

# Understanding the nanoscale structure of hexagonal phase lyotropic liquid crystal membranes

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## 1 Introduction

Nanostructured membrane materials have become increasingly popular for aqueous separations applications such as desalination and biorefinement because they offer the ability to control membrane architecture at the atomic scale permitting the design of solute-specific separation membranes [1]. Most membrane-based aqueous separations of small molecules can be achieved using reverse osmosis (RO) or nanofiltration (NF) [2]. While RO and NF have seen many advances in the past few decades, they are far from perfect separation technologies.

Current commercial RO and NF membranes suffer from inherent limitations of their fabrication. Although scalable, each process has a degree of stochasticity which makes overcoming the permeability-selectivity tradeoff a challenge. Namely, it is difficult to increase the permeability of a desired species, while maintaining the same retention of an undesired species.

Commercial RO membranes are thin film composite membranes with a porous support layer and an active layer made of a polymer matrix formed by interfacial polymerization of a diamine. During the membrane fabrication, aqueous diamine solution is allowed to penetrate into the polysulfone support layer which is then immersed in trimesoyl chloride, a compound that is immiscible in water. Diamine polymerizes with trimesoyl chloride at the solution interface and creates a thin film that physically adheres to the polysulfone support. The polymer matrix is dense and highly crosslinked which leads to low permeability.

NF membranes are typically made by a phase inversion process. During phase inversion, a thin polymer film is precipitated out of a polymer solution. Through the use of a non-solvent, a polymer-rich and polymer-poor phase is formed. A membrane is created as the polymer-poor phase forms pores in the polymer-rich

phase. Resultant pores are polydisperse in size which hurts membrane selectivity. A second technique used to create NF membranes is call track etching in which a polymer film is bombarded with charged particles, then chemically etched to create pores. The pores are uniform which benefits selectivity, however the membrane has a low porosity and subsequent low permeability.

The permeability-selectivity tradeoff has the potential to be overcome by designing membranes at the molecular level. Next-geneartion nanostructured membranes with high selectivity permitted by a precisely controlled pore size and high permeability allowed by its porous architecture, have the potential to replace traditional RO and NF membrane technologies.

Development of nanostructured materials has been limited by the ability to synthesize and scale various fundamentally sound technologies. Graphene sheets are atomically thick which results in excellent water permeability but defects during manufacturing severely impact selectivity [6]. Molecular dynamics (MD) simulations of carbon nanotubes show promise [1] but synthetic techniques are unable to achieve scalable alignment and pore monodispersity. [7, 8] Zeolites have sub-nm pores with a narrow pore size distribution and MD simulations exhibit complete rejection of solvated ions, [9] however, experimental rejection was low and attributed to interstitial defects formed during membrane synthesis. [10] There is a need for a scalable nanostructured membrane.

Self assembling lyotropic liquid crystals (LLCs) are a suitable candidate for aqueous separation applications. LLCs share the characteristic ability of nanostructured membrane materials to create highly ordered structures with the added benefits of low cost and synthetic techniques feasible for large scale production. [11] LLC systems created by the monomer Na-GA3C11 (Fig. 1a) have been extensively studied experimentally. [12, 13, 14, 11, 15] Neat liquid crystal monomer forms the thermotropic, Col<sub>h</sub> phase (Fig.1). The presence of ca. 10 wt % water results in the H<sub>II</sub> phase. In both cases, monomers assemble into mesophases made of hexagonally packed, uniform size, cylinders with hydrophilic head groups oriented inward towards the cylinder center. The hydrophilic region can act as a pore for aqueous separations. One can envision tailoring the pore region for specific separations by changing the monomer chemistry.

Research into LLC membranes has been revived in recent years. During early stages of exploration, mesophases formed by Na-GA3C11 could not be macroscopically aligned, resulting in low flux membranes, and no clear route towards scalable and economical filtration. In 2014, Feng et al. showed that the mesophases could be aligned using a magnetic field with subsequent crosslinking to lock the structure in place [11]. In 2016, Feng et al. showed that the same result could be obtained using a technique termed soft confinement [15].

Our current understanding of LLC systems is not rich enough to be able to precisely design membranes for specific separations. Over the past 20 years, H<sub>II</sub> phase LLC membrane studies have been limited primarily

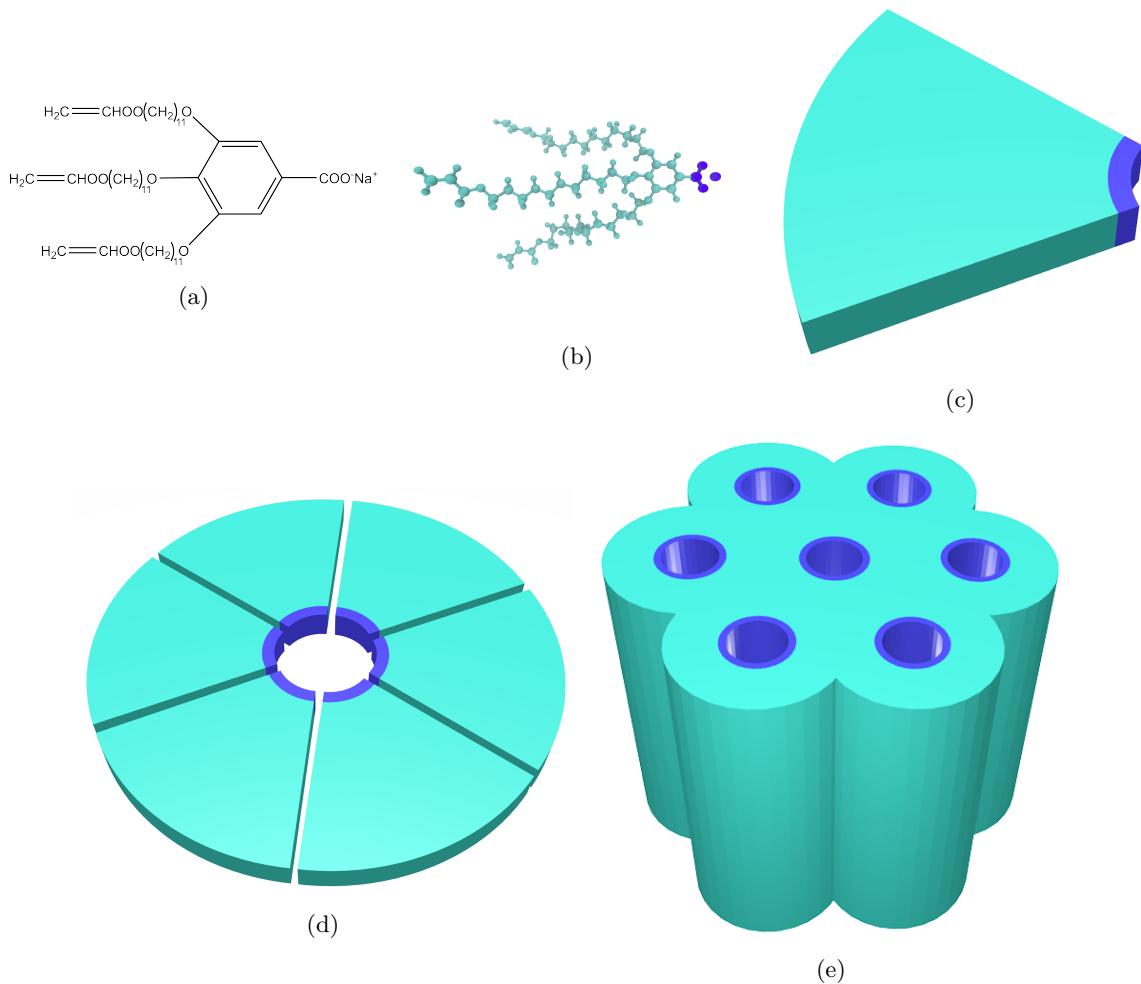


Figure 1: The liquid crystal monomer Na-GA3C11 (a) rendered atomistically (b) exhibits wedge-like character (c). Monomer wedges assemble into disks (d) with hydrophilic head groups (blue) facing towards the disk center. The disks assemble into hexagonally packed columnar mesophases (e)

to Na-GA3C11 with some characterization done after minor structural modifications. Resel et al. varied the length of the monomer tails and the counterion used and observed its affect on pore spacing [16]. Their study offers no insight into dynamics within the pore. In a later study of rejection performance, it was shown that membranes formed by Na-GA3C11 cannot perform separations of solutes less than 1.2 nm in diameter because the pores are too large [13]. We do not yet understand how to controllably reduce the effective pore size or how to tune the chemical environment in the nanopores for effective water desalination and small organic molecule separations. The only source of predictive modeling for LLC systems have been macroscopic models which likely do not adequately describe transport at these length scales [17]. It will be challenging to efficiently narrow down the large design space in a laboratory setting without a robust model.

In this study, we build a significantly more realistic atomistic model of LLC membranes than, to our knowledge, has ever previously been done, and explore what new structural information can be gained and what structure hypotheses are supported by this model. We validate the model using as much experimental information as possible. We are most interested in reproducing the conclusions about structure which have been drawn from X-ray diffraction (XRD) experiments and in matching ionic conductivity measurements [15].

A molecular level understanding of LLC membrane structure, enabled by molecular dynamics simulations, can provide guidelines to reduce the large chemical space available to design monomers for creation of separation-specific membranes. A good molecular model should incorporate a detailed picture of the nanoscopic pore structure which will be crucial to understanding the role of monomer structure in solute transport and membrane design. Models resulting from molecular dynamics simulations will provide the required level of detail (Fig. 2). We can directly observe solute transport and suggest governing mechanisms. We can observe how the choice of head group may influence pore size for size exclusion driven separations. We can interchange counterions which may influence both the pore size and the strength of the Donnan potential which affects the degree to which the membrane can exclude charged species.

In order to appropriately model transport, we must first gain a thorough understanding of the nanoscopic structure of LLC membranes. Our approach to constructing a general model will follow the development of a model of the assembly formed by Na-GA3C11 since it has sufficient experimental characterization. We have also narrowed our scope to the development of a model of the Col<sub>h</sub> phase membrane. Compared to the H<sub>II</sub> phase, the Col<sub>h</sub> phase is a simpler starting point, due to the absence of water, and has detailed experimental wide-angle X-ray scattering (WAXS) patterns useful for reconstructing structural data.

Despite having structural data, there is still information which experiment cannot definitively answer. There are several key questions that we will investigate.

