

Understanding the nanoscale structure of hexagonal phase lyotropic liquid crystal membranes

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Abstract

Nanostructured porous membranes made from the cross-linked hexagonal phase of self-assembled lyotropic liquid crystals (LLCs) are a promising material for selective separations. In this work, we develop an atomistic molecular model of an experimentally characterized LLC membrane. While it is relatively straightforward to create a stable hexagonal phase model, we demonstrate that closely reproducing the experimental pore structure requires a carefully constructed initial configuration in order to avoid falling into a metastable basin. We use simulated X-ray Diffraction (XRD) patterns in order to ensure maximum consistency between our structures and experiment. We show that pores are likely composed of 5 columns of stacked LLC monomers which surround each hydrophilic core. Although this system has been reported as dry, we show that small amounts of water are necessary to fully reproduce the experimental XRD pattern due to asymmetries introduced by hydrogen bonds between monomer head groups and water molecules. We explore, in depth, the composition and structure of the nanopores and reveal that there exists a composition gradient rather than a hard partition between the hydrophilic and hydrophobic regions. The clearer picture of the nanoscopic structure of these membranes provided in this study will enable a better understanding of the mechanisms of small molecule transport within these nanopores.

1 Introduction

More highly selective membranes would be extremely useful for the recovery of valuable products from complex aqueous and organic solutions. For example, flowback water (FW) produced during hydraulic fracturing is a complex wastewater full of potentially valuable dissolved organic compounds such as acetate.¹ There is increasing pressure to reuse hydraulic fracturing water rather than dispose of it in order to reduce social and environmental impacts as well as cost.² Rather than dispose of the wastestream generated in the recycling process, we can instead use highly selective membranes in order to successfully recover useful

compounds.

Current commercial RO and NF membranes suffer limitations to their selectivity which is inherent to their fabrication. Although scalable, each of these two types of membranes has a degree of stochasticity that makes overcoming well-known the permeability-selectivity tradeoff a challenge. 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

Selective separation by a semipermeable membrane barrier is a function of the geometric and chemical interactions of solutes with the membrane material. A molecule's size, shape, charge and polarity combine to determine the degree to which a solute partitions into a membrane and how fast it travels through the membrane. To separate a component from a mixture, one must understand how to design membranes in order to tune the relative transport rates of desired and undesired solutes.^{4,5}

Crosslinked lyotropic liquid crystal (LLC) membranes may be capable of performing highly selective separations. LLCs are amphiphilic molecules that have the ability to self-assemble into porous nanostructures⁶ which can be crosslinked to create mechanically strong membrane films with pores on the order of 1 nm in diameter.⁷ Unlike most commercial NF membranes, LLC membrane pores are uniform in size because they are self-assembled. Since LLC membranes lack a pore size distribution, they inherently exhibit high selectivity due to their strict molecular weight cut-off (MWCO).⁷ Additionally, the LLC monomers described in this paper are salts, and therefore lead to Donnan exclusion of ions in solution. The membrane gains a net surface charge when counterions from the head groups that line the pore walls escape into the feed solution in order to balance the gradients of concentration and electric potential.⁸

The feasibility of nanostructured LLC membranes for selective separations has been demonstrated using LLCs that form the type 1 bicontinuous cubic (Q_I),^{9–11} and the inverted hexagonal (H_{II})⁷ phases (See Figure ??). 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.¹ 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.⁷

The H_{II} phase pore geometry has a higher theoretical capacity for transport than the Q_I phase. The H_{II} phase forms at room temperature in the presence of c.a. 10 wt% water and consists of hexagonally packed, hydrophilic pore columns.⁶ In the absence of water, neat monomer will form the same hexagonal columnar structure which, in literature, has been referred to as the Col_h thermotropic phase¹² (See Figure ??). Q_I phase membranes consist of a tortuous network of three dimensionally interconnected pores that prevent optimal through-plane transport. The densely packed, non-tortuous and uniform sized pores of H_{II} phase membranes represent the ideal geometry for achieving high solute flux.¹³ Despite the promise of the H_{II} phase, the hexagonally packed liquid crystalline domains, formed when Na-GA3C11 monomers self-assemble, are isotropically aligned which is detrimental to membrane permeability.

Recently, researchers have learned how to macroscopically align the hexagonal domains which has revived research into H_{II} phase LLC membranes. Previously, research efforts were focused on the Q_I phase, whose geometry does not require alignment. In 2014, Feng et al. showed that one can align Col_h hexagonal domains using a magnetic field with subsequent cross-linking to lock the structure in place.¹² In 2016, Feng et al. showed that one could obtain the same result using a second technique termed soft confinement.¹⁴ Current efforts are focused on extending the method to the H_{II} phase and characterizing the performance of these newly aligned systems.

Our current understanding of the molecular details of LLC membrane nanostructure is not sufficient to be able to precisely design them for specific separations. Over the past 20 years, H_{II}-phase LLC polymer membrane studies have been limited primarily 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.¹⁵

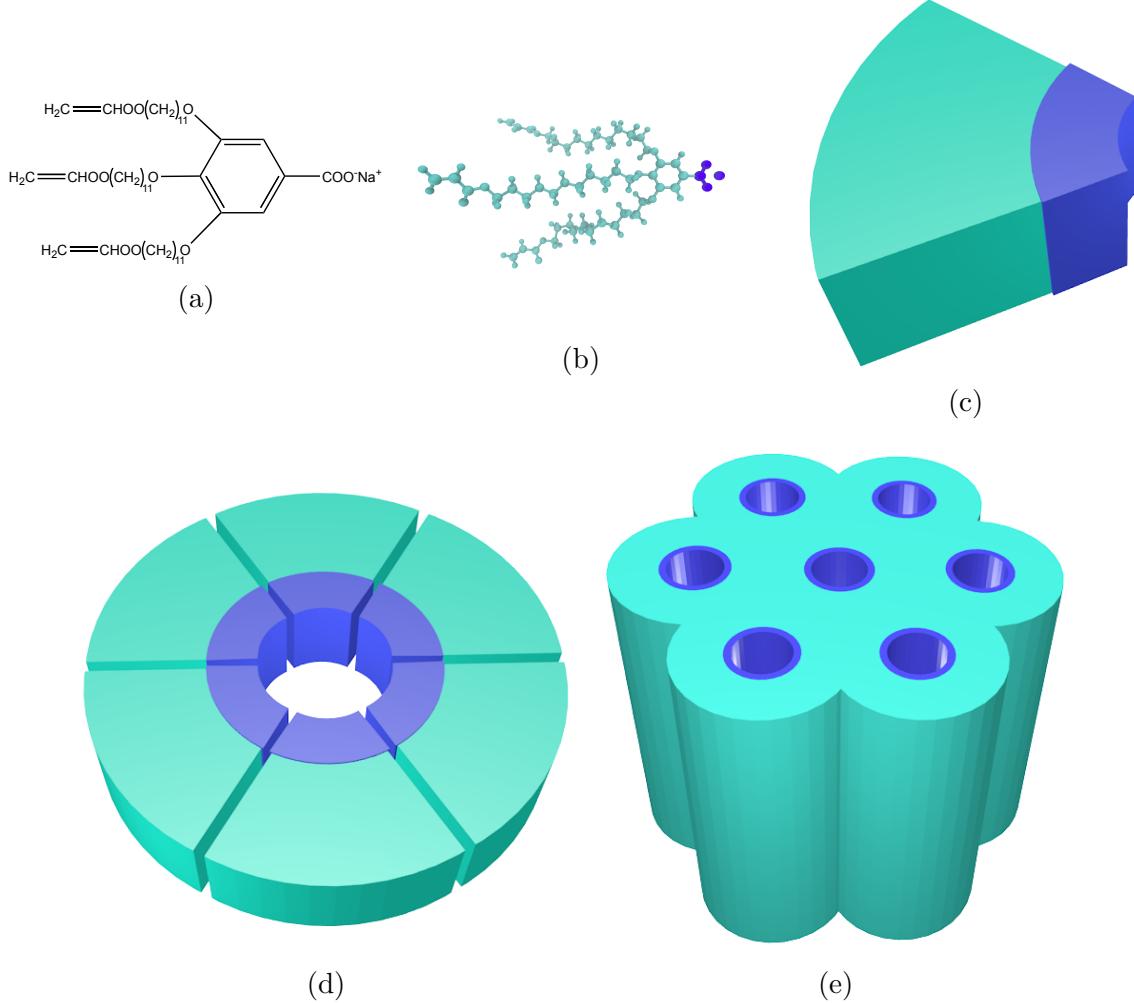


Figure 1: The LLC monomer Na-GA3C11 (a) rendered atomistically (b) exhibits wedge-like character (c). Monomer wedges assemble into disks (d) with hydrophilic head groups (blue) facing towards the disk center. The disks assemble into hexagonally packed columnar mesophases (e).

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.⁷ 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.⁹ 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 LLC polymer membrane structure, 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. A good molecular model 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. Models resulting from molecular dynamics simulations can provide the required level of detail (Fig. 2), 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 observe how the choice of head group interacts with solutes of interest. We can interchange counterions which may influence both the pore size and the strength of the Donnan potential.

In this study, we build a significantly more realistic atomistic model of LLC membranes than, to our knowledge, has ever previously been created, 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 drawn from small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) experiments as well as in matching ionic conductivity measurements.¹⁴

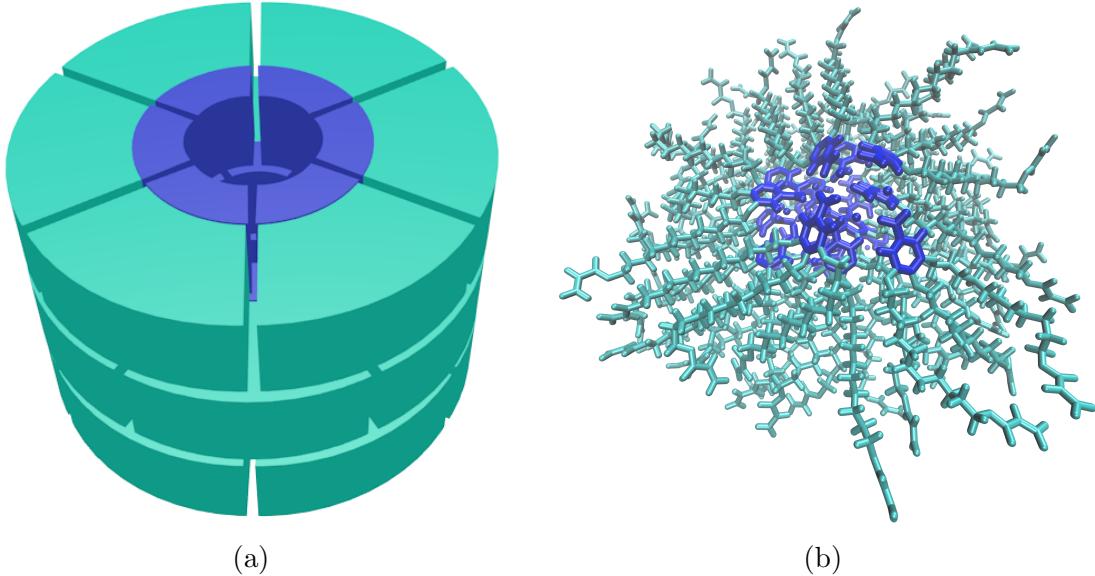


Figure 2: (a) Previous understanding of the pores are essentially speculations based on limited chemical and experimental data. (b) We use a detailed molecular model in this paper in order to appropriately model the pore’s complex architecture which is crucial to understanding the mechanism of solute transport. In both pictures, the head group region is colored blue and the tail region is colored cyan.

