subsectionHow do water and ions move in nanostructured charged polymeric membranes?

Background

The ability to design nanostructured membranes with concomitant high chemical specificity is an important goal of the membrane separations community. [?] The ability to control the nanoscale architecture of membranes will allow membranes to be designed precisely for the purpose of separating specific compounds. [?, ?] The membranes being studied in this project have pores sizes smaller than 1 nanometer, allowing size-selective filtration of small molecules and gases, as well as desalination of salt water based on charge repulsion and size-exclusion of hydrated salt ions.

The membrane system we propose to model in this project is composed of lyotropic liquid crystals (LLCs) which self-assemble into hexagonally packed, cylindrical pores with acidic groups facing toward the cylinder center, complexed to counterions. Subsequent cross-linking to forms a mechanically strong structure (Fig. ??). [?, ?, ?] The pores, at the level of resolution obtained by SAXS and TEM, appear to be straight and uniform in size (Fig. ??). This is very different from most commercially available membranes which have a pore size distribution with tortuous pathways that reduce selectivity and flux respectively. The ordered structure exhibited by LLC membranes makes them well suited for modeling using molecular dynamics simulations because the system has a defined structure that can be studied in a reasonably sized unit cell.

Our initial systems were built by first parameterizing a single monomer using the General Amber Force Field (GAFF). Because the self-assembly process is long relative to times which we can simulate, monomers were rotated into layers of six monomers and stacked into cylinders to give a starting configuration close to where we expect the system to settle at equilibrium. While a single lyotropic liquid crystal consists of a small number of atoms (138), the entire unit cell consists of about 66K atoms. This number increases to approximately 100K when water molecules are added to the system.

In order to assemble the structures shown in Fig. ??, a suitable monomer configuration needed to be chosen. Thermal annealing of the monomer using GROMACS yielded many low energy configurations close to what is expected.

Initial simulations have been performed which energy minimize and allow the system to stabilize over the course of 20 ns in vacuum. The final structure and trajectory are analyzed quantitatively by measuring pore size, distance between pores, and distribution of sodium ions in the pore. These measurements are compared to values measured experimentally with SAXS and TEM imaging in order to validate the final structure. SAXS and TEM images were taken using dry membrane which justifies our initial study of the system in vacuum.

Proposed Experiments and Justification of Resources

Vacuum simulations of this system with a unit cell consisting of 4 pores, each with twenty layers of six monomers, total 66K atoms. On Bridges, using MPI-enabled GROMACS 5.1.2, we obtain 99 ns/day using 224 cores, beyond which the scaling becomes mildly nonlinear (See Figure **??** in the "Code Performance and Scaling" document for more details). Simulations of the same system solvated in water results in a total of 100K atoms, which ran at 121 ns/day using 336 cores, at the limit of the near linear scaling regime. By creating a system with 80 layers, we reached 265K atoms, which scaled nearly linearly up to 29 ns/day on 224 cores. We will use these timings to estimate the time required for these experiments.

We repeated scaling studies with the same system using the GPU-enabled GROMACS 2016 which was compiled for optimal use with NVIDIA Tesla K80 accelerators. On Bridges we obtain 58 ns/day for the 66K atom system using 4 GPUs and 28 cores. Simulating the solvated configuration, we obtain 56.4 ns/day on 4 GPUs and 28 cores. Simulating the 265K atom system we obtain 10.1 ns/day on 4 GPUs and 28 cores.

In order to study the relative stability of the two metastable phases we have discovered, we need will need to perform a computationally intensive free energy calculation using the Multistate Bennett Acceptance Ratio (MBAR) technique. MBAR estimates free energy difference with current lowest variance when compared to other estimators. In order to make a reasonable estimate, we will need to conduct simulations all intermediate states which lead from one metastable state to another. Each configuration in the pathway mapping the two states must be sufficiently similar to adjacent configurations so that we achieve enough phase space overlap for a more precise calculation. We estimate that we will need at least 50 intermediate states, each run for 50 ns for a total of 2500 ns of simulation time. This will require (2500 ns / (99.2 ns/day))* 24 hrs/day * 224 cores = 135K SU using MPI on the RM partition. This will require (2500 ns / (58 ns/day)) * 24 hours * 4 GPUs = 4.1K SU on the K80 GPU nodes.

The resolution of simulated X-ray diffraction patterns is dependent on the size of the simulated unit cell. To create higher resolution patterns in the x, y or z directions, requires an increase in the respective dimension of the unit cell by adding more atoms. The fundamental reason for this limitation is the necessity of meeting the Bragg condition. When met, constructive X-ray interference occurs, producing a signal on a nearby detector. The lattice planes in the crystal, defined by the reciprocal space Miller indices h, k, and l, are separated by a distance, d. One can calculate all possible d values given unit cell parameters.

Once equilibrated and cross-linked, we will examine the effect of solvation of the membranes on the pores. We have learned that at least 1000 ns of total simulation is required to observe full penetration of water through pores resulting in a cost of (2000 ns / (86 ns/day)) * 24 hours * 224 cores = 124K required SU, if we assume the initial membrane simulation boxes are sufficiently

large.