Monomers in the Col<sub>h</sub> system are theorized to be partitioned into stacked layers which form columnar

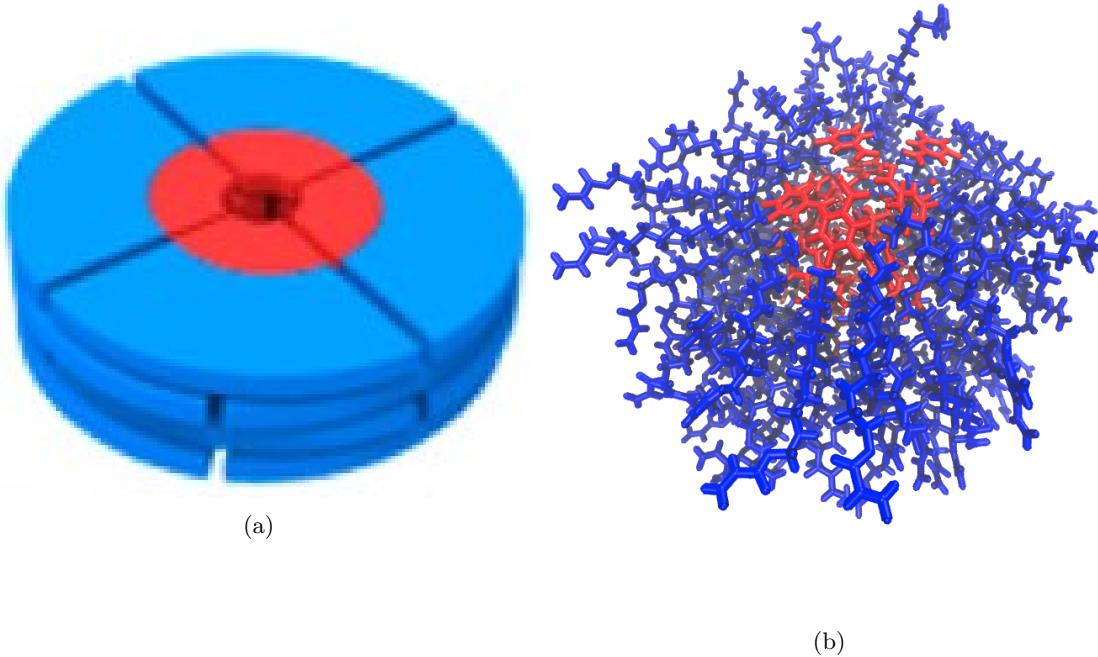


Figure 2: Our previous level of understanding of the pore structure (a) only allows us to speculate about transport behavior in the pore. A detailed molecular model (b) will allow us to directly observe solute transport. Here, four stacked layers of 5 monomers are pictured from atomistic simulations. The hydrophilic region is in red and the hydrophobic region is colored blue.

pores. We want to know

1. If layers do exist, how many monomers constitute a single layer?

A simple molecular simulation study of a similar molecule suggested that there are 4 monomers in each layer. Their estimation is based on a simulated system containing only 16 total monomers which likely does not sufficiently model the chemical environment present in the real system [18]. A separate calculation based on the volume of the liquid crystal monomers proposes that there are seven monomers in each layer [16]. A molecular model orders of magnitude larger than any other reported atomistic liquid crystal membrane simulations has the best chance of directly answering this question. We will directly change the layer composition and note its effect on membrane structure.

2. Does our model support the existence of layers and if so, how well defined are the layers?

Experimentally, their existence is supported by evidence of strong  $\pi$ - $\pi$  stacking interactions in the direction perpendicular to the membrane plane.  $\pi$ - $\pi$  stacking will only occur between the aromatic monomer head groups which leaves no description of what is happening in the monomer tail region. The tails may entangle isotropically while stacking order is maintained among headgroups.

3. How do monomers in each layer position themselves with respect to surrounding layers?

The  $\pi$ - $\pi$  stacking interactions may be a driving force of self assembly in this system [19]. Gas phase ab initio studies of benzene dimers have shown a clear energetic advantage for parallel displaced and T-shaped  $\pi$ - $\pi$  stacking conformations versus a sandwiched conformation [20]. Substituted benzene rings exhibit an even stronger  $\pi$ - $\pi$  stacking attraction which favors the parallel displaced configuration in all cases except where the substitutions are extremely electron withdrawing. [21, 22]. In this study, we compare simulated X-ray diffraction patterns to experiment in order to deduce which stacking configurations is most likely.

4. Can the system exist in other metastable states or phases that are not accessed during experiments?

There remains the possibility that there is more than one metastable state associated with a given LLC system. Simulating a membrane atomistically requires many atoms which limits the timescales accessible with MD. It is reasonable to expect that we will generate configurations which are kinetically trapped in a metastable free energy basin. We must be able to identify which state is produced experimentally.

5. What constitutes a pore and how well-defined are the pore regions?

The limited picture that experiment provides tells us that there are hexagonally packed, hydrophilic regions where transport is likely to occur. One may instinctively assume that these regions are tube-like pathways. We will explore the composition of the pores and the partition between the hydrophilic and hydrophobic regions.

#### 6. Is it necessary to include any water in order to appropriately model the Col<sub>h</sub> phase?

While the Col<sub>h</sub> phase is described as dry, it has been suggested by experimentalists, in unpublished communications, that it is likely that small amounts of ambient water are leached into neat monomer. Experimentally, achieving a hexagonal phase with a completely dry system has proven difficult. If neat monomer is allowed to sit in ambient conditions, its color turns from transparent to slightly opaque and a hexagonal phase forms. Although we will not explore whether water is necessary for self assembly, we hypothesize that the hydrogen bonding network formed by the water may play a role in structuring the pores and holding together the hexagonal phase. We can use simulated X-ray diffraction patterns to see if there is any meaningful structural difference between a “dry” and “wet” system.

We used experimental small-angle X-ray scattering (SAXS) data from [15] (Fig. 3a) and wide angle X-ray scattering (WAXS) data (Fig. 3b, produced as described in [11]) for comparison to our model. We rely primarily on the 2D WAXS data since it encodes all structural details down to the sub-nm scale. There are five major features of interest present in the 2D experimental pattern shown in Figure 3b.

1. The first is located at  $q_z = 1.7 \text{ \AA}^{-1}$ , corresponding to a real space separation of  $3.7 \text{ \AA}$ . The reflection is attributed to  $\pi$ - $\pi$  stacking between aromatic rings in the direction perpendicular to the membrane plane, or z-axis [11]. For simplicity, this reflection will be referred to as R- $\pi$ .
2. A weak intensity line is located at exactly half the  $q_z$  value of R- $\pi$  ( $q_z = 0.85 \text{ \AA}^{-1}$ ), corresponding to a real space periodic spacing of  $7.4 \text{ \AA}$ . This reflection has been interpreted as  $2_1$  helical ordering of aromatic rings along the z axis, meaning that if the positions of the aromatic rings can be traced by a helix, then for each full turn in the helix, one will encounter two aromatic rings. For this reason it will be referred to as R-helix.
3. A third major reflection is marked by a low intensity ring located at  $r = 1.4 \text{ \AA}^{-1}$ . The real space separation corresponds to  $4.5 \text{ \AA}$  which is characteristic of the average spacing between packed alkane chains. This reflection will be called R-alkanes.
4. Within R-alkanes, are four spots of higher relative intensity which will be called R-spots. All are located  $\sim 37$  degrees from the  $q_z$  axis in their respective quadrants. In many liquid crystal systems this can be explained by the tilt angle of the alkane chains with respect to the membrane plane.

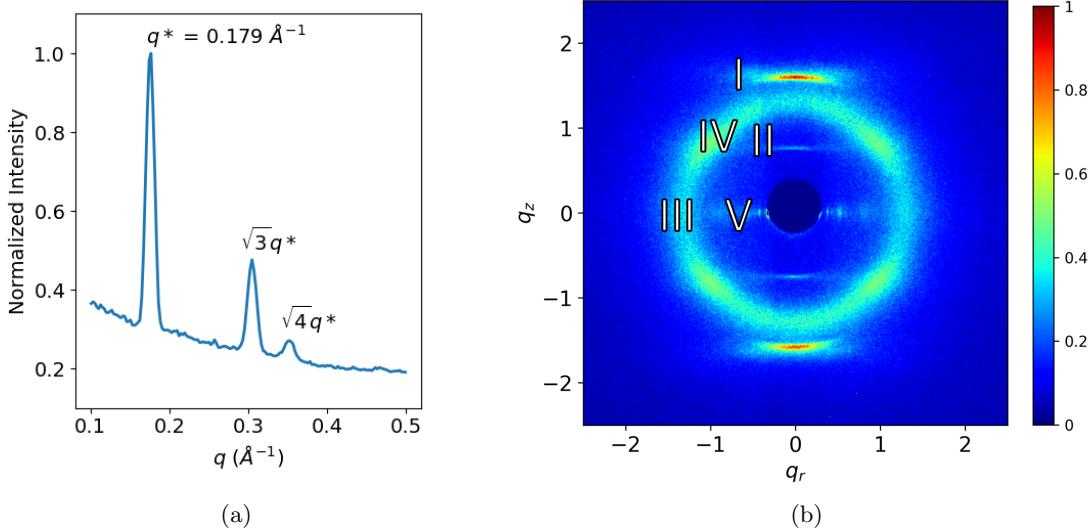


Figure 3: (a) The repeat spacing in the 1D small angle X-ray scattering pattern is characteristic of hexagonal packing. The leading peak represents the distance between the  $d_{100}$  planes. Using this distance, we know that the distance between pore centers is 4.12 nm. (b) 2D wide angle X-ray scattering gives details about repeating features less than 1 nanometer apart. Experimentalists have justified each of the 5 major reflections present as follows: (I) Aromatic head group  $\pi - \pi$  stack 3.7  $\text{\AA}$  apart. (II) Monomers arrange vertically in a  $2_1$  helix. (III) Alkane chain tails pack 4.5  $\text{\AA}$  apart. (IV) Monomer tails tilt with respect to the membrane plane. (V) As derived from SAXS, pores pack hexagonally and are spaced 4.12 nm apart

5. The final feature corresponds to the spacing and symmetry of the  $d_{100}$  plane which can be related to the distance between pores. The feature, which will be called R-pores, is characterized by dots along  $q_z = 0$ . The spacing between dots is indicative of the hexagonal symmetry of the packed pores. The same information at higher resolution is obtained using SAXS.