In this paper, we develop a molecular model of the Col_h assembly formed by Na-GA3C11. Compared to the H_{II} phase, the Col_h phase is a simpler starting point. The system has no water which will allow us to simulate longer timescales, and there exists detailed experimental characterization of the fully aligned state, including 2D wide-angle X-ray scattering (WAXS) patterns (Figure 3b) which are useful for reconstructing structural data. We will use this Col_h model in order to build an H_{II} model in the future.

There are five major features of interest present in the 2D experimental pattern shown in Figure 3b.

1. *R- π* : The location of the first is at $q_z = 1.7 \text{ \AA}^{-1}$, corresponding to a real space separation of 3.7 Å. Previous work¹² attributes this reflection to π - π stacking between aromatic rings in the direction perpendicular to the membrane plane, or z-axis.¹² For simplicity, we will refer to this reflection as R- π .

2. *R-double*: A weak intensity line, located at exactly half the q_z value of R- π ($q_z = 0.85 \text{ \AA}^{-1}$), corresponds to a real space periodic spacing of 7.4 \AA . Since this reflection corresponds to double the spacing of R- π in real space, will refer to this reflection as R-double. R-double has been interpreted as 2_1 helical ordering of aromatic rings along the z axis,¹² meaning that if one traces the positions of the aromatic rings with a helical curve, then for each full turn in the helix, one will encounter two aromatic rings.
3. *R-alkanes*: A low intensity ring located at $r = 1.4 \text{ \AA}^{-1}$ marks the third major reflection of interest. The real space separation corresponds to 4.5 \AA which is characteristic of the average spacing between packed alkane chains.¹⁶ We will call this reflection R-alkanes.
4. *R-spots*: Within R-alkanes, are four spots of higher relative intensity. Accordingly, we name these reflection R-spots. The location of all spots is $\sim 37^\circ$ from the q_z axis in their respective quadrants. In many liquid crystal systems one can explain the spots as the tilt angle of the alkane chains with respect to the membrane plane.¹⁷
5. *R-pores*: The final feature corresponds to the spacing and symmetry of the d_{100} plane. This plane is geometrically related the distance between pores. The feature, which we named R-pores, is characterized by dots along the equatorial axis defined when $q_z = 0$. The spacing between dots is indicative of the hexagonal symmetry of the packed pores. We observe the same information with higher resolution using SAXS (Fig. 3a).

Despite having structural data, there is still information which experiment cannot definitively answer. There are a number of structural questions we wish to answer in this article. We want to know:

1. What is the density of monomers that pack around each hydrophilic core?

Authors often describe this and similar systems as being made up of layers. 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

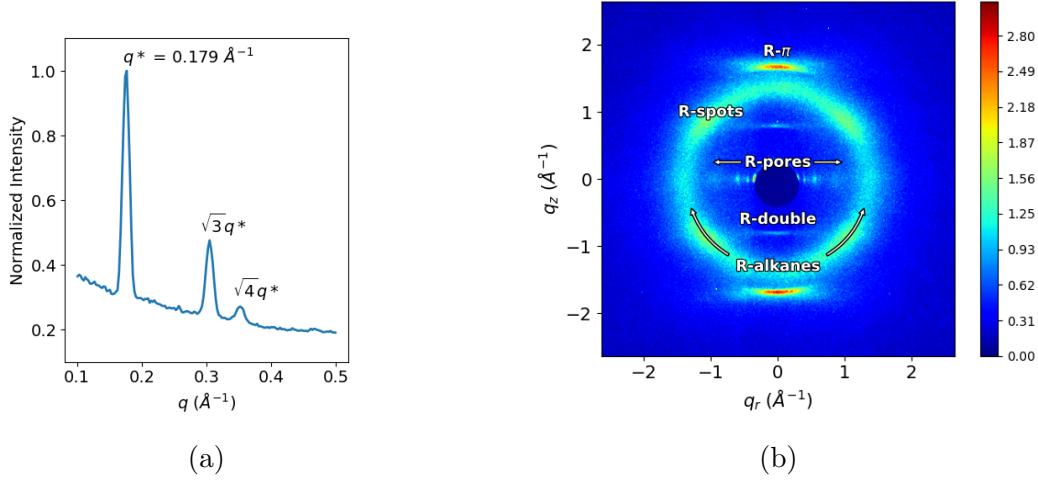


Figure 3: (a) (Reproduced from 14) The repeat spacing in the 1D small angle X-ray scattering pattern is characteristic of hexagonal packing. The leading peak, q^* , represents the distance between the d_{100} planes. Using this distance, we know that the distance between pore centers is 4.12 nm. (b) 2D WAXS gives details about repeating features on the order of angstroms. Experimentalists have explained each of the 5 major reflections present as follows: (R- π) Aromatic head groups $\pi - \pi$ stack 3.7 Å apart. (R-double) Monomers arrange vertically in a 2_1 helix. (R-alkanes) Alkane chain tails pack 4.5 Å apart. (R-spots) Monomer tails are tilted with respect to the membrane plane. (V) As derived from SAXS, the pores are spaced 4.12 nm apart and pack hexagonally

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.¹⁵

We are careful to avoid the term 'layers' since many liquid crystalline systems have long range order in 1 or 2 spatial dimensions and short range order in the other dimensions.¹⁹

In the system we are studying, there are long-range 2D correlations in the hexagonal array of pores (xy plane) and short range correlations in the z-direction. In this study, we use our atomistic molecular model to study how the system's structure is affected by the density of monomers surrounding each pore's hydrophilic core.

2. What structural motif best matches experimental 2D WAXS patterns?

On the short timescales accessible to MD (even the 100's of nanoseconds of simulation performed here are short compared to experimental timescales), we observe distinct

metastable configurations which depend on starting configuration. We simulated XRD patterns of our system and compared them to experimental 2D WAXS patterns (Figure 3b) so that we ensure our model creates a nanoscopic chemical environment maximally consistent with experiment within the constraints of our forcefield. Using this approach, we are able to confirm some previous interpretations of the WAXS pattern and refute others.

3. What is the chemical composition of the pores?

The limited picture that experiment provides tells us that there are hexagonally packed, hydrophilic regions where transport is likely to occur. One may instinctively imagine these regions as tube-like pathways with well-defined boundaries. We will explore the composition of the pores, the partition between the hydrophilic and hydrophobic regions, and its sensitivity to initial configuration.

4. Is it necessary to include any water in order to appropriately model the Col_h phase?

While the Col_h phase is described as dry, it is likely that small amounts of ambient water may be leached into the system. The hydrogen bonding network formed by the water may play a role in structuring the pore. We used simulated X-ray diffraction patterns to see if there is any meaningful structural difference between a "dry" and "wet" system.

2 Methods

2.1 Monomer Parameterization

We parameterized the liquid crystal monomer Na-GA3C11 using the Generalized AMBER Force Field (GAFF)²⁰ with the Antechamber package²¹ provided with AmberTools16.²² We assigned atomic charges using the am1bccsym method of `molcharge` shipped with

QUACPAC from Openeye Scientific Software. We ran all molecular dynamics simulations using GROMACS 2016.^{23–26}

We generated an ensemble of characteristic, low-energy vacuum monomer configurations by applying a simulated annealing process to a parameterized monomer. We cooled monomers from 1000K to 50K over 10 nanoseconds. We randomly pulled a low energy configuration from the trajectory then reassigned charges using `molcharge`. Using the new charges, we annealed the monomer system again and pulled a random monomer configuration from the trajectory which we used for full system construction (Figure 4a). See section S-2 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-grained model self assemble into the H_{II} phase configuration in ∼1000 ns.²⁷ We attempted atomistic self-assembly by packing monomers into a box using Packmol.²⁸ Simulations of greater than 100 ns show no indicators of progress towards an ordered system (See section S 1). To bypass the slow self-assembly process, we use Python scripts 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 columns of stacked monomers with periodic continuity along the pore axis, avoiding any edge effects and creating an infinite length pore ideal for studying transport. We prefer a small number stacked monomers in order to reduce computational cost and to allow us to look at longer timescales. Ultimately, we chose to build a system with 20 monomers per column in order to obtain sufficient resolution when simulating X-ray diffraction patterns.

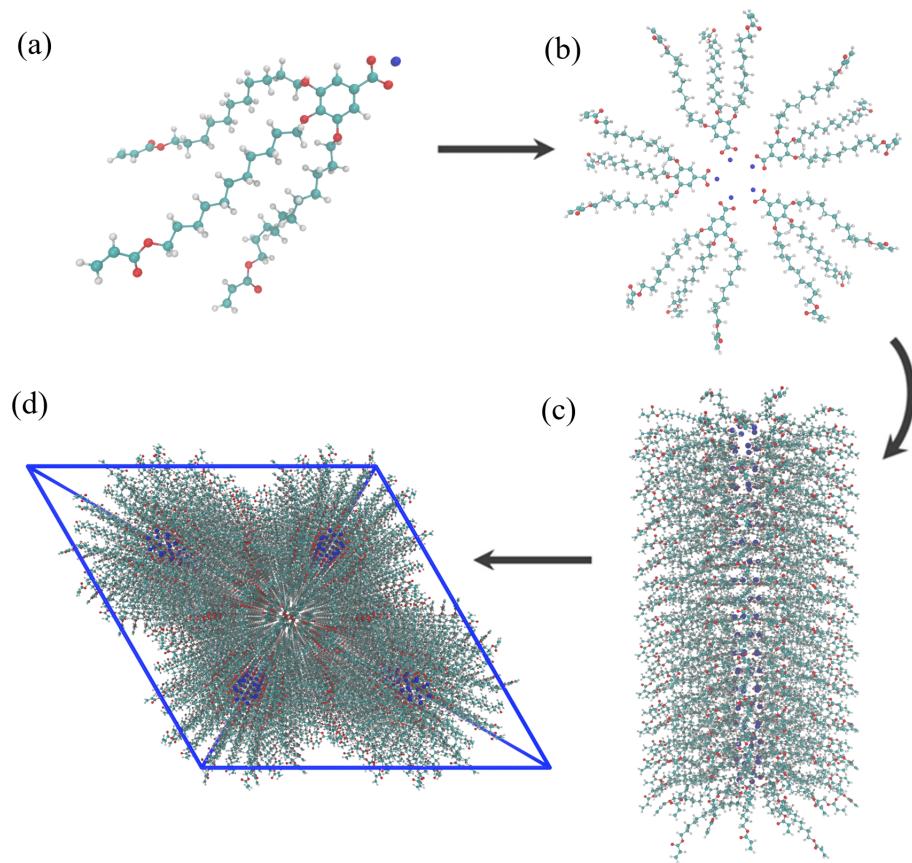


Figure 4: (a) We parameterized a single monomer and annealed it to produce a low energy configuration. (b) A Python script assembles monomers into columns which are duplicated and rotated to surround hydrophilic pore centers. (c) We chose to stack twenty monomers into each column. (d) The pores are duplicated and placed into a monoclinic unit cell.

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 if one chooses a reasonable value. The pore radius is chosen to be 0.5 nm in our initial configurations. The initial distance between pores, within a wide range, 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, \sim 10% larger than the experimental value of 4.12 nm. A sensitivity analysis of both parameters is presented in the Supporting information, section S-4. The distance between vertically stacked monomers, the position of monomers with respect to vertically adjacent monomers, and the number of columns per pore do influence the equilibrated structure and require further justification for their choices. We rely on experimental data to inform them.

