structure in place[13].

- In 2016, Feng et al. showed that one could also obtain the same result by confining the neat monomer between PDMS or glass substrates since hexagonal mesophases preferentially anchor perpendicular to both surfaces[16].

Unfortunately, reproducing the work of Feng et al. with the H_{II} has been an experimental challenge. Therefore, the primary focus of experimental research efforts has been with the Q_I phase.

2   Project Objectives

Our current understanding of the molecular details of LLC 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.[17]

- 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.

A molecular-level understanding of structure of and transport in LLC polymer membranes, enabled by molecular dynamics (MD) simulations, can provide guidelines to reduce the large chemical space available to design monomers for creation of separation-specific membranes.

- Using a sufficiently accurate molecular model, we can directly observe transport of solutes within LLC membrane nanopores and infer mechanisms.

- Based on this information we can intelligently design new membranes by screening new liquid crystal monomer designs.

- Our most promising designs can be tested experimentally.

There are five primary objectives of our work.

1. Develop techniques to build and understand the nanoscopic structure of LLC membranes.

   Useful molecular-level modeling should incorporate a detailed picture of the nanoscopic pore structure, which is crucial to understanding the role of monomer structure in solute transport and membrane design. We will generate simulated X-ray diffraction patterns from MD trajectories and compare them to an experimental 2D wide angle X-ray scattering (WAXS) spectrum of a Col_h phase membrane. We

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will assess the extent to which we can apply our understanding to the H_{II} phase, as well as systems built with alternate monomers.

2. Determine dominant solute-membrane interactions that give rise to transport mechanisms.

   We will observe transport of a relatively large set of small polar solutes placed within the H_{II} membrane nanopores. We will observe the time series of each solute's position as well as directly measure the physical interactions, such as hydrogen bonding and ion coordination, between solutes and LLC monomers.

3. Create a stochastic model which can project long timescale transport behavior.

   We will combine our general knowledge of the solute transport mechanisms with simulation data in order to inform a stochastic model. This model should closely reproduce the time series that we observe in our simulations. Due to the low computational cost of a stochastic model relative to MD simulations, we will be able to project long timescale transport behavior and make well-converged predictions of macroscopic transport properties.

4. Adapt the same analysis to the Q_I phase.

   Over the course of this project, experimental research surrounding LLC membranes has shifted nearly all focus towards the Q_I phase due to its more facile synthesis. Although most of our work has been applied to the H_{II} phase, we expect that much of the same analyses can be applied to the Q_I phase. The biggest challenge will be adapting our techniques to its more complex geometry.

5. Enable easy continuation of our work with a dedicated and well-documented python package.

   Although molecular simulations have become popular for studying systems at the atomic level, LLCs used in this context have not been heavily investigated. Consequently, much of the analysis developed for this project is not widely applied. Therefore, it is important for us to make available the scripts that reproduce the exact results presented in our published papers along with detailed documentation of the scripts. This will ensure near-seamless continuation of this project and accelerate the development of LLC membranes.

3 Progress to Date

Objective 1: *Build and understand nanoscopic structure of LLC membranes* (Complete)
We have developed a procedure for building an LLC membrane unit cell.
We have created a molecular model that is maximally consistent with experimental WAXS data.
Water is necessary to fully reproduce all features in the WAXS pattern.
An ensemble of simulation trajectories best capture the system's time averaged behavior.
Objective 2: *Determine transport mechanisms* (Complete)

We added additional water to our model to create the H_{II} phase

Water partitions into the distal tail region

The pore structure changes

We place 20 small polar solutes

The mean squared displacements are not a monotonic function of solute MSD

Solute behavior is subdiffusive.

Subdiffusive behavior is a consequence of a hopping and trapping mechanism.

There are three mechanisms of entrapment.

Objective 3: *Create a stochastic model* (**In Progress**)

We are in the process of developing the theory required to build a stochastic model.

The distribution of dwell times is power law distributed.

The distribution of hop lengths is approximately gaussian

The model will likely have a radial dependence.

Objective 4: *Apply analyses to Q_I phase* (**In Progress**)

We have developed a procedure to build the Q_I phase.

Objective 5 *Create a well-documented python package* (**In Progress**)

Python scripts used to simulate X-ray diffraction patterns are available in the following GitHub repository: `https://github.com/joeyelk/MD-Structure-Factor`. Documentation is forthcoming.
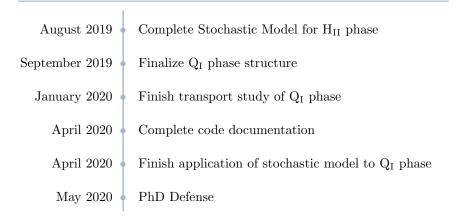
Python scripts used to conduct all other post-simulation trajectory analysis are also available on GitHub: `https://github.com/shirtsgroup/LLC_Membranes`. Documentation is a work in progress. It is available for viewing in its current state at `https://llc-membranes.readthedocs.io/en/latest/`.

4 Timeline for Completion of Objectives

A schematic of the estimated timeline that will be followed for the completion of tasks pertinent to finishing all objectives is given in Table 1.

- Simulations required to study the structure of the bicontinuous cubic phase will be run in parallel while working out the details of our stochastic model of transport in the H_{II} phase.

- Simulations and analysis required for Q_I phase solute transport studies analogous to those of Objective 2 will be carried out throughout Fall 2019.

- Finalization of code documentation and application of a stochastic model to the Q_I phase will be finished by May 2020

TABLE 1   Estimated Timeline for Completion of Objectives

August 2019	Complete Stochastic Model for H_{II} phase
September 2019	Finalize Q_I phase structure
January 2020	Finish transport study of Q_I phase
April 2020	Complete code documentation
April 2020	Finish application of stochastic model to Q_I phase
May 2020	PhD Defense

5   Resource Requirements

The remainder of our work will require the use of high performance computing (HPC) resources.

- We will continue using Bridges, an XSEDE resource as well as Summit, a supercomputer located at CU Boulder.

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