## 2 Methods

### 2.1 Monomer Parameterization

Liquid crystal monomers were parameterized using the Generalized AMBER Forcefield [23] with the Antechamber package [24] provided with AmberTools16 [25]. Atomic charges were assigned using the am1bccsym method of molcharge shipped with QUACCPAC from Openeye Scientific Software. All molecular dynamics simulations were run using Gromacs 2016. [26, 27, 28, 29]

An ensemble of characteristic, low-energy vacuum monomer configurations were constructed by applying a simulated annealing process to a parameterized monomer. Monomers were cooled from 1000K to 50K over 10 nanoseconds. A low energy configuration was randomly pulled from the trajectory and charges were reassigned using molcharge. Using the new charges, the monomer system was annealed again and a random

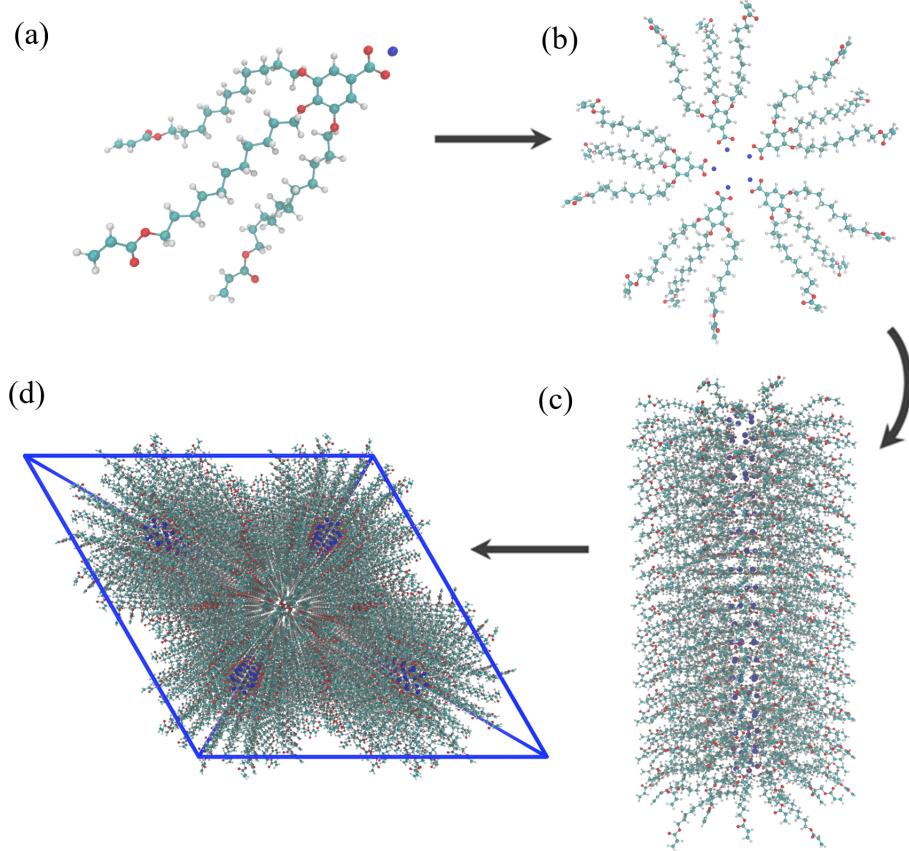


Figure 4: (a) A single monomer was parameterized and annealed to produce a low energy configuration. (b) Monomers are rotated and assembled into layers with hydrophobic centers. (c) Twenty layers are stacked on top of each other to create a pore. (d) Pores are duplicated and placed into a monoclinic unit cell

monomer configuration was pulled from the trajectory to be used for full system construction (Figure 4a). See supplemental information for further detail.

## 2.2 Unit Cell Preparation

The timescale for self assembly of monomers into the hexagonal phase is unknown and likely outside of a reasonable length for an atomistic simulation, calling for a more efficient way to build the system. Previous work has shown a coarse grain model self assemble into the  $H_{II}$  phase configuration in  $\approx 1000$  ns [30]. We attempted atomistic self-assembly by packing monomers into a box using Packmol [31]. Simulations of greater than 100 ns show no indicators of progress towards an ordered system To bypass the slow self-assembly process, python scripts are used to assemble monomers into a structure close to one of a number of hypothesized equilibrium configurations (Figure 4).

A typical simulation volume contains four pores in a monoclinic unit cell, the smallest unit cell that maintains hexagonal symmetry when extended periodically. Each pore is made of twenty stacked monomer

layers with periodic continuity in the z direction, avoiding any edge effects and creating an infinite length pore ideal for studying transport. A small number of layers is preferred in order to reduce computational cost and to allow us to look at longer timescales. Ultimately, we chose to build a system with 20 monomer layers in each pore in order to obtain sufficient resolution when simulating X-ray diffraction patterns.

### 2.3 Monomer Placement

When constructing an initial configuration, there are a number of variables which require careful consideration while placing monomers. The equilibrium configuration is sensitive to some while insensitive to others. The starting pore radius, defined as the distance of a chosen head group carbon from the pore's central axis, does not influence the equilibrium structure when a reasonable value is chosen (See Supplemental). The pore radius is chosen to be 0.6 nm in our initial configurations because the pore size is estimated to be  $\approx$  1.2 nm. The initial distance between pores also has little effect on the equilibrated structure. However, one should not start them too close or there will be high energy repulsions during early equilibration. We chose an initial pore spacing of 4.5 nm,  $\approx$  10 % larger than the experimental value of 4.12 nm. The distance between layers, the rotation of the layers with respect to adjacent layers, and the number of monomers per layer do influence the equilibrium structure and require further justification for their choices. We rely on experimental data to inform them.

We chose the layer spacing for the initial configuration based on R- $\pi$  and then allowed the system to readjust during equilibration. Each monomer was rotated so the plane of the aromatic head groups would be coplanar with the xy plane. We explore two different initial layer spacings. The first is exactly equal to R- $\pi$  with layers placed so aromatic rings are stacked 3.7 Å apart in the z-direction. A second system is explored with an initial layer spacing of 5 Å. A third system with an initial layer spacing of 10 Å was briefly explored. When layers are spaced out too far, they will collapse on each other while simultaneously slipping in between layers of adjacent pores which leads to an artificially thick membrane with pores spaced closely together. Further details of simulations with large layer spacing are in the supplemental information.

The relative interlayer orientation was chosen based on clues from diffraction data as well as the various known stacking modes of benzene and substituted benzene rings: sandwiched, parallel-displaced and T-shaped [20] (Figures 5a to 5c). The T-shaped configuration was ruled out because its  $\approx$  5 Å equilibrium stacking distance [20] is inconsistent with R- $\pi$ . It is also infeasible for the monomers to orient in the T-shaped conformation because of the bulky tail groups. The system's preference towards the sandwiched vs. parallel displaced stacking modes will be explored in some detail. Both have reported stacking distances near the R- $\pi$  value of 3.7 Å. Headgroups in our sandwiched initial configuration are stacked directly on top

of each other while stacked headgroups in the parallel displaced initial configuration are offset by  $180/nmon$  degrees where  $nmon$  equals the number of monomers per layer.

As outlined in (1) the number of monomers in each layer is unknown. We tested configurations constructed with a varied number of monomers per layer. Systems were built in the offset and parallel displaced configurations with 4, 5, 6, 7 and 8 monomers per layer.

## 2.4 Equilibration

We developed equilibration schemes to create dry and wet configurations. Both schemes start with an initial configuration generated according to the previous guidelines. To create a dry configuration, we fix monomer head groups in the sandwiched or parallel-displaced configuration using position restraints with a force constant of  $10^6 \text{ kJ mol}^{-1} \text{ nm}^{-2}$ . We run a 50 ps simulation in the NVT ensemble which allows the monomer tails to settle without disrupting the ordering of the head groups. Doing so also mitigates system dependence on initial monomer configuration. Every 50 ps, we reduce the force constants by the square root of its previous value. Once the force constant is below  $10 \text{ KJ mol}^{-1} \text{ nm}^{-2}$ , the restraints are reduced in a sequence with values of 8, 3, 2, 1, and 0  $\text{KJ mol}^{-1} \text{ nm}^{-2}$  respectively. The resulting unrestrained structure is allowed to equilibrate for 5 ns in the NPT ensemble with pressure controlled by the berendsen barostat. Next, we run long NPT equilibration simulations for at least 400 ns using the Parrinello-Rahman barostat with a time constant of 10 ps.

In order to create a wet system, we solvated an initial configuration with water using `gmx solvate`. All water molecules placed outside the pore region are removed. Waters inside the pore region are randomly removed until the desired concentration of water in the pores is reached. The remainder of the equilibration follows the same procedure as the dry system.

## 2.5 Crosslinking

In order to fully match synthetic procedures, we created a crosslinking algorithm that can be applied to equilibrated structures. The purpose of crosslinking is to maintain macroscopic alignment of the crystalline domains, ensuring aligned, hexagonally packed pores. For that reason, we are not concerned with replicating the kinetics of the reaction, but instead emphasize the consistency of the final structure with experimental structural data. The algorithm was developed based on the known reaction mechanism. Crosslinking of this system is a free radical polymerization (FRP) taking place between terminal vinyl groups present on each of the three monomer tails. FRPs require an initiator which bonds to the system, meaning new atoms are introduced into the system. For simplicity, the initiator was simulated as hydrogen and made present in the

simulation by including them in all possible locations where an addition could occur as dummy atoms. The crosslinking procedure is carried out iteratively. During each iteration, bonding carbon atoms are chosen based on a distance cut-off. The topology is updated with new bonds and dummy hydrogen atoms are changed to appropriate hydrogen types. Head-to-tail addition was the only propagation mode considered due to its dominance in the real system. Direction of attack was not considered because the resultant mixture is racemic.

Our implementation requires long simulation times to achieve high degrees of crosslinking. A typical crosslinking procedure can take up to 24 hours. In order to collect equilibrated data, further NPT simulation is necessary. We typically run a crosslinked system for an additional 100 ns to allow the system to readjust. For those reasons we did not crosslink all systems tested, but only the most promising structure. We show that crosslinking does not significantly change any of our drawn conclusions in Section 3.6.

## 2.6 Equilibrium Calculations

Using equilibrated structures, we carry out various calculations to characterize the system. We define the point at which a system is equilibrated based on when the distance between pores stops changing. We determined when the distances stopped changing by applying the statistical test, `pymbar.timeseries.detectEquilibration`, to the time series. Simulations of 400 ns give at least 50 ns of equilibrated simulation trajectory.

To calculate the equilibrated pore spacing, we measured the distance between pore centers. Pore centers are located by averaging the coordinates of sodium ions in their respective pores. Pore spacing statistics were generated using the bootstrapping technique (See Supplemental Information).