We chose the vertical spacing between monomers 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 its aromatic head groups would be coplanar with the xy plane. We explored three different initial monomer spacings. The first is exactly equal to $R-\pi$ with layers placed so aromatic rings stack 3.7 Å apart in the z-direction. We explore a second system with an initial spacing of 5 Å. We briefly explored a third system with an initial spacing of 10 Å. However this spacing yields non-physical behavior which is detailed in the Supporting Information, section S-4.3.

We chose the relative orientation between vertically adjacent monomers in each column 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.²⁹ We ruled out the T-shaped configuration because its \sim 5 Å equilibrium stacking distance²⁹ 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. We will explore the system’s preference towards the sandwiched vs. parallel displaced stacking modes in some detail. Both have reported stacking distances near the $R-\pi$ value of 3.7 Å. Head groups in our sandwiched initial configuration stack directly on top of each other while head groups in the parallel displaced initial configuration stack with an offset of $180^\circ/ncol$ where $ncol$ is the number of columns per pore. See the Supporting Information, Figure 5 for a detailed illustration of the initial configurations in each mode.

The number of columns per pore is unknown, as stated in question (1). We tested configurations constructed with a varied number of columns per pore. We built systems 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 kJ mol $^{-1}$ 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 KJ mol $^{-1}$ nm $^{-2}$, we reduce the restraints in a sequence with values of 8, 3, 2, 1, and 0 KJ mol $^{-1}$ nm $^{-2}$ respectively. We allow the resulting unrestrained structure 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`. We remove all water molecules placed outside the pore region. Then we

randomly remove water molecules inside the pore region until the pores reach the desired concentration of water. The remainder of the equilibration follows the same procedure as the dry system.

2.5 Equilibrium Calculations

2.5.1 *Determining equilibration time*

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.^{30,31} Typically, the pore-to-pore distance equilibrates between 200 and 350 ns. We used data collected after equilibration to do all subsequent analysis.

2.5.2 *Calculation of pore spacing*

To calculate the equilibrated pore spacing, we measured the distance between pore centers. We located the pore centers by averaging the coordinates of sodium ions in their respective pores. We generated pore spacing statistics using the bootstrapping technique (See section S-3 of the Supporting Information).

2.5.3 *Pair distribution functions and correlation length*

The normalized pair distribution function, $g(\mathbf{r})$, describes the probability of finding a pair of particles separated by \mathbf{r} ,

$$g(\mathbf{r}) = \frac{1}{\rho N} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \delta(\mathbf{r} + \mathbf{r}_j - \mathbf{r}_i) \right\rangle \quad (1)$$

where ρ is the average number density of particles and $\delta(\mathbf{r})$ is the Dirac delta function.³² We applied equation 1 in three dimensions and then extracted one dimensional distribution

functions using slices of the grid along the appropriate axis.

We measured the one dimensional pair distribution function, $g(z)$, between centers of masses of aromatic head group rings along the z-axis (perpendicular to the membrane plane). We averaged all 1D slices in the z-direction of the full 3D correlation function within 2.1 Å of $(x, y) = (0, 0)$. We chose 2.1 Å as a crude approximation of the radius of the phenyl ring plane. We calculated the radius as the sum of the longest C-C distance within a phenyl ring (2.8 Å) and two times the carbon atom radius (0.7 Å).

Here, $g(z)$ is characterized by an oscillatory function with a period equal to the average distance between stacked monomers, and an amplitude that decays exponentially (See Figure 12). The rate of decay is related to the correlation length, L, between monomer head groups. We estimated L by fitting the peaks of $g(z)$ to a decaying exponential function of the form:

$$Ae^{-z/L} \quad (2)$$

where A is a fitting parameter for amplitude, z is the independent variable of $g(z)$ and L is the fit correlation length. The error in the estimated value of L is calculated as the square root of the diagonal entry of the covariance matrix of optimized fit parameters.

We also used $g(z)$ to calculate the equilibrated vertical stacking distance between monomers, d_{equil} . We fit a decaying sinusoidal function to $g(z)$ of the form:

$$1 - A \cos\left(\frac{2\pi}{d_{equil}}z + B\right) e^{-z/L} \quad (3)$$

where A and B are fit parameters for the function's amplitude and phase shift respectively. This function could be used in place of Equation 2, however it does not fit the peaks of $g(z)$ from parallel displaced configurations well enough to extract a reliable value of L.

2.5.4 Radial distribution functions

We explored the pores' compositions 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. We binned the radial distance of all atoms in each group from the pore centers, then normalized by the volume of the annulus defined by the bin edges and the z box vector (See Figure 19 in the Supporting Information).

2.5.5 Simulated structure factor calculations

Simulated X-ray diffraction patterns were 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 electronic radius. 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. The experimental WAXS measurement was made using a vertically aligned film whose pores were oriented perpendicular to the direction of the incident X-ray beam. Although the pores were vertically aligned, the crystalline domains were still misaligned with respect to the xy plane. To account for this, we averaged 2D slices of the structure factor at all angles about $|\mathbf{q}| = (0, 0, z)$.

We normalized all diffraction patterns 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} and divide all intensities by this values. In this way, the average intensity of the alkanes is equal to 1. When calculating I_{avg} , we excluded intensities within $\pm 30^\circ$ of the meridional axis defined by $q_r = 0$, since the simulated patterns differ from experiment in those regions in all cases. Specifically, in contrast to the experimental WAXS pattern, R- π appearing in simulated diffraction patterns intersects with

R-alkanes (See Fig. 7). We set an upper bound on the colorbar by multiplying I_{avg} by a scaling factor, f . Intensities that appear in the patterns $\geq f \times I_{avg}$ are colored uniformly. We apply the same scaling method to the simulated patterns. We carefully chose a scaling factor of $f = 3.1$ in order to visibly display all features in the all patterns.

2.5.6 *Ionic conductivity calculations*

We calculated ionic conductivity using the Nernst-Einstein relationship, which relates the DC ionic conductivity, σ , to ion diffusivity, D , concentration, C , ion charge, q , the Boltzmann constant, k_b , and temperature, T :

$$\sigma = \frac{q^2 C D}{k_b T} \quad (4)$$

We measured sodium ion diffusion coefficients by calculating the slope of the linear region of the z-direction mean square displacement curve as indicated by the Einstein relation.³³ We visualized the MSD plot to determine where to begin and end a linear fit. We measured ion concentration with respect to the volume of the entire unit cell.

2.6 Cross-linking

In order to maximally match the experimental membrane synthesis process, we created a cross-linking algorithm that one can apply to equilibrated structures. The primary purpose of cross-linking is to create a mechanically robust membrane. For that reason, we are not concerned with replicating the kinetics of the reaction, but instead emphasize understanding how much and in what way cross-linking modulates the system's structure.

We developed the algorithm based on the known reaction mechanism. Cross-linking of this system is a free radical polymerization (FRP) taking place between terminal vinyl groups present on each of the three monomer tails. The reaction mechanism is drawn out in Figure S-23. FRPs require an initiator which bonds to the system, meaning new atoms are introduced into the system. For simplicity, we simulated the initiator as hydrogen and made

it present in the simulation by including them as dummy atoms in all possible locations where an addition could occur. We carry out the cross-linking procedure iteratively. During each iteration, the algorithm selects eligible bonding carbon atoms 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.³⁴ We did not consider direction of attack because the resultant mixture is racemic.

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

3 Results and Discussion

3.1 Density of monomers around pores

Our simulations best support a model built with 5 monomer columns per pore based on the measured equilibrated pore-to-pore distances. To discern the composition of the monomer layers, addressing question 1, we ran simulations of systems created with 4–8 columns per pore. We built systems in both the parallel displaced and sandwiched configurations and equilibrated them according to the dry equilibration procedure. We tested all systems with an initial vertical monomer spacing, d , of 3.7 Å in accordance with R- π . We tested 4 additional systems with monomers initially spaced 5 Å apart vertically (See section 4.1 of the supporting info for more details on sensitivity to initial layer spacing). We considered the pore-to-pore spacing to be equilibrated as defined in section 2.5.1. Figure 5 shows the equilibrated pore-to-pore distances for all systems tested.

All systems tested, although equilibrated from the perspective of the metrics used here, are frozen in metastable basins. Not all make physical sense or fit the experimental profile that we are trying to match. In the limit of infinite simulation time, all systems will in theory converge to a single equilibrium configuration, but that time is far beyond the 100's of nanosecond simulated here. For simplicity, we group the systems studied here into the ordered and disordered basins. Any system where $d = 3.7 \text{ \AA}$ will be included in the ordered basin and any system where $d = 5.0 \text{ \AA}$ will be included in the disordered basin. The reason for these names will become clearer as we progress through our analysis.

Systems built with 5 columns in each pore 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 columns per pore. Ordered basin systems built with 6 columns per pore, have an equilibrated pore spacing ca. 0.50 nm higher than experiment. Ordered basin systems built with 4 columns per pore equilibrate to an average pore spacing 0.25 nm lower than experiment.

Disordered basin systems built with 6 columns-per-pore are not compact in the z-direction. The final pore spacing is close to experiment within its uncertainty. Relative to ordered basin 6 column-per-pore systems, the unit cell is elongated in its z dimension and contracted in its x and y dimensions, however the box volume stays nearly constant in all cases (Figure 6). The system is likely not fully equilibrated and may eventually rearrange into something that resembles a 5 column-per-pore system. Further investigations into this are beyond the scope of this paper.

3.2 Structural refinement with 2D WAXS data

We further refined our structural understanding of the system by simulating X-ray diffraction patterns produced from equilibrated MD trajectories and comparing them to experiment. We tested systems built with 5 columns per pore in the parallel displaced and sandwiched configurations at 300 K in the ordered and disordered basins. We extended each simulation

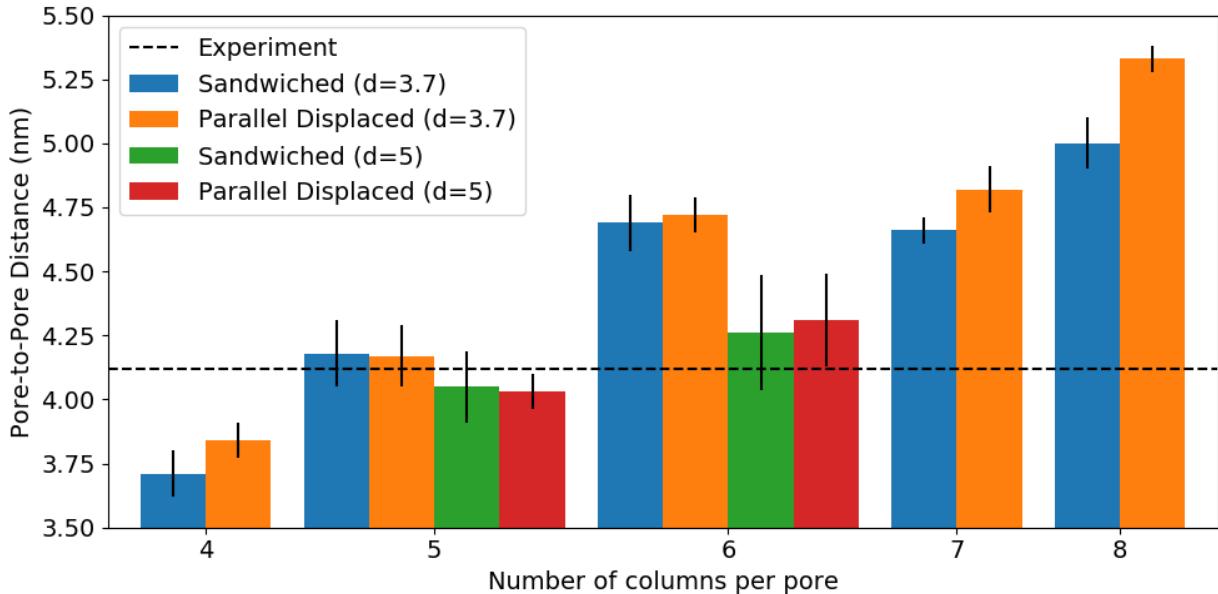


Figure 5: Systems with 5 columns per pore have equilibrated pore spacings closest to the experimental value of 4.12 nm. The equilibrated pore spacing of the model increases as the number of columns in each pore increases.

by 100 ns in order to get more equilibrated data. We generated simulated patterns using the extended simulation trajectories. The patterns for all structures are shown and compared to experiment in Figure 7.

