Supporting Information: Time Series Modeling of Solute Transport in an H_{II} Phase Lyotropic Liquid Crystal Membrane

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September 9, 2019

S1 Setup and analysis scripts

All python and bash scripts used to set up systems and conduct post-simulation trajectory analysis are available online at `https://github.com/shirtsgroup/LLC_Membranes`. Documentation for the `LLC_Membranes` repository is available at `https://llc-membranes.readthedocs.io/en/latest/`. Table S1 provides more detail about specific scripts used for each type of analysis performed in the main text.

Script Name	Section	Description
`/setup/param.sh`	2.1	Parameterize liquid crystal monomers and solutes with GAFF

Table S1: The first column provides the names of the python scripts available in the `LLC_Membranes` GitHub repository that were used for system setup and post-simulation trajectory analysis. Paths preceding script names are relative to the `LLC_Membranes/LLC_Membranes` directory. The second columns lists the section in the main text where the output or usage of the script is first described. The third column gives a brief description of the purpose of each script.

S2 Choosing a transport model

We used the toolbox created by Meroz and Sokolov in order to justify our choice of transport model.[**?**] The solutes in our systems exhibit anomalous transport properties characteristic of a Continuous Time Random Walk (CTRW).

Mean Squared Displacement

The general form of a mean squared displacement (MSD) curve is:

$$\langle x^2(t) \rangle \sim t^\alpha \tag{1}$$

For brownian motion, $\alpha = 1$ and the MSD is linear. When $\alpha \neq 1$, the particle of interest exhibits anomalous diffusion. Values of α greater than 1 give rise to superdiffusion, while values of α less than 1 give rise to subdiffusion.

We can calculate the ensemble-averaged MSD curve by averaging the MSDs of each particle trajectory, where each MSD is calculated using:

$$\delta^2(t) = \|\mathbf{r}(t) - \mathbf{r}(0)\|^2 \tag{2}$$

where $\|\cdot\|$ represents the Euclidean norm.

The mean squared displacement of solutes in our model is a non-linear function of time, with $\alpha < 1$ which is indicative of anomalous subdiffusion. Figure S1a plots the ensemble-averaged MSD curve for 24 ethanol molecules diffusing in a 10 wt% water H_{II} LLC membrane system. We fit a power law of the form Ae^α to the MSD curve. We performed 2000 bootstrap trials by randomly sampling 24 MSD curves with replacement from the 24 total ethanol MSD curves. The bootstrapped average value of α is 0.75 for this system.

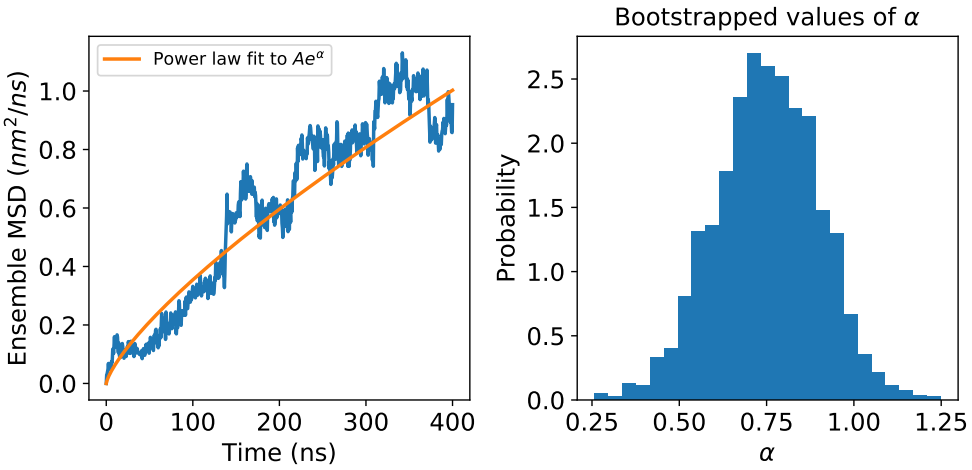


Figure S1: (a) We fit a curve with the form of Equation 1 to the ensemble-averaged MSD curve. (b) The average value of α, obtained using fits to MSDs calculated from bootstrapped ensembles, is less than 1 suggesting that ethanol molecules in our model exhibit subdiffusive behavior.