To quantify the degree of layering and the equilibrium distance between layers in our system, we calculate a spatial correlation function,  $g(z)$ , measured along the z-axis (perpendicular to the membrane plane). To calculate  $g(z)$ , we binned the z-component distances between the center of mass of each component and all others of the same pore over at least 50 ns of equilibrated trajectory and then normalized by the average number density. To extract the average distance between layers we applied a discrete Fourier transform to  $g(z)$  and extracted the highest intensity frequency.

Simulated X-ray diffraction patterns are generated based on atomic coordinates in order to make a direct experimental comparison. All atomic coordinates were simulated as Gaussian spheres of electron density corresponding to each atom's atomic number. A three dimensional Fourier transform (FT) of the array of electron density results in a three dimensional structure factor which represents the unit cell in reciprocal space. We matched experimental 2D WAXS patterns by adjusting the initial spacing between layers and the orientation of the head groups with respect to adjacent layers.

The colorbars on all diffraction patterns are normalized relative to R-alkanes. We believe that the alkane-alkane density, averaged over all angles, is the feature most likely to be replicated between experiment and simulation. Other features are dependent on system ordering which is likely to have some dependence on initial configuration. We calculated the average intensity within R-alkanes of the experimental pattern,  $I_{avg}$ . We exclude intensities within  $\pm 30^\circ$  of the  $q_r = 0$  axis, since the simulated patterns differ from experiment in those regions. In contrast to the experimental WAXS pattern, R- $\pi$  appearing in simulated diffraction patterns intersects with R-alkanes (See Fig. 8). We multiplied  $I_{avg}$  by a scaling factor of 2.5. Intensities that appear in the experimental pattern  $\geq 2.5*I_{avg}$  receive colorbar values of 1. We apply the same scaling method to the simulated patterns. We carefully chose a scaling factor of 2.5 in order to (1) visibly display all features in the experimental pattern and (2) to allow us to compare the relative intensities of features between simulated and experimental diffraction patterns.

We explored the pore composition by measuring the average number densities of various monomer components as a function of distance from the pore centers. We looked at the average number density of sodium ions, aromatic rings and carbon atoms making up the monomer tails. The radial distance of all atoms in each group from the pore centers are binned, then normalized by the volume of the annulus defined by the bin edges and z box vector.

We calculated ionic conductivity using two different methods for robustness. The Nernst-Einstein relation relates the DC ionic conductivity to ion diffusivity,  $D$ , concentration,  $C$ , ion charge,  $q$ , the Boltzmann constant,  $k_b$ , and temperature,  $T$ :

$$\sigma = \frac{q^2 C D}{k_b T}$$

Sodium ion diffusion coefficients were found by calculating the slope of the linear region of the z-direction mean square displacement curve as indicated by the Einstein relation [32]. We visualized the MSD plot to determine where to begin and end a linear fit. Ion concentration was measured with respect to the volume of the entire unit cell.

The second method, termed the Collective Diffusion model, measures the movement of the collective variable,  $Q$ , which is defined as the amount of charge transfer through the system and can be thought to represent the center of charge of the system. The conductance,  $\gamma$  of the system can be calculated as:

$$\gamma = \frac{D_Q}{k_b T}$$

Conversion to ionic conductivity is achieved by multiplying by channel length and dividing by the membrane cross sectional area.  $D_Q$  is the diffusion coefficient of the collective variable  $Q$ . It can be calculated using

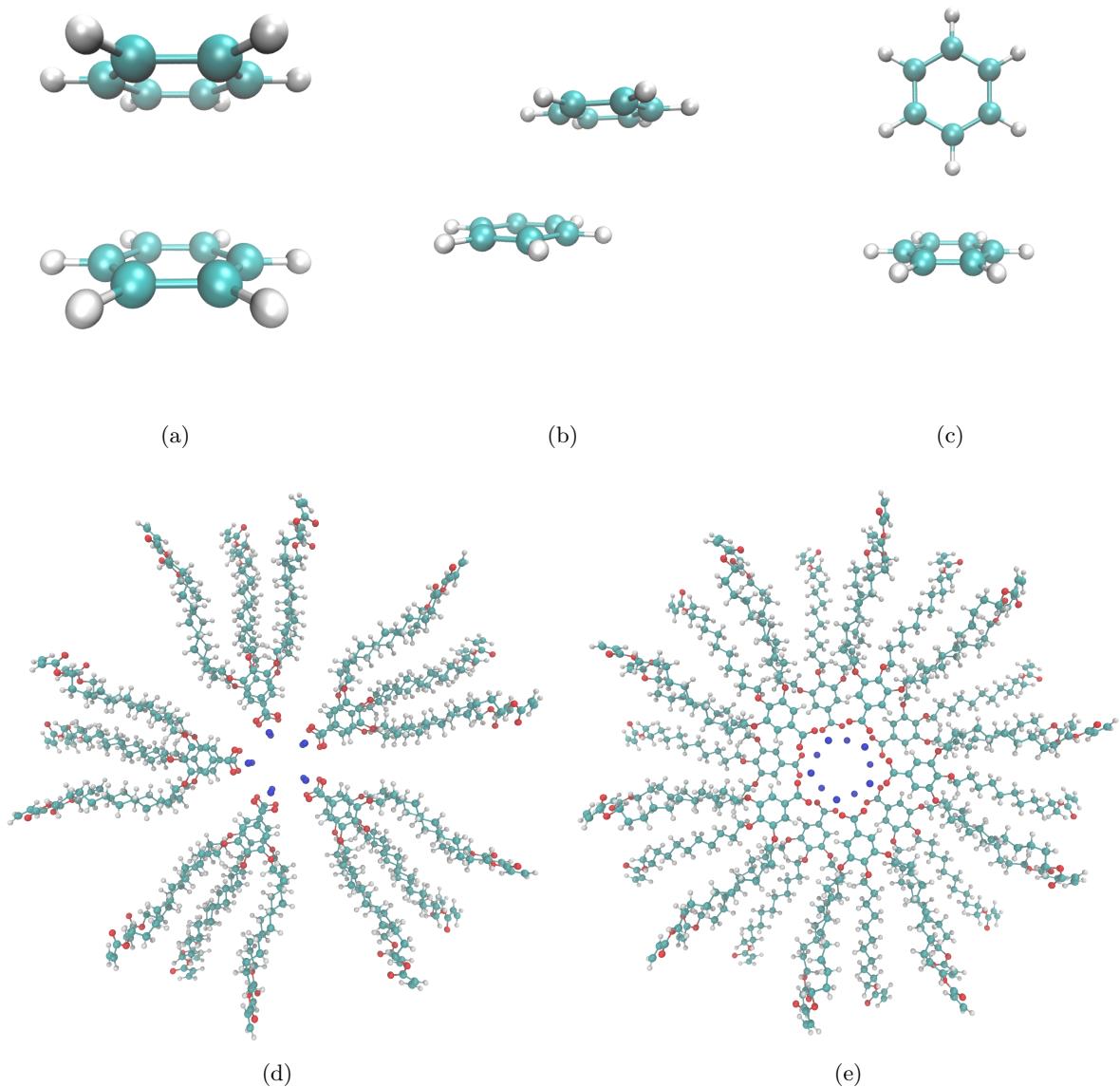


Figure 5: (a) Sandwiched benzene dimers stack 3.8 Å apart. (b) Parallel-Displaced benzene dimers stack 3.4 Å vertically and 1.6 Å horizontally apart. (c) T-shaped benzene dimers stack 5.0 Å apart. (d) Two monomer layers stacked in the sandwiched configuration (e) Two monomer layers stacked in the parallel-displaced configuration

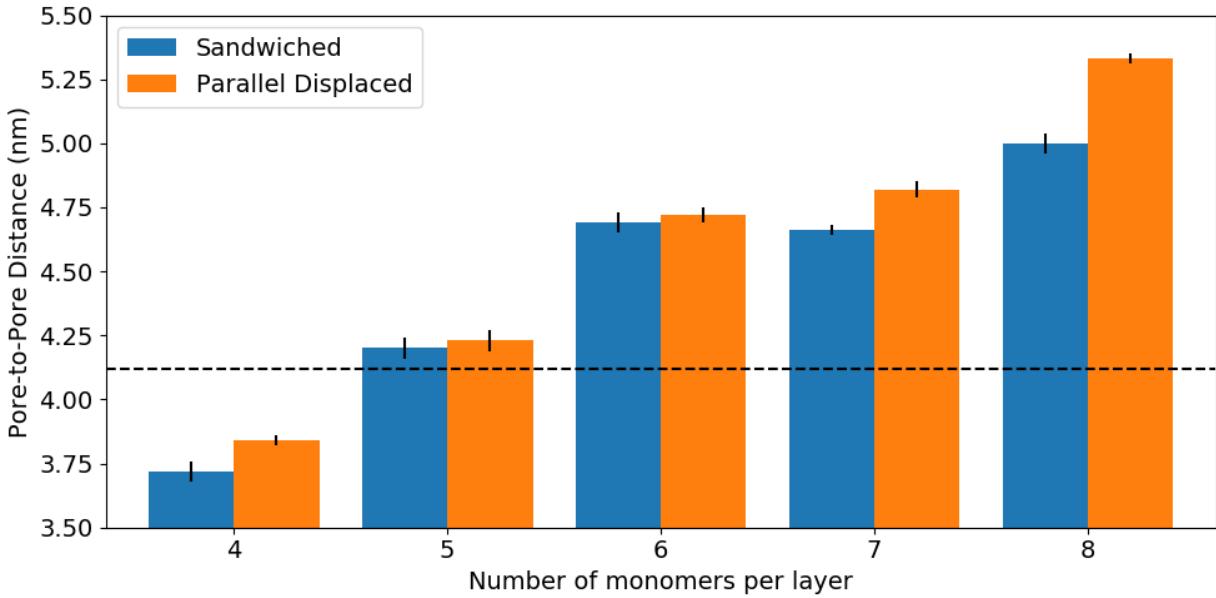


Figure 6: Systems built with 5 monomers per layer in a parallel displaced configuration result in a pore spacing closest to the experimental value of 4.12 nm. The pore spacing of the model increases as number of monomers in each layer increases. The pore spacing of a system starting in the sandwiched configuration is systematically lower than that started in an offset configuration.

the Einstein relation. A full derivation of the model can be accessed elsewhere [33].