The diffraction patterns show some noise, especially along the axis where $q_r=0$. There are two main reasons for this noise. First is that we angle averaged the 3D structure factor (see section 2.5.5) which inherently gives less data as \mathbf{q} approaches 0. Second, our simulations are not long enough to sample enough truly independent configurations within their respective metastable basins. By sampling more uncorrelated equilibrium configurations, we can suppress some of the noise (See section S7).

The simulated XRD patterns show moderate qualitative agreement with experiment. R-alkanes and R-pores appear in the expected location. R-pores is more intense than experiment, likely because we are simulating a near perfect, infinite hexagonal array. The real system has defects and domain misalignment which decreases the overall intensity. R-spots appears to be weaker, except for the ordered basin sandwiched configuration, in the simu-

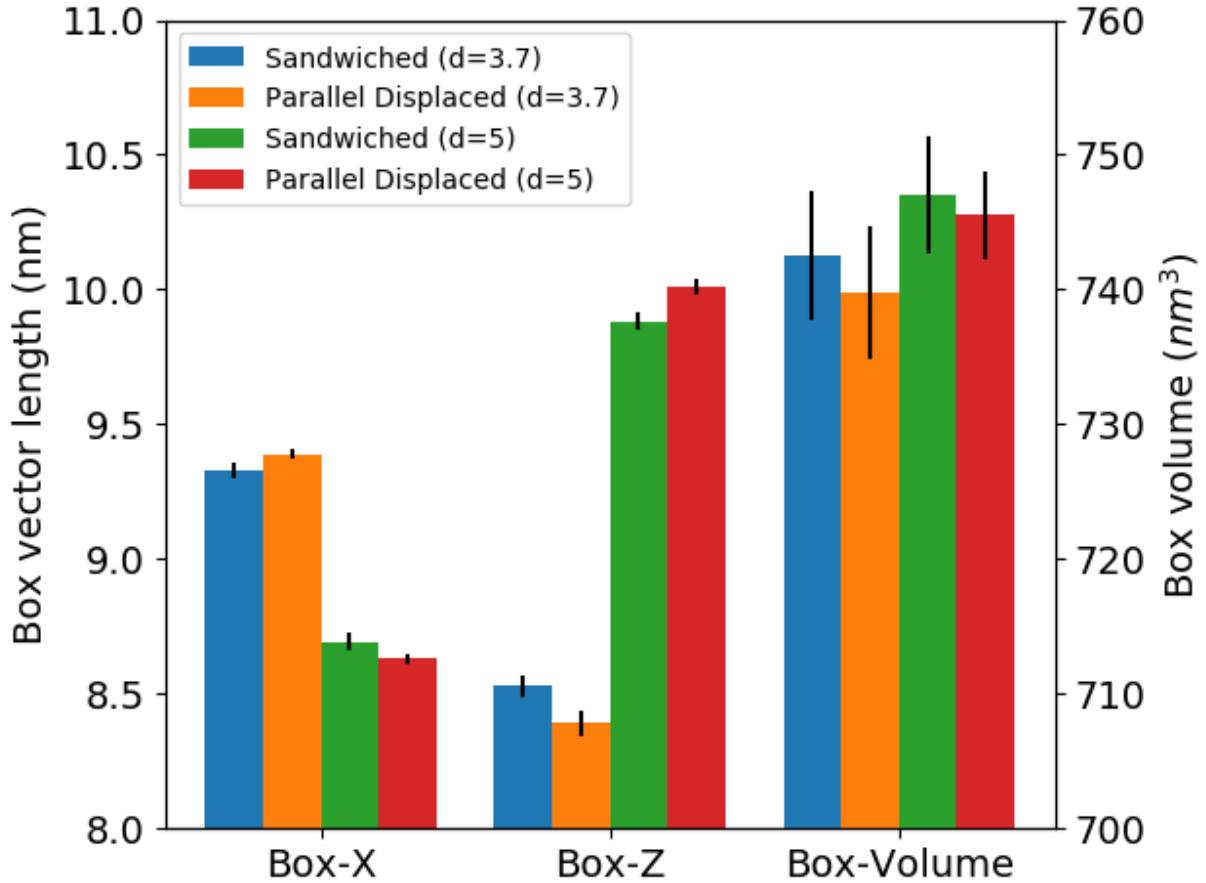


Figure 6: When monomers are initially stacked 5 Å apart ($d = 5 \text{ \AA}$), the unit cell expands in the z direction and contracts in its x and y dimensions. The volume remain nearly constant across all cases. The y dimension box vectors are not included since we use semiisotropic pressure coupling which requires that the x and y box vectors change uniformly.

lated patterns. R-spots is also partially engulfed by the wide R- π reflection. R- π appears at a lower q_z value than experiment. In all systems, the reflection reaches its maximum at $q_z < 1.5 \text{\AA}^{-1}$ which means that monomers prefer to stack at least 4.2 Å apart rather than 3.7 Å. R-double does not appear in any of the patterns.

The simulated XRD patterns of the parallel displaced configurations show an additional reflection due to their helical structure. There are horizontal reflections near $|q_z| = 0.7 \text{\AA}^{-1}$, half of the q_z value of R- π . The reflection does not cross through $q_r = 0 \text{\AA}^{-1}$ so it does not necessarily appear for the same reason as R-double. This type of pattern is characteristic of a helix (reference something). It is possible that these reflections contribute to the diffuse

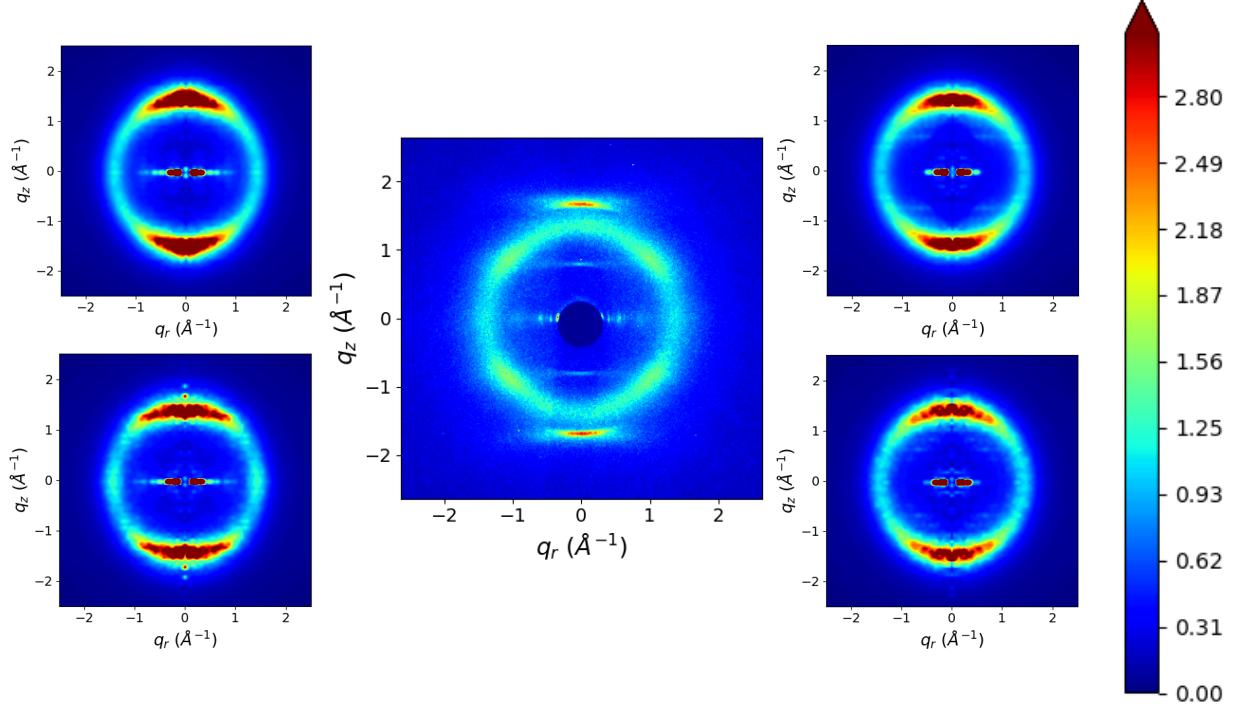


Figure 7: Simulated X-ray diffraction patterns show some qualitative agreement with experiment. Shown is a comparison of the (a) Sandwiched, ordered basin (b) Sandwiched, disordered basin (d) Parallel Displaced, ordered basin and (e) Parallel Displaced, disordered basin configurations with (c) experimental WAXS. Quantitative comparisons of the relative intensities of reflections of interest are present in Table 1. In all cases, R-double is not present.

reflections that connect R-spots and R-double in the experimental pattern.

We quantified the numerical discrepancies present when comparing the relative intensities of each reflection of interest between experimental and simulated patterns. Table 1 shows the relative intensities of each reflection for all systems tested. The patterns are normalized so that the average intensity of R-alkanes must equal 1. We measured the approximate intensity of R- π and R-double by measuring the intensity of the appropriate peaks of the cross-section of the 2D pattern at $q_r = 0$. The relative intensity of R- π is significantly higher than experiment in our simulations. R-spots is measured as the average intensity within the region bounded by a 'spot'. We identified spots based on visual inspection. If the spots were not easily discernible, then the intensity was taken as that of the intersection of R-alkanes at half the q_z value of R- π , since that is where it appears experimentally. The intensity of

R-spots is slightly lower than experiment in all cases. There is no R-double intensity to be measured. Figures are provided in section S6 to make these measurements clear.

Table 1: The simulated XRD patterns of the systems tested, normalized so that the average intensity of R-alkanes equals 1, show R- π reflections that are significantly higher than experiment and R-spots reflections that are slightly lower than experiment. R-double does not appear in any patterns, and thus has no measurable intensity.

Reflection	Configuration					
	Experiment	Sandwiched	Parallel	Disordered	Disordered	
			Displaced	Sandwiched	Parallel	Displaced
R-alkanes	1.0	1.0	1.0	1.0	1.0	1.0
R-spots	1.3	1.3	1.2	1.1	1.2	
R- π	2.8	44.0	7.7	8.4	10.1	
R-double	0.9	—	—	—	—	

There are clear differences between simulated and experimental results that must be addressed and justified. We will explore the possible origin of each experimental reflection and form structural hypotheses related to their appearance in our simulated patterns. Specifically, we want answer:

1. What is the origin of R-spots?
2. Why is the intensity of R- π so much greater than experiment?
3. What is the origin of R-double?

3.2.1 Origin of R-spots

We observe an increase in the intensity of R-spots when we simulate systems at 280K. R-spots is most intense in the ordered basin sandwiched configuration (Figure 8b). The relative intensity of R-spots is slightly higher than in experiment (1.5 vs. 1.3). R-double is still not present. We will use the system simulated at 280K to more thoroughly explore the origin of R-spots.