Ergodicity

The ergodicity of a system can help us narrow down the possible anomalous diffusion mechanisms. In an ergodic system, the time-averaged behavior of an observable should yield the same result as the ensemble average of the same observable. Examples of anomalous diffusion processes that are ergodic include random walks on fractals (RWF) and fractional brownian motion (FBM). Non-ergodic systems generally give rise to CTRWs with the possibility of combination with a RWF and/or FBM.[**?**]

We tested the ergodicity of our system by comparing the ensemble-averaged and time-averaged MSD curves. We calculated the MSD of each ethanol trajectory using Equation 2 and a time-averaged algorithm:

$$\delta^2(t) = \frac{1}{N-t} \sum_{i=0}^{N-t-1} \|\mathbf{r}(i+t) - \mathbf{r}(i)\|^2 \tag{3}$$

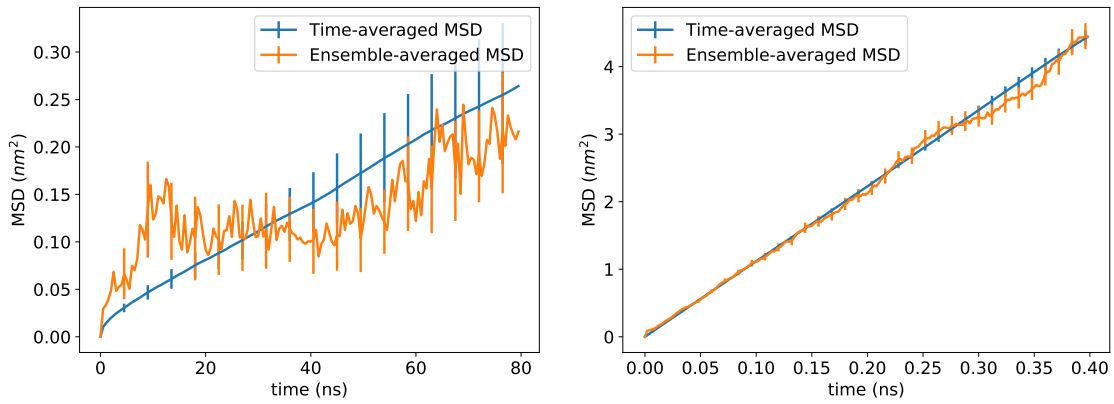
where N is the total number of simulation frames, and t represents the length of subinterval or number of frames per subinterval. We averaged the MSD curves from each trajectory in order to create final MSD plots.

The ethanol molecules exhibit non-ergodic behavior because their time-averaged and ensemble-averaged MSDs do not agree with each other (Figure S2a). We validated our analysis using a 1 ns simulation of a box of tip3p water molecules. As expected, since the particles exhibit Brownian motion, the time-averaged and ensemble-averaged MSDs agree with each within error (Figure S2b).

Autocorrelation of steps

Based on the previous two sections, our model can likey be studied as a CTRW. However, it is still possible that our CTRW model might also be convoluted with an FBM or a RWF process. In a pure CTRW, the steps are uncorrelated. Both FBM and RWF exhibit anti-correlated steps.

The steps in our system are not correlated. We showed this by calculating the autocorrelation function (ACF) of the step lengths in the z-direction. The ACF of a representative trajectory is shown in Figure S3.



(a) (b)

Figure S2: (a) The time-averaged and the ensemble-averaged MSDs for ethanol in an H_{II} nanopore are not in agreement, implying non-ergodicity. (b) A box of tip3p water molecules is expected to be ergodic and it is shown to be true here because both MSDs are in agreement.

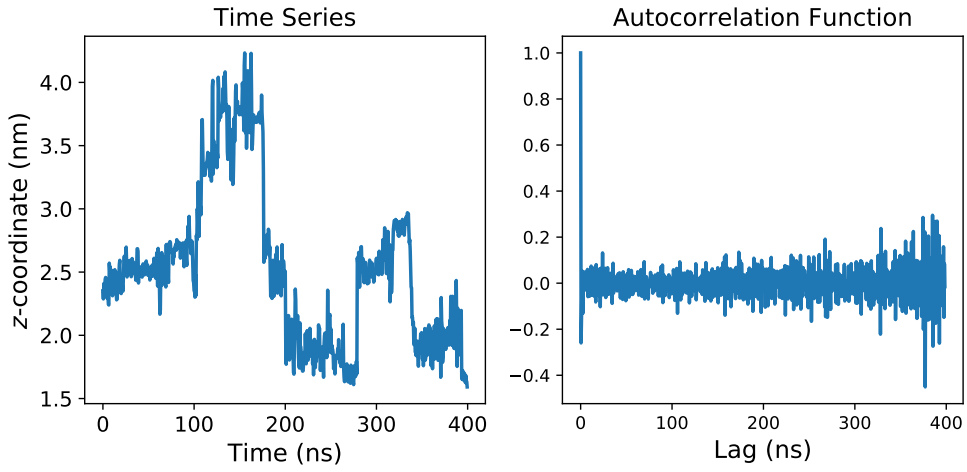


Figure S3: The autocorrelation function (right) of a representative ethanol center of mass z-coordinate trajectory (left) almost immediately decays to zero, indicating a complete loss of memory of it's previous position. Noise increases at large time lags due to decreased sampling.

References