### 3 Results and Discussion

#### 3.1 Determining the Spatial Configuration of Monomers

Our simulations best support a model built with 5 monomers per layer based on the measured equilibrated pore-to-pore distances. To discern the composition of the monomer layers, addressing (1), we ran simulations of systems created with 4 - 8 monomers per layer. Systems were built in both the parallel displaced and sandwiched configurations with layers initially spaced 3.7 Å apart. Equilibrated configurations were prepared according to the dry equilibration procedure. All systems are stable after 400 ns of simulation. In a sense, all systems are at least metastable, addressing (4), however not all will make physical sense or fit the experimental profile that we are looking to match. Figure 6 shows the pore spacing for all systems tested. Systems built with 5 monomers in each layer equilibrate to a pore spacing that is most consistent with the experimental value of 4.12 nm derived from SAXS measurements (Figure 3a). The remainder of this discussion will focus on the analysis of systems built with 5 monomers per layer.

We learned that layers are well-defined and persistent, answering (2). We established our conclusion by

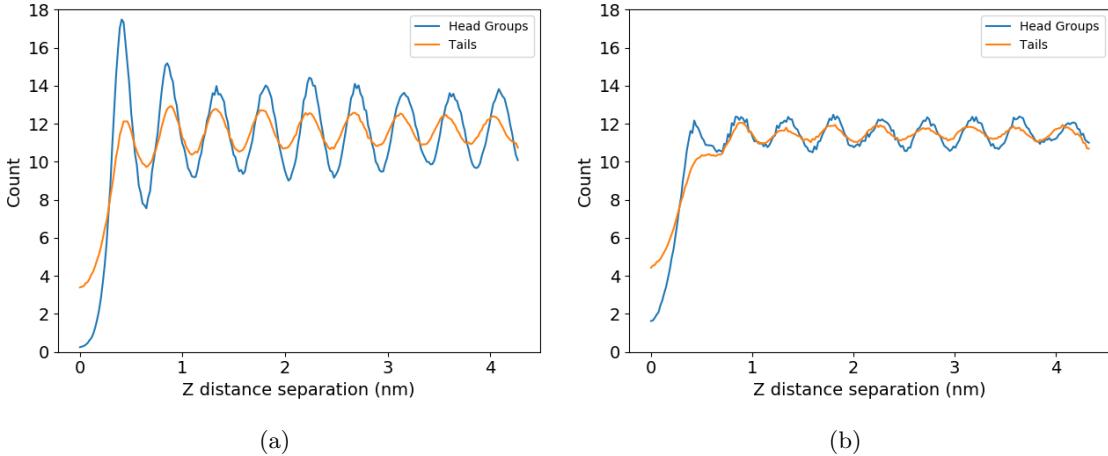


Figure 7: Pair distribution functions of aromatic carbons for the (a) 5 monomer per layer, sandwiched and (b) 5 monomer per layer, parallel displaced configurations. Clear periodic maxima in the  $z$  number density indicate distinct layers. The magnitude of the spikes with respect to the average suggest that the 5 monomer per layer, sandwiched configuration possesses a higher degree of layer partitioning.

plotting the pair correlation function,  $g(z)$ , calculated between atoms along the length of the pores (Fig. 7). We measured  $g(z)$  with respect to aromatic rings in the head groups and, separately, with respect to carbon atoms in the alkane chains. Using a Fourier transform of  $g(z)$ , we see that sandwiched configuration layers stack  $4.39 \text{ \AA}$  apart while parallel displaced configuration layers stack  $4.38 \text{ \AA}$  apart.

We answer question (3) by simulating X-ray diffraction patterns produced from equilibrated MD trajectories. We tested systems built with 5 monomers per layer in the parallel displaced and sandwiched configurations. Simulated patterns were generated using portions of simulation trajectory after equilibration. The patterns for both structures are shown and compared to experiment in Figure 8.

Simulated XRD of the sandwiched configuration contains all experimental features except for R-helix. R-alkanes, R-spots and R-pores appear close to their expected locations. R- $\pi$  is also present, however it intersects R-alkanes at a  $q_z$  value lower than experiment meaning the head groups in our model prefer to stack farther apart.

The parallel displaced configuration results in a simulated XRD pattern with the closest match to experiment. It produces the only pattern that exhibits all major reflections. R-alkanes and R-pores appear as they do in the sandwiched configuration. R-spots and R- $\pi$  appears, however with a lower intensity relative to R-alkanes when compared to the sandwiched configuration. R-helix appears due to the parallel displaced aromatic rings. It is a subharmonic of R- $\pi$  since the nearest vertically stacked head group to any given head group is  $7.4 \text{ \AA}$  away.

In both the parallel displaced and sandwiched configurations, we noted that R- $\pi$  appears in a location which corresponds to a real space separation larger than experiment. We attribute this discrepancy to

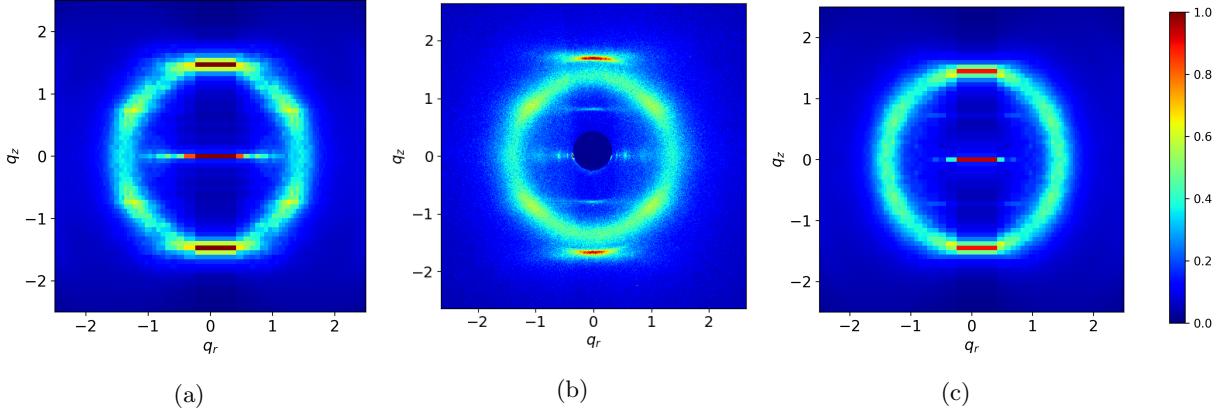


Figure 8: The simulated X-ray diffraction patterns for simulations run in the sandwiched (a) and parallel-displaced (c) configurations are compared to experiment (b). The parallel displaced configuration is the only one that exhibits all major reflections of interest to some degree

GAFF’s inability to appropriately model the aromatic interactions which would be necessary to achieve the correct  $\pi$ - $\pi$  stacking distance. Systems have been modeled that exhibit the correct stacking distance, however they are typically made of planar molecules spanning a large area. The system we have modeled has bulky tails whose entropic contributions compete with the  $\pi$ - $\pi$  stacking interaction energy. There have been efforts to model systems that contain  $\pi$  interactions in a classical mechanical context using polarizable forcefields. We could implement a polarizable force field, however it is likely not worth the extra computational cost. If our model proves to be inadequate when simulating transport, we will revisit our current choice of forcefield.

The R-spots signal, which appears in both simulated XRD patterns, is a result of hexagonal alkane chain packing. Previously, the spots in the diffraction pattern had been explained as the product of tilted alkane chains. We measured the tilt angle of the alkane chains and showed that our system equilibrates to an average tilt angle close to zero degrees (Fig. 9). To understand the origin of the spots, we determined which atoms gave rise to the feature. Since R-spots is present as higher intensity spots within R-alkanes, it is likely that the spots arise as a consequence of the tails. By removing all non-tail atoms from the trajectory and simulating a diffraction pattern, we were able to isolate the cause of the spots to the tails (Figure 10). Since the tails stay nearly flat, we plotted the centroids of the tails and measured the angle between each centroid and its nearest neighbors with respect to the plane of the membrane. We see distinct peaks in the distribution of these angles (Figure 11).

The peaks in the nearest neighbor angle distribution are consistent with the location of R-spots. The peaks of interest in Figures 11a and 11c are located at  $\pm 33^\circ$  which is the same location where the highest intensity of spots are located on the simulated patterns. We confirmed this conclusion by radially integrating the 2D WAXS pattern for  $|\mathbf{q}|$  values between 1.4 and 1.57 (between 4 and 4.5 Å in real space). We observe

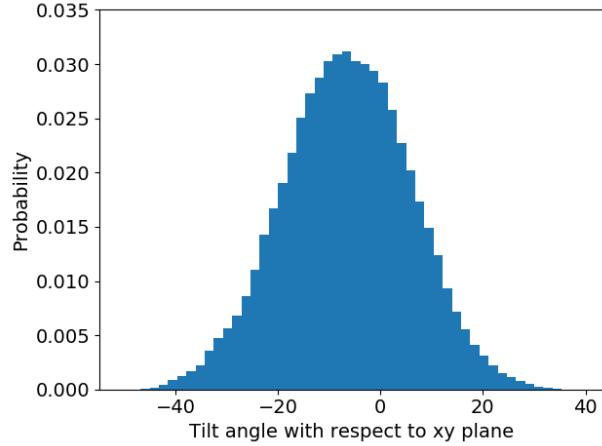


Figure 9: The tilt angle distribution of alkane chain tails with respect to the membrane plane indicates an average tilt angle near  $7^\circ$  which is far from the  $37^\circ$  tilt angle previously used to explain R-spots.

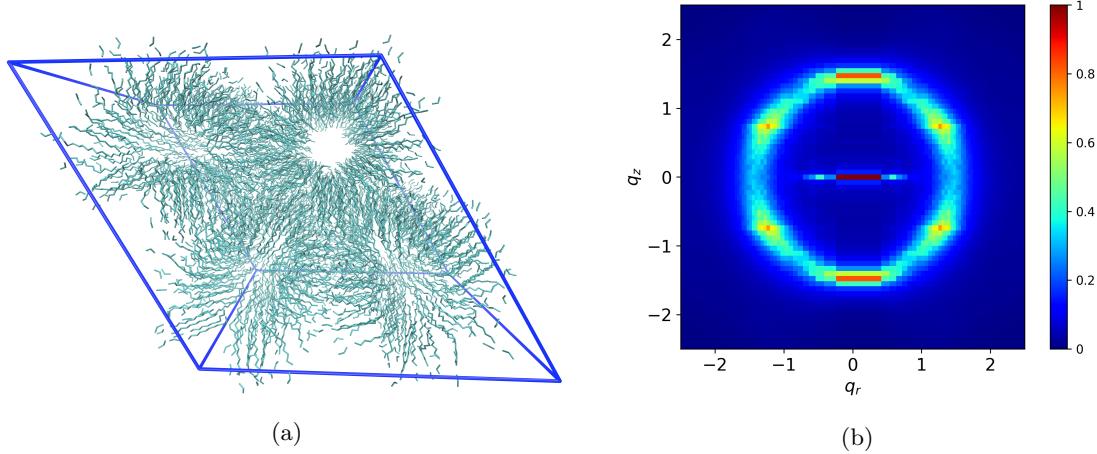


Figure 10: (a) All atoms except carbon atoms making up the tails are removed from a sandwiched configuration trajectory. (b) The simulated diffraction pattern of the tail-only trajectory still shows R-spots

that distinct peaks appear ca.  $30^\circ$ , in close agreement with the previously measured angle distribution (Figs. 11b and 11d). We performed the same integration on the raw experimental data and found the angle at which R-spots reaches its highest intensity to be  $\pm 37^\circ$  which is a reconcilable difference with our simulated results.