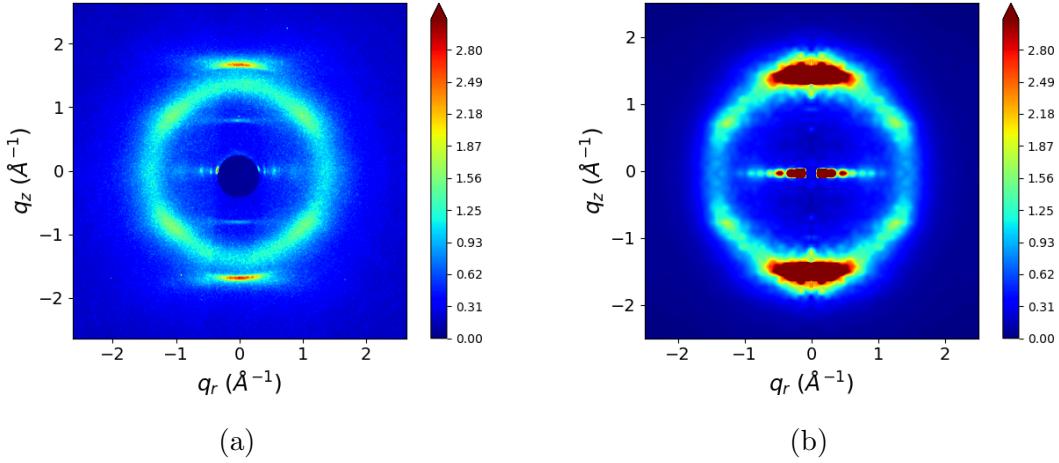


Figure 8: R-spots increases in intensity when the temperature of the system is lowered to 280K. In this case, the simulated R-spots is more intense than experiment.

Evidence strongly suggests that the R-spots signal is not a result of alkane chain tilt. Previous literature has attributed the spots in this particular WAXS pattern as the product of tilted alkane chains.¹² We looked closer at the sandwiched configuration simulated at 280K. We measured the tilt angle of the alkane chains and showed that our system equilibrates to an average tilt angle of -2°(Fig. 9).

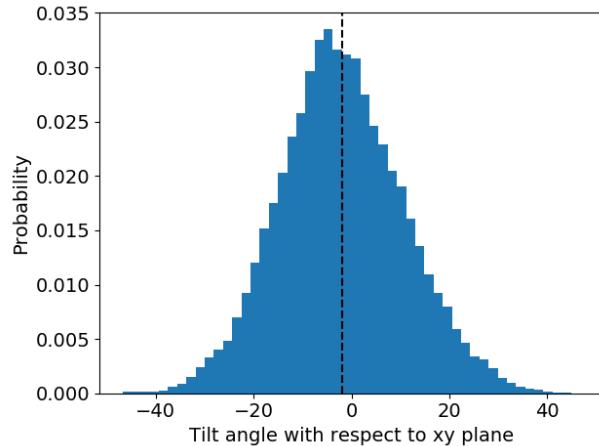


Figure 9: We measured the angle made between each monomer alkane tail and the membrane plane. The average tilt angle (dashed line) is near -2° which is far from the 37° tilt angle previously used to explain R-spots.

To understand the origin of R-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 with the remaining atoms, 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 (Figure S18) 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 Figure 11a 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 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 distinct peaks ca. 30° , in close agreement with the previously measured angle distribution (Figure 11b). 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.

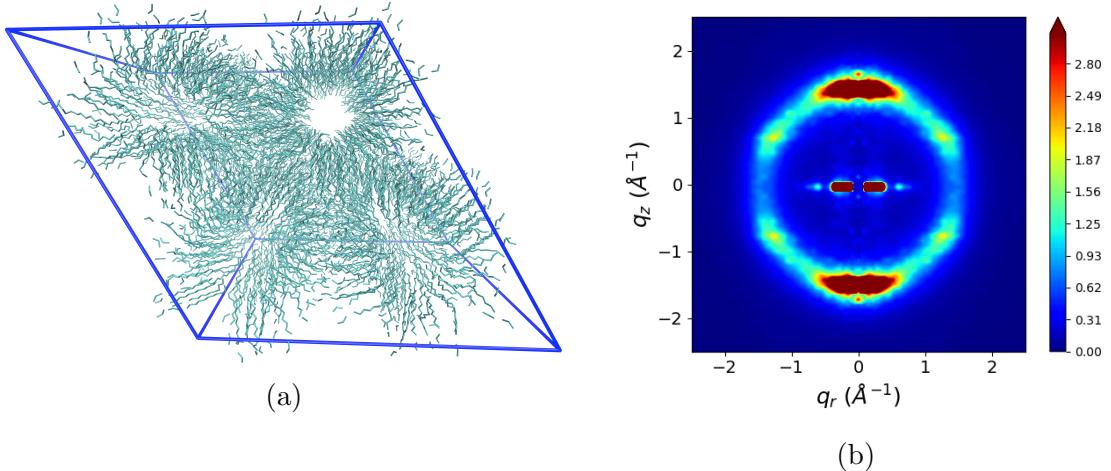


Figure 10: (a) We removed all atoms except carbon atoms that constitute the tails from a sandwiched configuration trajectory. (b) The simulated XRD pattern of the tail-only trajectory still shows R-spots

There are two reasons why we see stronger ordered chain packing at 280 K compared to experimental conditions of 300 K.

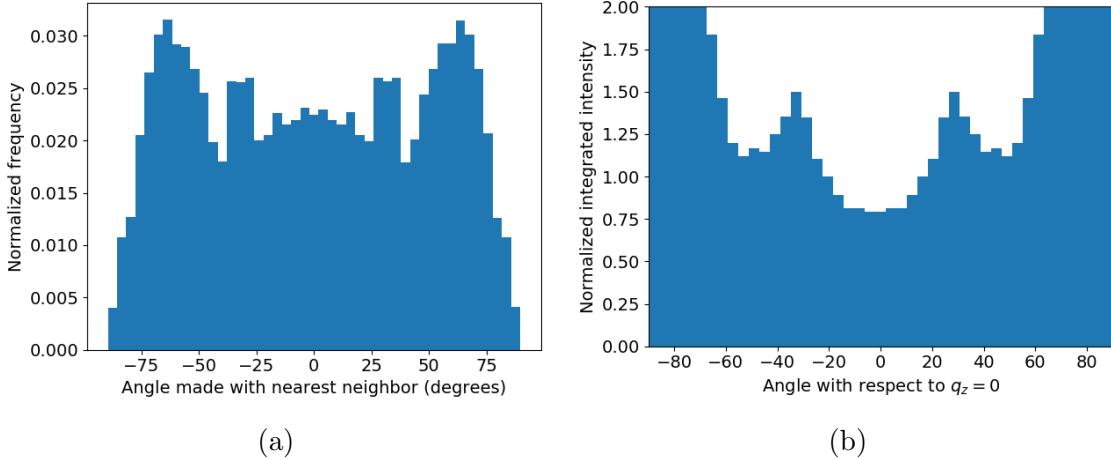


Figure 11: We hypothesize that R-spots is the result of ordered tail packing. Defining the membrane plane to be 0° , we measured the angles between each alkane chain tail centroid and its nearest neighbor centroids for the equilibrated sandwiched configuration simulated at 280K. Peaks that appear in each distribution are centered near $\pm 33^\circ$. We radially integrated the simulated XRD patterns of the parallel displaced and sandwiched configuration within the region bounding R-alkanes. Peaks appear in the same location as the angle distributions which corroborates our hypothesis.

1. The difference between 280 K and 300 K is relatively small. Our forcefield parameters may not correctly model the behavior of the tails at 300 K (citation?).
2. Monomers aren't as confined at 300 K in our simulations versus experiment. If the head groups packed 3.7 Å apart, the tails would be more confined and forced to pack between vertically adjacent monomer tails. In our case, the tail region is less dense than experiment which gives the tails freedom to organize in a more entropically favored disordered state.

3.2.2 Discrepancies between experimental and simulated R- π

We plotted the one-dimensional pair distribution function, $g(z)$, for the centers of mass of monomer phenyl rings (Figure 12). We used this information to understand how far apart monomers stack within monomer columns and the degree to which they are correlated.

Monomers in the ordered basin stack closer together than those in the disordered basin

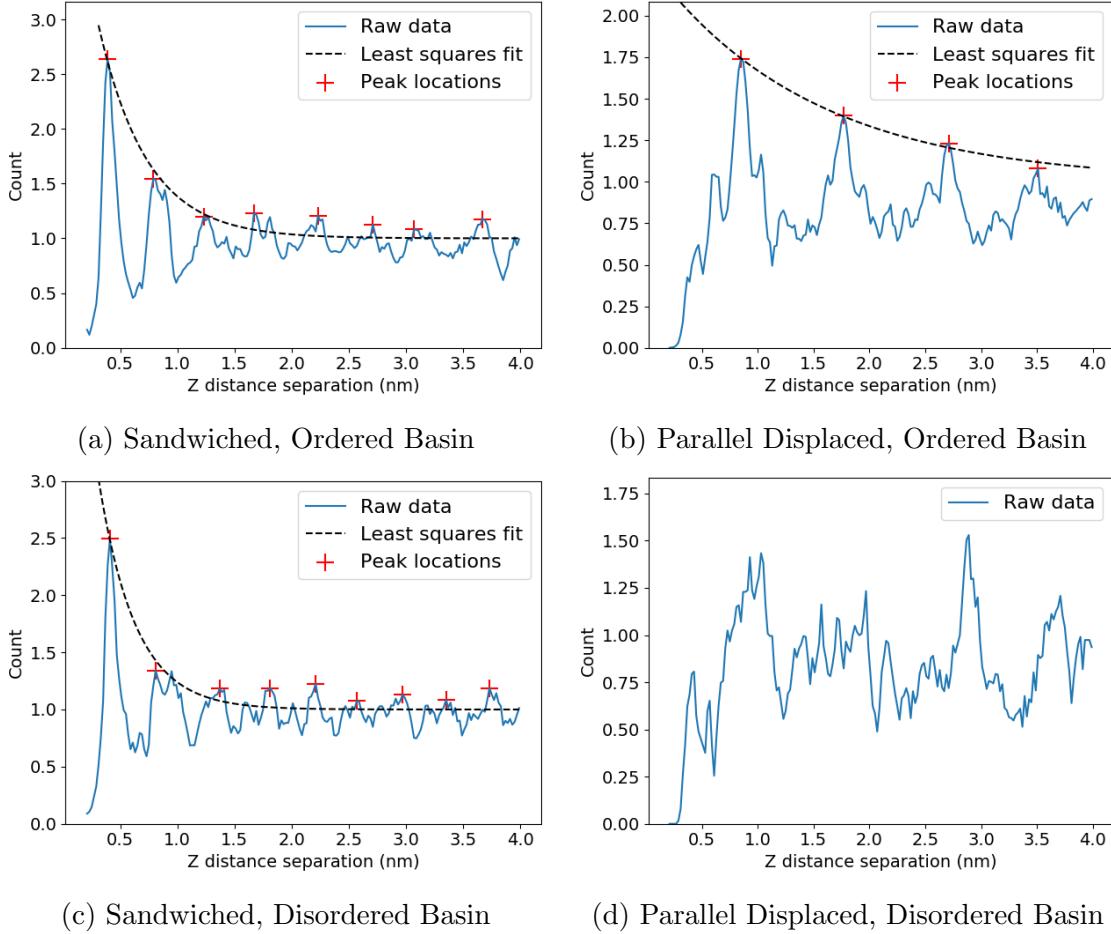


Figure 12: 1D correlation functions of the center of masses of aromatic head groups, $g(z)$, show decaying oscillatory behavior. We calculated the correlation length by fitting a decaying exponential function (Equation 2) to the peaks of $g(z)$. The correlation length is longer for ordered basin systems (Table 2). We did not attempt to calculate the correlation length for (d) because there are no clear peaks. We assume that its correlation is less than the vertical distance between monomers.