We will carry out the same procedure with a set of new monomers. In addition to the simulations outlined above, we will need to equilibrate each system using the developed procedures. Equilibration for 500 ns
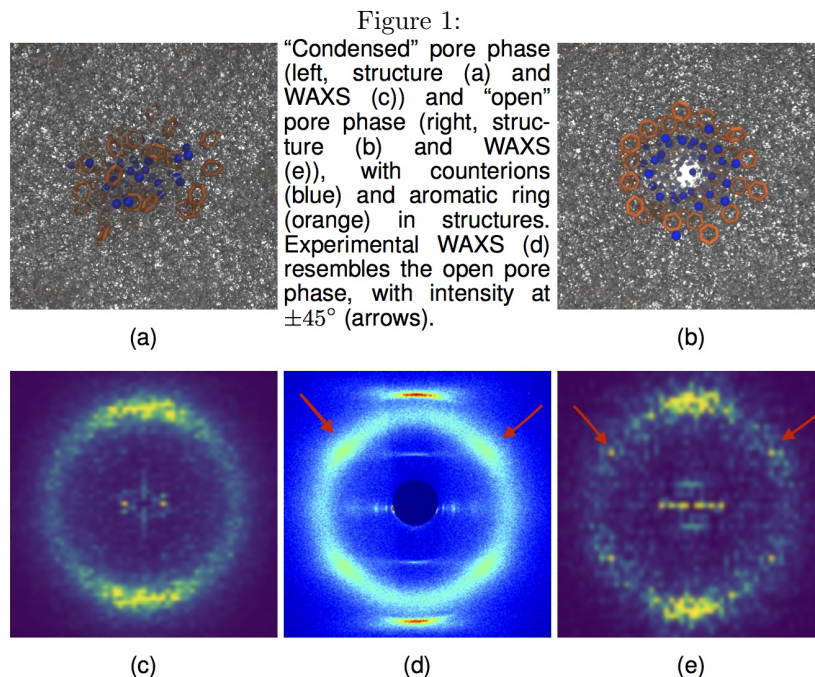
Summary of Scientific Discoveries

Simulations of transport in nanostructured polymer membranes

Our understanding of the microscopic structure of this type of LLC membrane has greatly increased with the aid of simulations run using Bridges.

Equilibration simulations of greater than 500 nanoseconds yield stable membrane configurations with the expected HII phase morphology. Various methods have been developed to characterize the equilibrated system. Generally, all equilibrium properties are compared to experimental measurements. We validated two methods for measuring ionic conductivity from atomistic simulations. Both methods require long simulations (at least 500 ns) in order to give accurate statistics. The distance between pores is an important structural parameter which we have measured using atomic coordinates and by simulating X-ray diffraction (XRD) experiments, a relatively undeveloped technique in MD for periodic systems such as ours. We have been able to generate structures which match experimental pore spacings within reason.

The X-ray diffraction simulations also give detailed information about membrane structure on the angstrom lengthscale. Our simulations have produced two dimensional X-ray diffraction patterns that contain all major features present in experimental studies. Producing a matching pattern was not trivial and resulted in the discovery of two metastable states. The two states are defined by the degree of local order inside the pore regions. The state which we had initially studied is characterized by a disordered pore region, however the X-ray diffraction pattern does not match experiment. We altered the starting configuration so that the benzene rings in the head group of each monomer were stacked in a parallel displaced configuration relative to each other. The resulting X-ray diffraction pattern of the new configuration, after equilibration, is a much closer match to experiment. Additionally, we were able to explain the spots that appear (red arrows in figure xx) contrary to how it was originally reported. The spots were assumed to be caused by the 40 degree tilt angle of the alkyl tails with respect to the plane of each stacked monomer layer, a common feature of liquid crystal systems. However, we were able to produce the same spots using configurations with an average tilt angle close to zero. Our most impactful finding remains as the discovery of two metastable states. This will be the subject of a publication which will be submitted in the coming months. In the future, we will conduct free energy calculations that will help explain the difference between the two states and and help predict what experimental conditions might lead to each.

The next step for our system is to solvate it with water. In parallel to the preceding work, we have worked to develop methods which will be used to study the solvated system. While measuring ionic conductivity and running XRD simulations will work just the same, equilibration is non-trivial. We do not know exactly the equilibrium content of water or where the water is situated. While it is clear that most water should be in the hydrophilic pore region,

4

Figure 1:
"Condensed" pore phase (left, structure (a) and WAXS (c)) and "open" pore phase (right, structure (b) and WAXS (e)), with counterions (blue) and aromatic ring (orange) in structures. Experimental WAXS (d) resembles the open pore phase, with intensity at $\pm 45°$ (arrows).

(a)

(b)

(c)

(d)

(e)

simulations have shown that an appreciable amount of water can exist in the tail region near the slightly hydrophilic ester group. The best way to figure out how much water should be in the pore is to run very long equilibration simulationsand allow the simulations to tell us. Our current approach is to create water baths at each face of the membrane and allow water to diffuse into the membrane. We have learned that we can equilibrate a membrane with water in 1000 nanoseconds. Studies of the hydrated, 'lyotropic', phase will be the subject of a subsequent publication.