### 3.2 Initial Layer Spacing Affects System Equilibration

When systems are built with layers stacked  $5.0 \text{ \AA}$  apart then equilibrated, we observe long-term stability of a qualitatively different configuration, suggesting that we have found another metastable free energy basin, further corroborating (4). We studied this type of system in both the parallel displaced and sandwiched

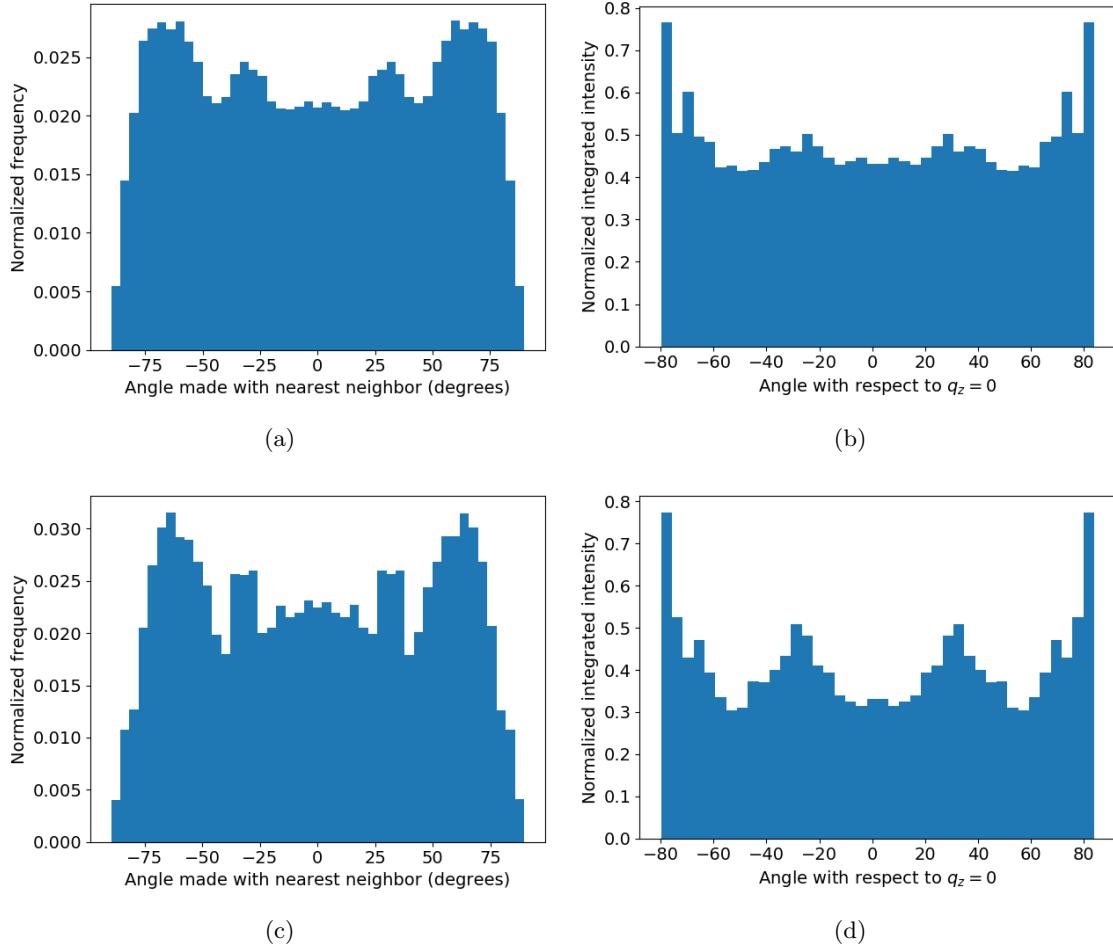


Figure 11: The distribution of angles w.r.t. the xy plane between alkane chain tail centroids and nearest neighbor centroids for equilibrated parallel displaced (a) and sandwiched (c) configurations. The same peaks are visible when the 2D simulated diffraction data is radially integrated in the R-alkanes region, (b) and (d) respectively.

configurations.

Structural properties are different when layers are initially spaced 5 Å apart. In both configurations, we observe a decrease in pore spacing (Fig. 12b) and a corresponding increase in the equilibrated distance between layers (Fig. 12a). The simulated X-ray diffraction patterns indicate further structural differences. In the parallel displaced configuration, almost all contrast between R-spots and R-alkanes is faded (Fig. 12c). In the sandwiched configuration, R-spots are weakly present, but in different locations, showing higher intensity at the top and bottom of the pattern as well as at the intersection of R-alkanes with  $q_z = 0$  (Fig. 12d).

The sandwiched and parallel displaced assemblies do not deviate from their initial head group arrangement. R-helix is still faintly visible in the parallel displaced configuration and is absent in the sandwiched

simulated diffraction pattern. The spectroscopic signatures are unique to the two different head group configurations.

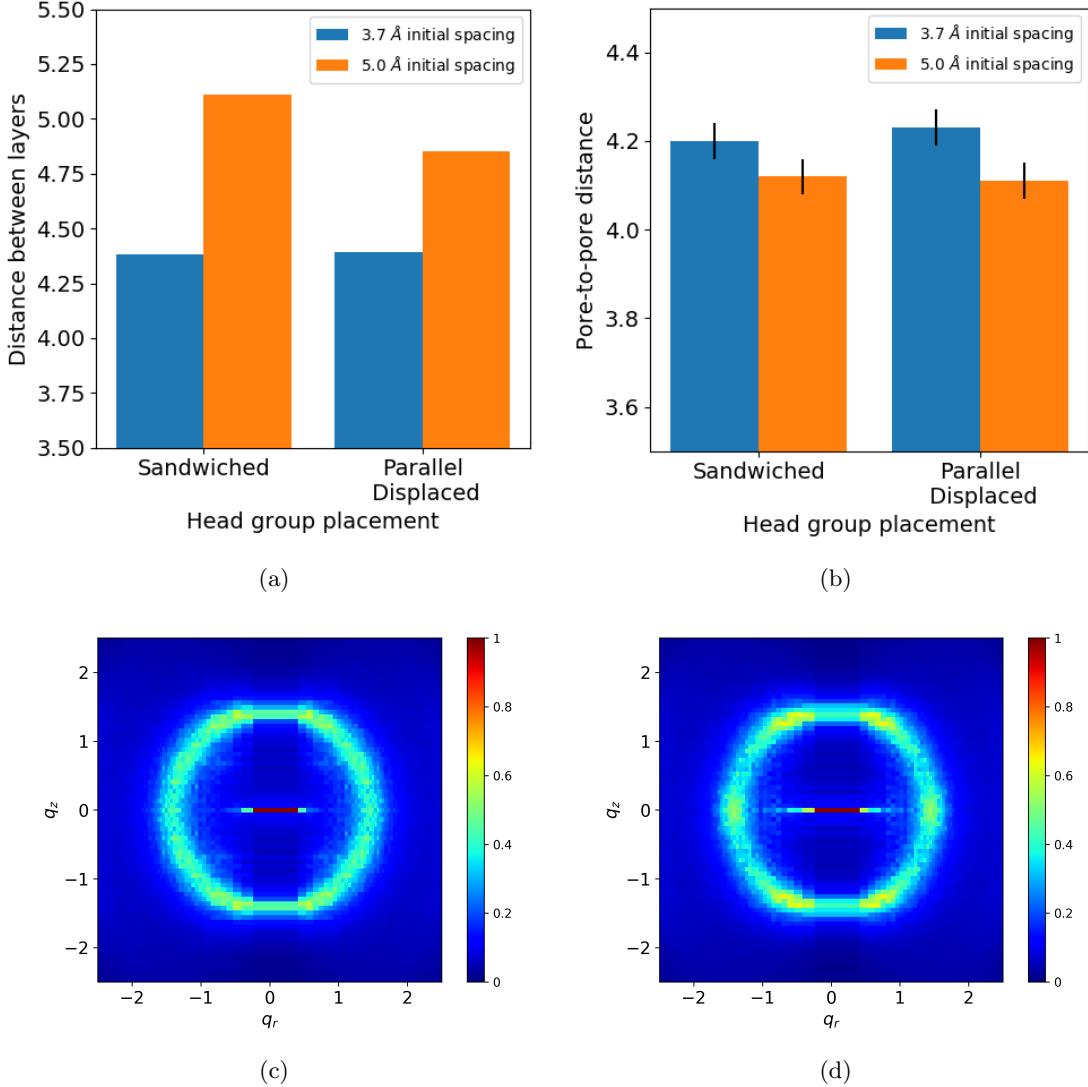


Figure 12: In comparison to systems built with  $3.7 \text{ \AA}$  initial layer spacing, the simulated X-ray diffraction patterns of the parallel displaced (a) and sandwiched (b) configurations are different when systems are built with a  $5 \text{ \AA}$  initial layer spacing, most notably in the region bounded by R-alkanes. When layers are stacked further apart, the distance between layers increases (c) and the pore spacing decreases (d).

### 3.3 Pore Structure Depends on Initial Configuration

In order to address (5), we plotted the number densities of heavy atoms in the head group, carbon atoms in the tail region and the sodium ions (Figure 13). For the head group region, we used the carbon atoms making up the aromatic ring. For the tail region we used only carbon atoms of the monomer tails (See Supplemental

Information for diagram). Histograms are averaged over at least 50 ns of equilibrated trajectory.

In all cases, the space in the pore region is filled with sodium ions and head groups. When systems are spaced 3.7 Å apart, there is less density in the center of the pore indicating a more ordered pore structure. In both the sandwich and parallel displaced configurations, we see the density of head groups and sodium ions fall to less than 50 % of its maximum at  $r = 0$  (Fig. 13b). The situation is most pronounced in the sandwiched configuration where the maximum head group density occurs 0.44 nm from the pore center. The parallel displaced configuration reaches its maximum 0.35 nm from the pore center. In contrast, both system built with layers initially spaced 5 Å apart show verly little difference in density from its maximum. This implies a more uniform distribution of head groups within the pore center.