(Table 2). We calculated the equilibrated vertical distance, d_{equil} , between monomers using Equation 3. Monomers in the ordered basin stack ca. 0.2 and 0.3 Å closer than those built in the disordered basin in the sandwiched and parallel displaced configurations respectively. The distance between stacked monomers is greater than experiment by 0.5 - 0.9 Å across all cases. This behavior is not surprising since GAFF models atoms as point charges and does not appropriately model the aromatic $\pi - \pi$ interactions which would cause the monomers to stack closer together. Additionally, it is possible that the tails prevent close stacking of

Table 2: The correlation length is larger for systems in the ordered basin. The equilibrated vertical stacking distance, d_{equil} , is also smaller.

System	d (Å)	d_{equil} (Å)	Correlation Length (Å)
Sandwiched	3.7	4.27 ± 0.03	4.2 ± 0.8
Parallel Displaced	3.7	4.33 ± 0.04	14.5 ± 1.3
Sandwiched	5.0	4.48 ± 0.07	3.2 ± 0.9
Parallel Displaced	5.0	4.60 ± 0.08	$< d_{equil}$
Experiment	–	3.70	10 ± 1

monomer head groups and we do not achieve the timescales necessary for them to rearrange into a necessarily more tightly packed configuration. Ordered basin systems are likely the best choice for transport studies.

The correlation length between stacked monomer head groups of the ordered systems also show closer agreement with experiment (Table 2). We calculated the correlation length of each system using Equation 2. We could not extract a reliable correlation length from the disordered parallel displaced configuration since the peaks do not show clear patterns than can easily be fit to exponential decay. In general, we see that correlation length increases as monomers stack closer together. The same trend has been seen in molecular dynamics studies of polymer fluids.[?] We hypothesize that the correlation length of the sandwiched configuration would increase to a value near experiment if monomers packed closer together.

The persistent oscillatory behavior of the correlation function may in part explain the high intensity of R- π relative to experiment. The way we calculate correlation length is unique to the rate of decay of $g(z)$ but not its exact shape. $g(z)$ for our simulated systems, especially the sandwiched configurations, shows peaks which persist across the entire correlation function. If the peaks, at large values of z, instead decay to 1 uniformly, the correlation length could remain nearly the same, but R- π would have a reduced intensity. The monomer head groups in our simulations do not move enough to create the noise which would cause such behavior. See Section S9.1 of the supporting information for illustrative examples.

The system size does not significantly alter the intensity of R- π . We equilibrated a

sandwiched system with twice as many monomers per column so that the system size doubled in the z-direction. The correlation length increases modestly from 4.5 ± 0.4 to 7.3 ± 1.2 Å, and the intensity of R- π decreases from 44.0 to 39.4. Visually, the correlation functions are nearly identical (See Figure 24).

The simulated intensity of R- π is also more intense than experiment because our system models near-perfectly straight pores with no defects. Nearly all of the intensity in R- π of our simulated patterns is concentrated at a single point. Figure 13a shows the simulated pattern of the ordered sandwiched configuration with the upper boundary on the colorbar adjusted to be 6x higher than those shown in Figure 7. The only distinguishable reflections are those of R- π and R-pores. In the experimental pattern (Figure 13b), the intensity is more evenly spread out over all of R- π .

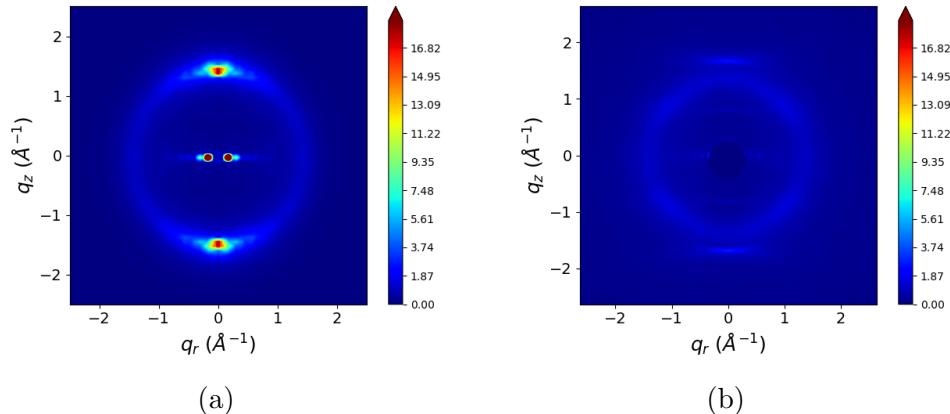


Figure 13: R- π and R-pores are far more intense than the other major reflections in simulated diffraction patterns (a). Here, the colorbar was scaled so that the max is 6x higher than all other plots.

3.2.3 Origin of R-double

The appearance of R-double implies a vertical modulation in electron density every 7.4 Å. We are not able to achieve such modulation using our simple initial configurations. Although the position of monomers in parallel displaced configurations alternate every other layer, we know that such a helical configuration will not produce R-double, but only off-axis reflections

at the same q_z value.⁷ There is not a unique solution that describes the origin of R-double. Extracting the exact relationship between a diffraction pattern and its real space configuration is well-known as the phase problem.⁷ We have proposed configurations that result in the appearance of R-double below, and we can speculate which makes the most physical sense. We explore both dry and wet configurations.

We can produce R-double if we rotate monomers with respect to vertically adjacent monomers. In this configuration, monomers are rotated so that the vector created by the bond extending from the carboxylate carbon to the phenyl ring is oriented $\pm 15^\circ$ with respect to the vector extending from the carboxylate carbon to the pore center (Figure 14b). Every other monomer layer is rotated $+15^\circ$ and those in between are rotated -15° . This configuration allows monomer tails to sit between adjacent monomer tails which may be the most favorable way for them to pack. This configuration is stable short-term while unrestrained however R-double quickly fades after a few nanoseconds of simulation. The long-term stability of a configuration similar to this may be feasible if monomers stay stacked 3.7 Å apart.

We can also produce R-double if layers are not uniformly spaced. Rather, monomers might form pairs that stack less than 3.7 Å apart, and whose center of masses are spaced 7.4 Å from the next pair of monomers (Figure 14a). To our knowledge, there have been no studies that specifically address the possibility of a configuration like this. Our forcefield causes our system to tend towards uniformly spaced layers. Simulations of unevenly spaced systems are only stable if position restraints are applied to heavy atoms of the phenyl rings.

Adding water to the system facilitates the appearance of R-double. We added water to the parallel displaced and sandwiched configurations in the ordered basin and equilibrated them according to the wet equilibration procedure. There is no experimental measurement of water concentration in these membranes so we tested a range of water concentrations from 1% to 5%. R-double appears transiently in the simulated XRD pattern of the parallel displaced configuration with 1 wt% water (Figure 14c). It is not initially present, but appears after 200 ns of simulation time. After 450 ns, it disappears again. Simulated XRD patterns

of all other solvated systems tested are shown in Figure S ??.

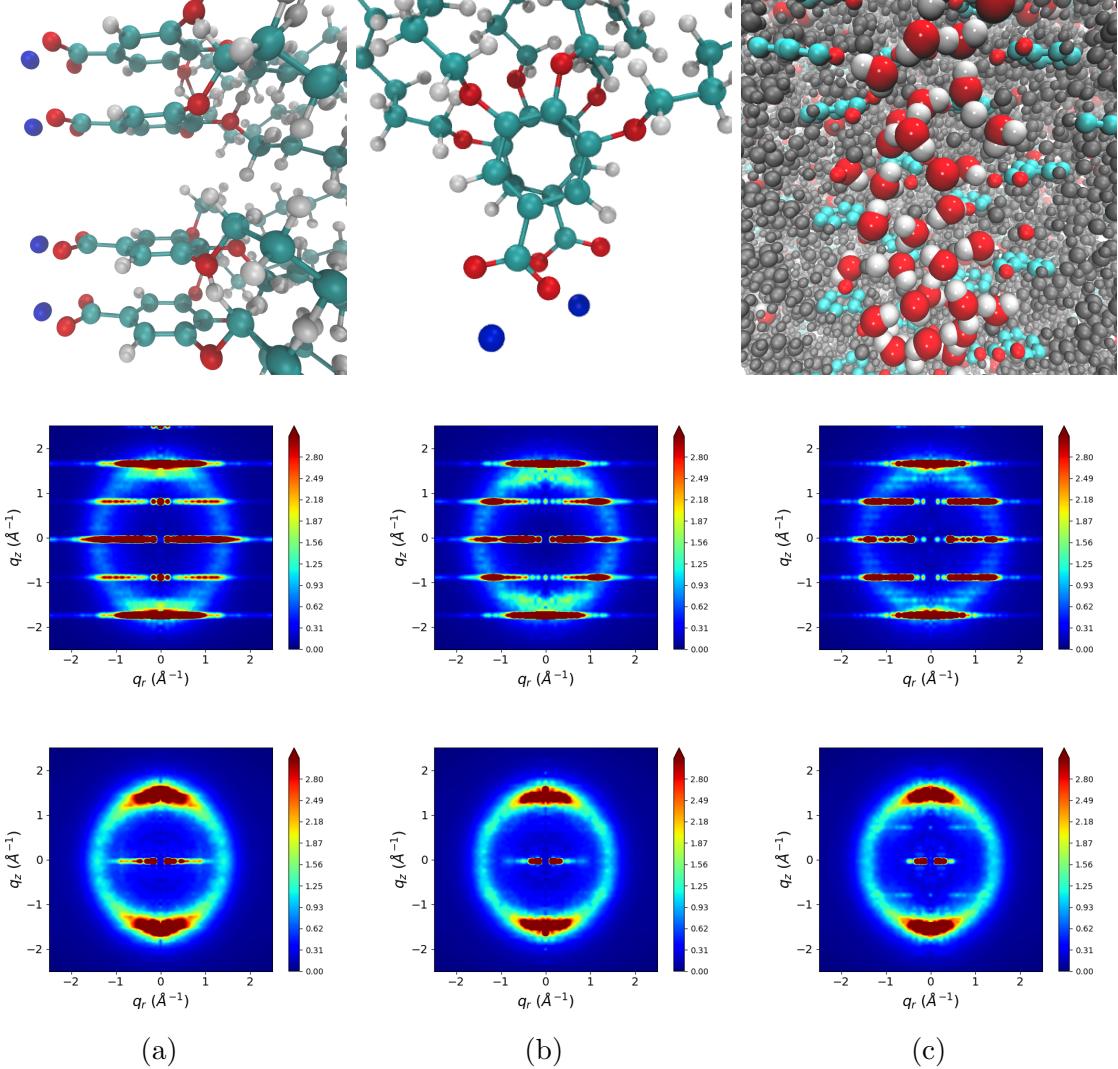


Figure 14: (a) When monomers are non-uniformly spaced (top), R-double appears if all heavy atoms of the head groups are held in place with position restraints (middle). R-double quickly fades once the position restraints are released (bottom). (b) When monomer head groups are rotated with respect to vertically adjacent monomers (top), R-double is visible while the heavy atoms of the head groups are held in place with position restraints (middle). Again, R-double fades once the position restraints are released. (c) When we add 1 wt% water to the parallel displaced configuration in the ordered basin (top) R-double is not initially present during the restrained portion of equilibration (middle). After 200 ns of equilibration, R-double becomes visible and persists for another 200 ns (bottom).