There is a partition between the hydrophobic and hydrophilic regions, however it is a gradient in composition, rather than an abrupt division. Sodium ions and head groups are not confined to just within the pore region. In all cases, 19 % of sodium ions exist outside the pore region whose radius is assumed to be 0.6 nm for this calculation (except sandwiched, 3.7 Å initial layer spacing, where 16 % are outside the pore). Additionally, we see that in all cases, about 3 % of the plotted tail density is located within the pore region (except sandwiched, 3.7 Å initial layer spacing, where 1.5 % are within the pore region). These observations bring into question how one should define a pore in these types of systems. One usually measures a membrane's pore radius based on the size of a molecule it can reject, however it is not clear where the edges of the pores are and what size molecule would fit through. We leave these investigations for a future study.

### 3.4 Affect of Water on Structure

We explored the affect of water on pore structure, addressing 6 by preparing parallel displaced and sandwiched configurations according to the wet equilibration procedure. There is no experimental measurement of trace water concentration in the pores so we tested a range of water concentrations from 0.5 to 5 percent. Our lower bound models a system with on average 2 water molecules for each monomer layer. Figure 14 shows the simulated diffraction patterns resulting from each configuration.

In all cases, water disrupts structuring of the model. The plots in Figure 14 are normalized to have the same colorbar as the dry systems. The intensity of the reflections decrease when water is added to the system. In systems built with 5 wt % water, R- $\pi$  and R-spots become nearly indistinguishable from R-alkanes.

Water is not necessary to maintain an ordered pore structure. We do not eliminate the possibility that water is necessary in order to drive self-assembly, however, studying the mechanisms of self assembly is beyond the scope of this work. According to our model, once the system has formed the Col<sub>h</sub> phase, adding

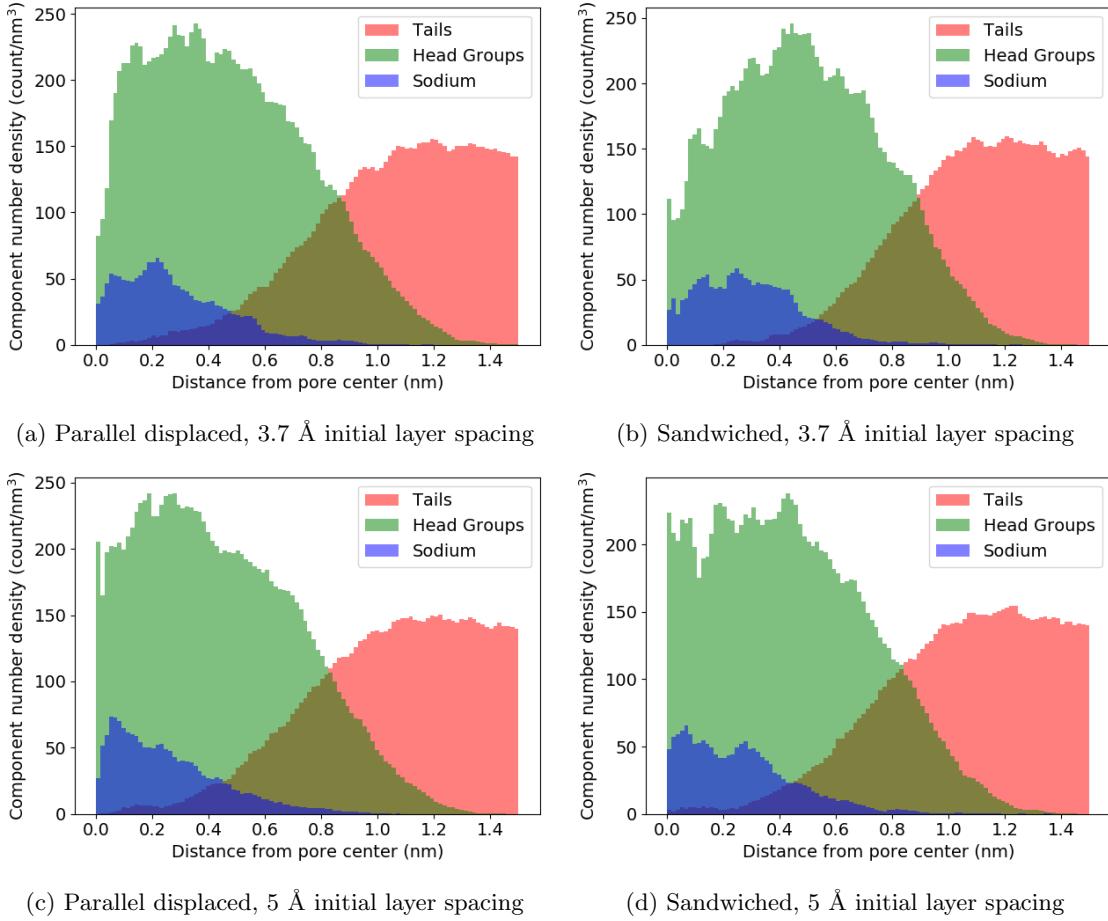


Figure 13: In all cases, the component radial distribution functions exhibit a composition gradient transitioning from the hydrophilic to the hydrophobic regions. Systems with layers initially spaced 3.7 Å apart in the parallel displaced (a), and sandwiched (b) configurations both show the highest concentrations of ions and head groups away from the pore center. Systems with layers initially spaced 5 Å apart (c) and (d), both show the highest concentrations of ions and head groups near the pore center, implying a more uniform, disordered pore.

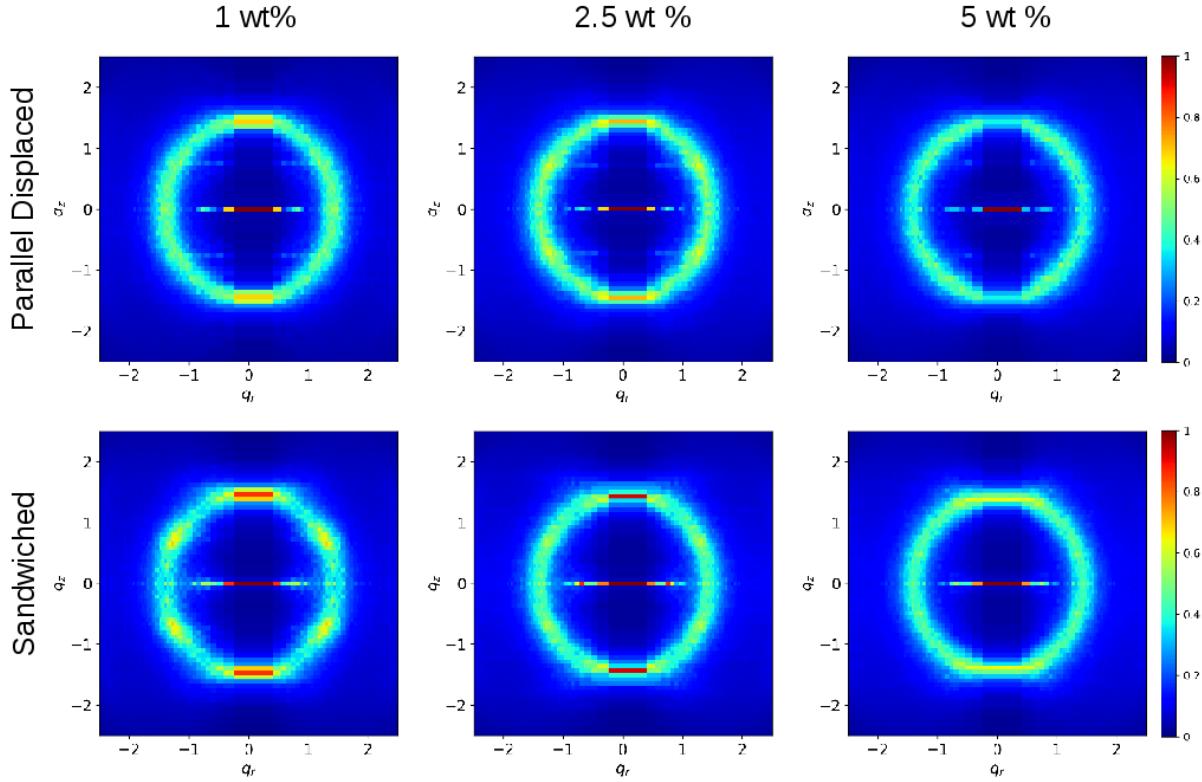


Figure 1: Simulated diffraction patterns generated from trajectories of systems built in the parallel displaced and sandwiched configurations as a function of water content shows weaker reflections than the dry system. All plots are scaled to use the same colorbar as their dry system counterpart

Figure 14

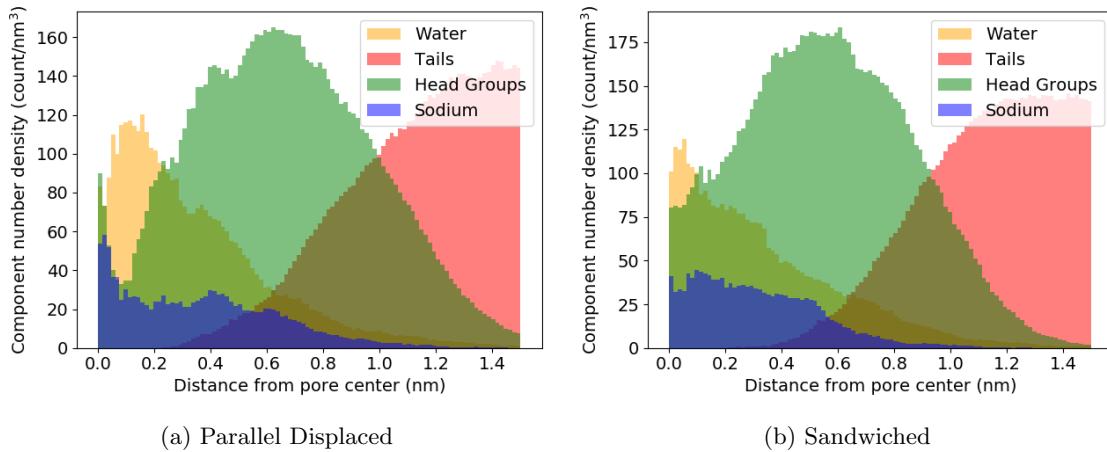


Figure 15: Water fills the membrane pores in the parallel displaced (a) and sandwiched (b) configurations. Sodium ions are distributed fairly uniformly within the pore region, defined by a radius of 0.6 nm.

water only drives disorder of the pore structure. In the true equilibrium configuration, if water exists, it is primarily confined to the pore region where there is no driving force for aggregation of water molecules. In the case of trace water, water molecules will be too sparse to form a hydrogen bonding network.

In systems built with 5 wt % water, the pore region becomes filled with water. We plotted the number density of components in this system. As with the dry systems, we see a gradual compositional transition from hydrophilic to hydrophobic. We see that the pores become a soup of water molecules and sodium ions (Fig. 15).

The membrane swells when water is introduced. The location of maximum head group density shifts from 0.35 to 0.62 nm and from 0.44 to 0.61 nm in the parallel displaced and sandwiched configurations respectively. We observe the existence of ions, head groups and water outside the pore region. In the hydrated system, the head groups drift beyond 1.5 Å from the pore center. In the dry systems, head groups did not wander beyond 1.4 Å from the pore center. Both observations suggest that all components are pushed radially outward from the pore center, characteristic of a swelling process.

This system is a closer representation of the H<sub>II</sub> phase which is typically synthesized with ca. 8 wt % water. Further investigation of hydrated systems can help unravel the mechanisms for selective transport in separations of aqueous solutions.

### 3.5 Model Ionic Conductivity Measurements

We used the equilibrated parallel displaced system to calculate ionic conductivity since its structure is the closest match to experiment. The model gives reasonable estimates of ionic conductivity when compared to experiment. Calculated values of ionic conductivity obtained using the Nernst-Einstein relation and

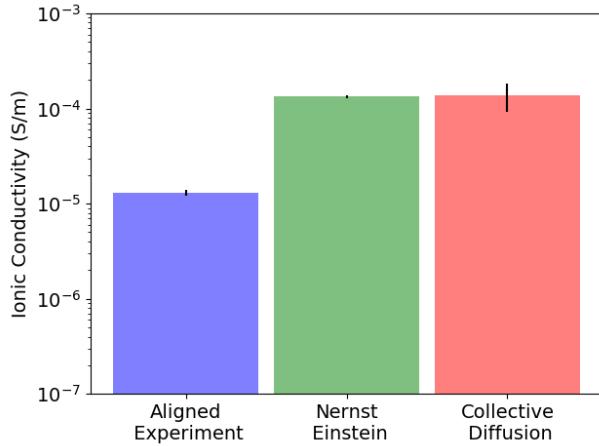


Figure 16: Calculated ionic conductivity using the Nernst-Einstein relation and Collective Diffusion model agree with error. Both methods give calculated values of ionic conductivity an order of magnitude higher than the experimental value.

Collective Diffusion model are compared in Figure 16. The two methods agree with each other within error, although the uncertainty obtained using the Collective Diffusion model is much higher. Much longer simulations are needed to lower the uncertainty, however it is not feasible to do so with a large system. We will only use the Nernst-Einstein relation in future calculations of this type.

The calculated values of ionic conductivity are higher than experiment by an order of magnitude. One can justify the reason for this result by considering the real system studied experimentally. The ionic conductivity measurement to which we are comparing was done on a  $80\text{ }\mu\text{m}$  thick film, nearly 10,000 times thicker than our simulated system. The thick film likely has defects leading to non-contiguous pores and imperfect alignment. It has been shown that there is a large dependence of ionic conductivity on the alignment of the pores. The ionic conductivity of an unaligned film is ca. 85 times lower than that of a nearly aligned film referenced here. We hypothesize that a thin, perfectly aligned film would have a value of ionic conductivity in closer agreement with our model.

### 3.6 Effect of Crosslinking

The system's structure and physical characteristics did not change significantly when we applied the crosslinking algorithm to the equilibrated parallel-displaced configuration built with 5 monomers per layer. We simulated the crosslinked system in the NPT ensemble for 100 ns. The distance between pores shrinks by  $0.4\text{ \AA}$  and the distance between layers increases by  $0.04\text{ \AA}$  after the system is crosslinked. All major features are still present in the simulated XRD patterns, however at lower intensities (Fig. 17a). We calculated the ionic conductivity using the Nernst-Einstein relation and found that it is lower in the crosslinked system

(Fig. 17b).

## 4 Conclusion

We have used a detailed molecular model of the Col<sub>h</sub> phase formed by Na-GA3C11 in order to study its nanoscopic structure. While there have been efforts to model formation of various liquid crystalline phases with molecular dynamics, to our knowledge there have been no studies which attempt to examine their structure with the same level of detail presented here.

Evidence strongly supports that monomers stay partitioned into layers which stack to create pores and that each layer contains 5 monomers. We see periodic spacing of layers based on the z-direction correlation function,  $g(z)$  of atoms in the tails and separately of atoms in the head groups. Systems not built with 5 monomers per layer result in assemblies whose pore-to-pore spacing is inconsistent with experiment.

We have explored the affect of two different  $\pi$ - $\pi$  stacking modes on the equilibrated membrane structure. Simulated diffraction patterns generated from MD trajectories suggest that the parallel-displaced configuration produces a structure with the closest match to experiment.

We have observed a number of metastable configurations. We witnessed long-term stability of systems built with a varied number of monomers per layer as well as in different  $\pi$ - $\pi$  stacking configurations. We also examined how the structure changes based on the initial distance between layers and showed how systems differ when built with layers spaced 5 Å versus 3.7 Å apart. The configuration that showed the greatest agreement with experiment was built in the parallel-displaced configuration, with 5 monomers per layer and an initial layer spacing of 3.7 Å.

We characterized the environment centered around the membrane pores and learned that the pores are generally filled by monomer head groups and sodium ions. Membranes prepared in the sandwiched configuration have more vacant pores. We also observed that there is not a hard partition between hydrophobic and hydrophilic regions, rather there is a gradient. This finding has raised questions about the nature of any size-exclusion separations.

We learned that water is not needed to create well-defined pore structures. Systems whose pores were filled with varying amounts of water showed a decrease in structuring relative to dry systems.

We justified that our system can reasonably estimate ionic conductivity. Our calculations are about 1 order of magnitude higher than experiment, however that is to be expected since we are simulating a perfectly straight and defect-free membrane.

Finally, we verified that our conclusions do not change when the system is crosslinked by the algorithm we implemented. The diffraction pattern weakens relative to the uncrosslinked system, the ionic conductivity

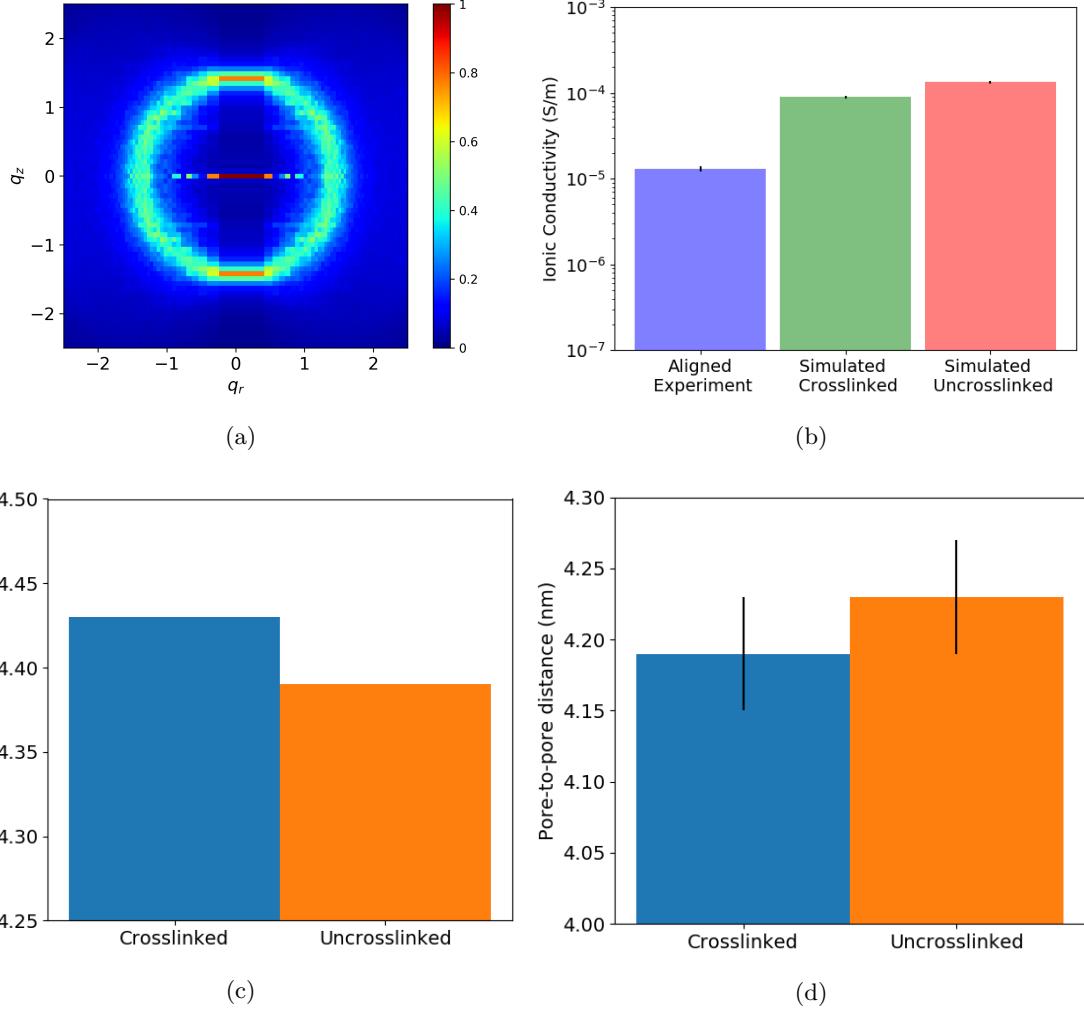


Figure 17: (a) Reflections produced by the crosslinked configuration fade relative to the uncrosslinked system. The colorbar shown is the same used for the uncrosslinked system. (b) The ionic conductivity is smaller relative to the uncrosslinked system, but still much larger than the experimental value. (c) The distance between layers increases when the system is crosslinked. (d) The pore spacing decreases when the membrane is crosslinked.

drops by a factor of ca. 1.5, in closer agreement with experiment, the pore spacing decreases and the membrane becomes thicker.

With the structural understanding gained by these simulations, we will evaluate transport of various solutes within the system. We will apply the knowledge gained from this study in order to suggest improvements to the existing system as well as to evaluate new unsynthesized LLC systems.

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