R-double appears in the solvated system due to the structure of the head groups. To prove this, we removed the head groups from the trajectory used to produce Figure 14c in order to produce that shown in Figure 15a. R-double does not appear without the influence

of the head groups. Water molecules must play a role in the structuring of the head groups since R-double does not appear in any dry simulations.

When two vertically stacked monomer head groups hydrogen bond with a shared water molecule, the monomers are drawn closer together (as illustrated in Figure 15b), which creates an asymmetry that allows R-double to appear. If a monomer head group shares a hydrogen bonded water molecule with a head group above itself, it will be less likely to share a water molecule with a head group below it due to steric constraints. The monomer head group below can just as easily share a water molecule with a head group below itself. In this scenario, the centers of each pair are 2 times the π -stacking distance apart which would lead to R-double (much like the configuration in Figure 14a). There are a modest number of occurrences of this scenario, shown in Figure 15c. Peaks in the distributions represent the scenario where a monomer head group shares a water molecule with a head group vertically above it. In Figure 15d, we calculated the discrete fourier transform of the distributions which we used as a rough indicator of whether the head group arrangement will lead to R-double. We see the strongest indicator of asymmetric monomer stacking in Pore 1 where the peaks at 0.5 layers^{-1} are clearly distinguished, meaning there is periodicity every two layers.

It is likely that R-double originates from water molecules as described above and it is the only mechanism that occurred without using position restraints. The extent of the hydrogen bonding network that forms is largely determined by the accuracy of the forcefield. It is possible that a more realistic forcefield would make the effect stronger or weaker. If this is truly the mechanism, it implies that the systems studied by Feng et al.^{12,14} were not truly thermotropic Col_h phases. Rather, they were very low water content H_{II} phases unintentionally created due to the neat monomers' hydroscopicity. This detail may be important for reproducing the results of Feng et al.

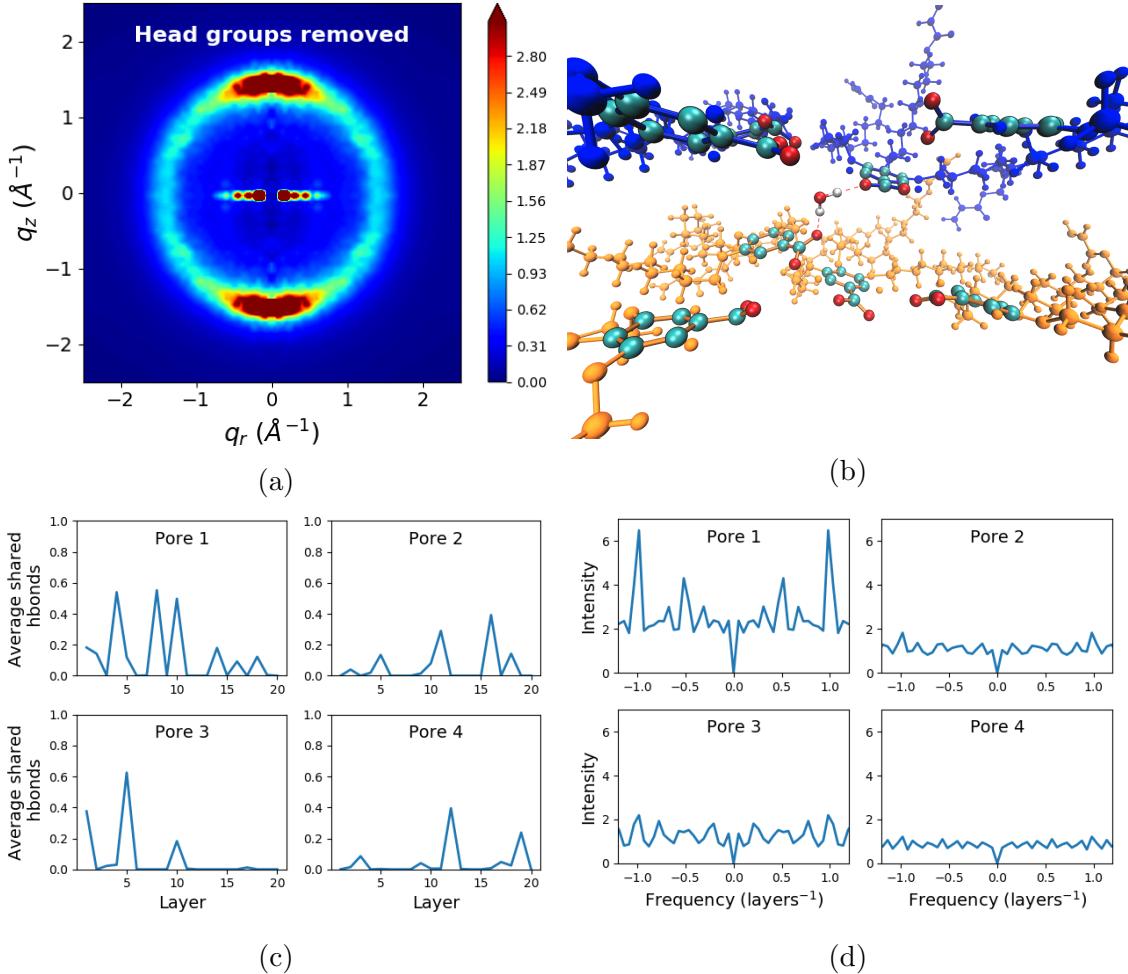


Figure 15: (a) The structure of the head groups is responsible for the appearance of R-double. When we remove head groups from the trajectory, the simulated diffraction pattern no longer shows R-double. (b) Monomer head groups above or below each other that hydrogen bond with a shared water molecule are drawn closer together. Blue monomers were stacked above orange monomers in the initial configuration. (c) Monomers in each column are numbered from 1–20. For simplicity, we define a layer to be composed of all same-number monomers. Peaks in the distributions indicate a shared hydrogen bonded water molecule between a monomer head group and one in the layer vertically above it. For example, in Pore 1, monomer 7 shares a hydrogen bond with a monomer in layer 8 (pictured in (b)). In this scenario, monomers are no longer evenly spaced in the z-direction since they are pulled closer together by hydrogen bonds. (d) We performed discrete fourier transforms on each distribution in (c). In all cases, the strongest peak represents periodicity every layer. In Pore 1, there is also periodicity every other layer as indicated by the strong peak at 0.5 layers^{-1} . In this case, the center of mass of two adjacent pairs is separated by twice the average monomer stacking distance, while the four monomers involved are unequally spaced. These conditions may give rise to R-double.

3.3 Chemical composition of pore columns

We are most interested in the structure and composition of the pores since we would like to study transport mechanisms within them. We have shown that the tails possess a certain degree of order which is necessary in order to create the complex WAXS pattern shown experimentally, but they will not be involved in a separation process. We aim to further understand the pore architecture and observe the differences, if any, between the different equilibrated configurations studied so far.

We plotted the number densities of heavy atoms in the head group, carbon atoms in the tail region and all sodium ions (Figure 16). For the head group region, we used heavy atoms making up the aromatic rings and carboxylate groups. For the tail region we used carbon atoms of the monomer tails (See Figure S3 for a diagram). We averaged the histograms over at least 50 ns of equilibrated trajectory.

There is a partition between the hydrophobic and hydrophilic regions, however it is a gradient in composition, rather than an abrupt division. The system does not confine sodium ions and head groups to just within the pore region. Based on size-exclusion experiments, we define the pore radius to be 0.6 nm.⁷ We see in all cases, that 19% of sodium ions exist outside the pore region (except sandwiched, ordered basin, 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 ordered sandwiched, 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.

In all cases, the space in the pore region is filled with a mixture of sodium ions and head groups. The ordered parallel displaced configuration has the highest density of sodium ions at the pore centers. Both the ordered and disordered parallel displaced configurations have higher concentrations of head groups in the center. This observation highlights that the pore

region is dense, not hollow, and may impede transport of solvent and solutes. We observe how this changes when water is added to the system.

In general, the composition of each region, particularly the pore region, is similar between all systems. We believe we can solvate and study transport in any of the systems presented here and extract similar transport mechanisms. We will need to verify that this assumption is true.

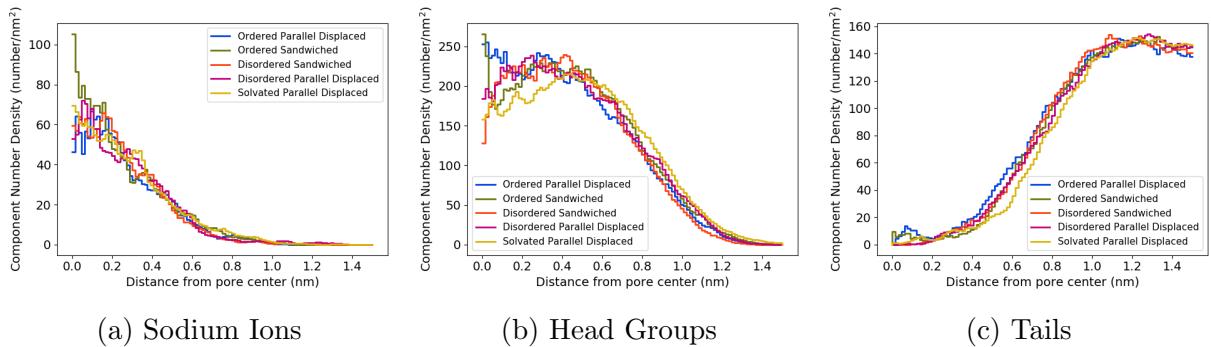


Figure 16: In all cases, the component radial distribution functions exhibit a composition gradient transitioning from the hydrophilic to the hydrophobic regions. Systems with layers initially spaced 3.7 Å apart in the parallel displaced (a), and sandwiched (b) configurations both show the highest concentrations 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.

3.4 Slow dynamics

We observe unusually slow dynamics in our system relative to other liquid crystal systems. Typical diffusion constants for columnar liquid crystals have been reported to be on the order of $10^{-11} \text{ m}^2/\text{s}$.³⁵ We measured the diffusion constants of monomers in each of the systems we studied (See Table S-2) and learned that they are all on the order of $10^{-14} \text{ m}^2/\text{s}$. Our systems may be frozen in a glassy state. It is also possible that we are simply observing characteristics of the experimental system. There has been no experimental work done to study diffusion of Na-GA3C11 monomers in the Col_h system and no measurement of the

glass transition temperature. Such a low diffusion constant is not unheard of. A more recent study reported a diffusion constant of $1.2 \times 10^{-14} \text{ m}^2/\text{s}$ for a different liquid crystal that formed a hexagonal columnar phase.³⁶

Consequently, there is not enough movement on the timescales we simulated for the system to consistently reach a structure equivalent to experiment. In all cases our monomers equilibrate to a stacking distance that is too large compared to experiment. While this may be in large part due to the forcefield's inability to model aromatic interactions, it is also possible that the monomer tails do have enough time to pack as tightly as they could. More densely packed tails could allow the monomers to stack closer together.

We quantified the movement of the tails during our simulations by calculating the auto-correlation function of the dihedral angle formed around the bond between the head groups and the ether oxygens which attach the tails to the head group (See Figure S4). We exclude the dihedral from the middle tail since it is fundamentally different than the two symmetric outside tails. We limited these studies to the sandwiched configuration for simplicity.

The ether dihedrals become decorrelated on a reasonable timescale when the temperature is raised. At 300K (Figure 17a), the autocorrelation function does not cross the x-axis until ≈ 105 ns meaning that tails might only fully rotate 4 times over the course of the 400 ns that we studied. Additionally, the correlation function plateau's near a value of -0.2 which indicates that the tails are starting in an unfavorable configuration. We implemented distance restraints between the centers of mass of monomer head groups to preserve the hexagonal phase, then rose the temperature of the equilibrated 300 K ordered basin sandwiched system to 500 K. We witnessed decorrelation of the ether dihedrals after ≈ 11 ns with a plateau at 0, (Figure 17b) indicating a complete loss of memory. We annealed the resultant configuration back down to 300 K over 200 ns to see if the increased rotational freedom might allow the system to relax into to a more tightly packed configuration.

Decorrelating the ether dihedrals at high temperature, followed by thermal annealing does not improve packing in our model. In the ideal case, if all monomers stacked 3.7 \AA apart,

the z-dimension of our unit cell should be 7.4 nm. In the ordered basin, sandwiched system studied in this paper, the z-dimension of the unit cell equilibrated to 8.87 nm, which is roughly consistent with the stacking distance reported in Table 2. After 200 ns of annealing from 500K to 300K, the z-dimension of the unit cell was 9.22 nm. We repeated the annealing procedure over the course of 400 ns and the final z-dimension of the unit cell was 9.20 nm. Much longer annealing simulations may get the system to the correct density, but we do not have the resources to further explore this approach.

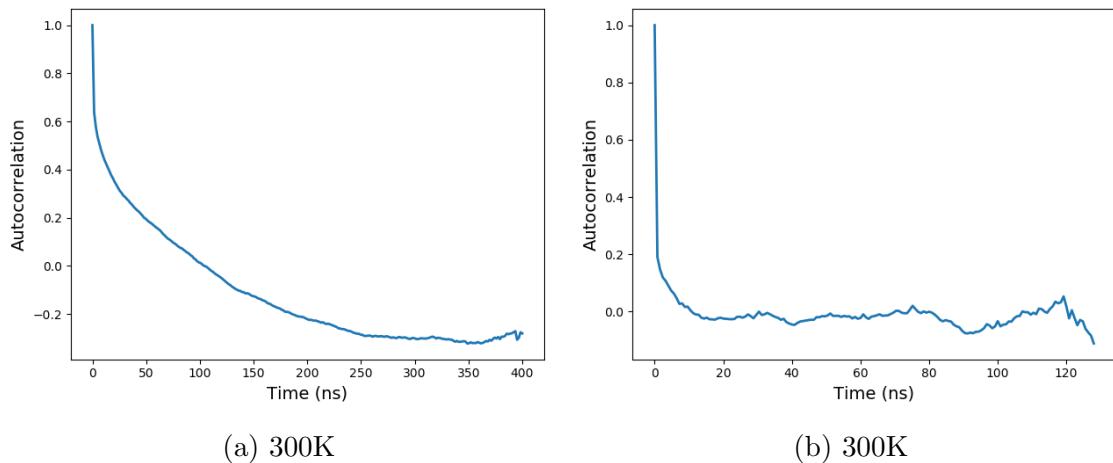


Figure 17

3.5 Model Ionic Conductivity Measurements

We calculated the ionic conductivity of the parallel displaced configuration in the ordered basin with 1 wt % water since we believe its structure is the closest match to experiment. Our model estimates the ionic conductivity within one order of magnitude of experiment (Figure 18). We verified the value calculated by the Nernst-Einstein relationship using a second method called the collective diffusion model³⁷ (See section S ??). The values calculated by the collective diffusion model agree with Nernst-Einstein values within error, however there is a much higher uncertainty that would require much longer simulations to lower.

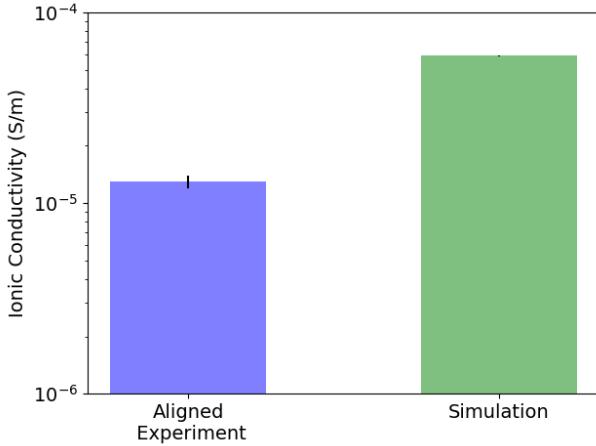


Figure 18: The calculated ionic conductivity of the simulated system is approximately one order of magnitude higher than experiment.

The calculate value of ionic conductivity is 5x higher than experiment because we simulated infinitely long, aligned pores. The ionic conductivity measurement to which we are comparing was done with a 80 μm thick film, nearly 10,000 times thicker than our simulated system. The thick film is likely imperfectly aligned and has defects leading to non-contiguous pores. It has been shown that there is a large dependence of ionic conductivity on the alignment of the pores. The ionic conductivity of an isotropically aligned film is ca. 85 times lower than that of the nearly aligned film to which we are comparing.¹² 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

We applied our crosslinking algorithm to equilibrated sandwiched and parallel displaced configurations in the ordered pore basin. We allowed the crosslinking algorithm to propagate until greater than 90% of vinyl groups were either involved in a crosslinking reaction or were terminated. See section S10 for further details on the crosslinking algorithm. We allowed the crosslinked configurations to simulate for 100 ns further in the NPT ensemble.

There are minor changes to the physical characteristics of these systems when they are

crosslinked (See Figure 19). The ionic conductivity of the sandwiched configuration decreases while that of the parallel displaced configuration stays the same. The pore spacing decreases in both systems by 0.07 nm. The vertical monomer stacking distance increases in the sandwiched configuration and decreases in the parallel displaced configuration, however the values of crosslinked configurations fall within uncertainty of their un-crosslinked counterparts. The correlation length decreases in both systems, but is most pronounced in the parallel displaced system.

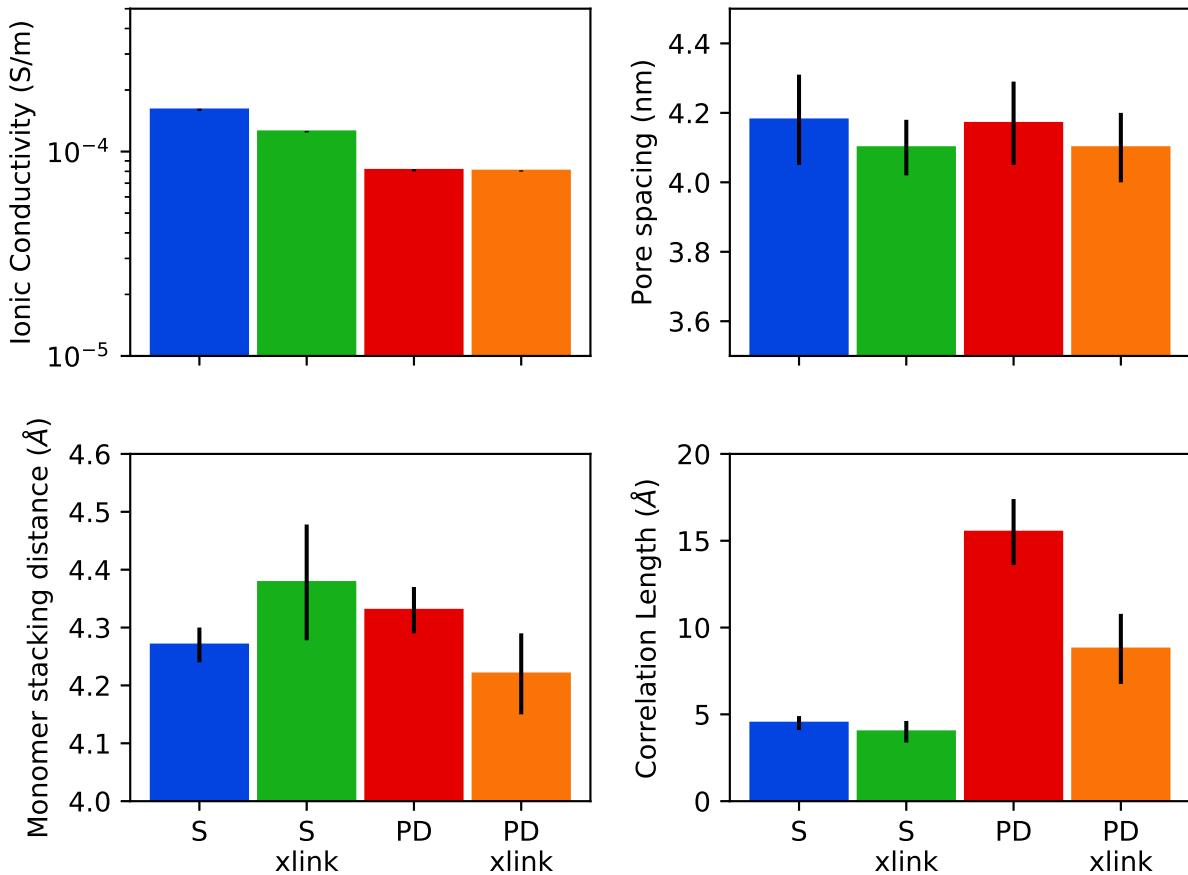


Figure 19: There are minor differences between the physical properties of a crosslinked (xlink) system versus an uncrosslinked system. The sandwiched configuration (S) exhibits a smaller decrease in its ionic conductivity, while the parallel displaced (PD) configuration remains constant. The pore spacing of both systems decreases upon crosslinking. The vertical distance between stacked monomers increases in the sandwiched configuration and decreases in the parallel displaced configuration. The correlation length decreases in both configurations.

4 Conclusion

We have used a detailed molecular model of the Col_h 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.

We observed a number of metastable configurations, stable for hundreds of nanoseconds, which do not fit the experimental profile we have tried to match. We explored two classes of metastable basins which are dependent on the initial vertical stacking distance between monomers : the ordered and disordered pore basins. We expect that these metastable configurations will eventually rearrange and converge to a single equilibrium structure. We conducted extensive analysis in order to isolate structures which most closely resembles the true equilibrium structure.

We achieve maximum structural consistency with experiment, as determined by simulated 2D structure factors, when we build our model in the ordered basin parallel displaced configuration with 5 monomer columns per pore and 1 wt% water. R-alkanes and R-pores appear where expected for the reasons originally predicted. We learned that R-spots is likely due to ordered alkane chain packing. R- π appears at lower q values than experiment because monomer stack too far apart. Finally, we observed that our model reproduces R-double only when we add 1 wt% water to the system. This observation has important implications for the reproducibility of the experimental results from Feng et al since they claim that their membrane is completely dry.

We characterized the environment centered around the membrane pores and learned that the pores are generally filled with monomer head groups and sodium ions. All dry systems studied showed a similar distribution of sodium, head groups and tails while the wet system shows evidence of swelling due to the presence of water molecules. 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 size-exclusion separations in systems without a well-defined pore size.

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 cross-linked by the algorithm we implemented. The diffraction pattern weakens relative to the uncross-linked system, the ionic conductivity 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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Graphical TOC Entry

