SLATT UNDERGRADUATE RESEARCH FELLOWSHIP
FINAL REPORT

SCHOLAR NAME:	Andrew Scott Manning
FACULTY ADVISOR:	Jonathan Whitmer
PROJECT PERIOD:	June-August 2021
PROJECT TITLE:	Using Molecular Simulations to Determine Structure of Ionic Liquid Crystals
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	**( ) Energy Conversion and Efficiency** **( ) Sustainable and Secure Nuclear** **(X) Smart Storage and Distribution** **( ) Transformation Solar** **( ) Sustainable Bio/Fossil Fuels** **( ) Transformative Wind**

MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Model CnTFSI- System using GROMACs software	The CnTFSI- system was successfully modeled in GROMACs. The process involved several model iterations designed to capture the shape and charge distribution of the molecule.	100
Conduct a Temperature Ramp on CnTFSI- material	Several temperature ramps were implemented on the CnTFSI- system. The temperature ramps yielded results that diverged from experimental results, so work for designing temperature ramps that accurately predict the temperature dependence of CnTFSI- is a work in progress. However, the code and machinery is in place to continue the research.	70
Study the Structural Properties of the CnTFSI- material	The next order of business is to simulate the CnTFSI- materials at constant temperatures and calculate ion transport and nematic order parameters to identify the potential of the material as a battery electrolyte.	10

RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS SUBMITTED	(Sponsor, Project Title, PIs, Submission Date, Proposal Amount)
EXTERNAL AWARDS RECEIVED	(Sponsor, Project Title, PIs, Award Date, Award Amount)
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s)
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	(Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s)
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	(Event, Presentation Title, Presentation Date, Location) Summer Undergraduate Research Symposium, Using Molecular Simulations to Determine Structure of Liquid Crystal Electrolytes, 7/14/21, University of Notre Dame (Remote)
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	(Purpose, Title, Date Received)
INTERNAL COLLABORATIONS FOSTERED	(Name, Organization, Purpose of Affiliation, and Frequency of Interactions) Professor Jennifer Schaefer, University of Notre Dame, coordinate experimental molecule results with simulation results, 2-3 times.
EXTERNAL COLLABORATIONS FOSTERED	(Name, Organization, Purpose of Affiliation, and Frequency of Interactions)
WEBSITE(S) FEATURING RESEARCH PROJECT	(URL)
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models,	(Please describe each item in detail)

curricula, instruments, education programs, outreach for ND Energy and other groups)	

RESEARCH EXPERIENCE

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

My research experience with the Slatt Fellowship allowed me to grow as a researcher and as a participant in the chemical engineering field. I worked closely with Professor Jonathan Whitmer over the Summer 2021, and each week I was introduced to new theoretical considerations and learned how to better use the simulation software. For the research I also worked with Michael Quevillon, a graduate student at Notre Dame. Michael and I met once every week to discuss how to implement coding challenges into the simulation software, and these meetings helped me to rapidly hone my research skills as the summer progressed. The experience was positive because I came to greatly enjoy simulation research and the challenges that new problems in the field present.

FINAL WRITTEN REPORT

(Please use the space below to describe your research project and objectives, any findings and results you can share, and graphs, charts, and other visuals to help us understand what you achieved as a result of this research experience.)

I used the Slatt Undergraduate Research Fellowship to continue my research with Professor Jonathan Whitmer in the Chemical and Biomolecular Engineering Department. Renewable energy technologies like wind and solar have made large strides in power performance, but these natural resources may be intermittent. Therefore, renewable energy technologies require improved battery technologies for implementation so that power can be stored and discharged as needed. The liquid crystal electrolyte is a promising battery material because it contains a smectic phase with more order than a pure isotropic liquid and less order than a crystalline solid; this intermediate phase allows for facilitated ion transport that could greatly improve battery performance. This research project focused on understanding how a type of liquid crystal electrolyte called [Li+][CnTFSI-] would function in a battery electrolyte using Linux-based GROMACS simulations.

In this fellowship, the research goals were to first model the CnTFSI- molecular system and then to measure properties of the electrolyte including the temperature dependence of the structure as well as degree of order in the structure. C10TFSI- was studied because Professor Jennifer Schaefer's lab can produce that specific length molecule. A remote Linux environment provided by the Notre Dame Center for Research Computing (CRC) was used to perform these simulations.

First, the [Li+][CnTFSI-] liquid crystal had to be modeled and implemented in GROMACs before any simulations could be run. The lithium ion is simple to implement in GROMACs, but the CnTFSI- ion is a complex anion containing a bulky head group and a long alkyl tail. Modeling this complex ion became the first challenge of the research project. As a first attempt, a 3D structure for C10TFSI- was generated using the Open Babel software package. The resulting molecular structure was in a high energy conformation, so the software was rerun using conformers that would identify the lower energy orientation of the molecule. The resulting C10TFSI- molecule is shown below:

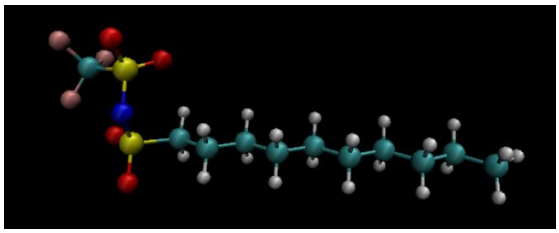

Figure 1. The C10TFSI- anion contains a bulky head (left in image) and an alkyl tail (right in image)

With the molecule successfully modelled, a force field needed to be implemented that would contain the important molecular components of the liquid crystal including charge dispersion, angles between atoms, and torsions between segments of the molecule. A Generalized Amber Force Field (GAFF) was chosen as the force field for the simulation, and the force field was implemented using Antechamber through the ACPYPE software package.

Next, the single molecules were packed into bulk 3D materials to better model an electrolyte in a battery. Liquid crystal electrolytes should demonstrate some degree of order in packing, so the molecules were packed in layers such that the polar head groups were layered apart from the nonpolar alkyl tails:

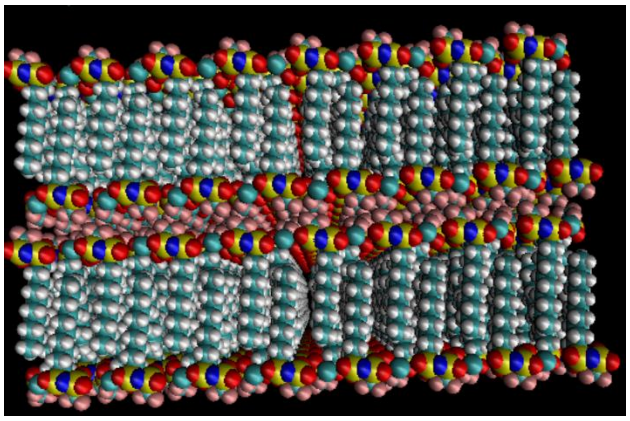

Figure 2. C10TFSI was packed into a bulk electrolyte with ordered layers.

With the liquid crystal electrolyte system properly modeled, the model was ready to be simulated using GROMACs. A series of energy minimization and initialization simulations had to be run to remove any energetically unfavorable conformations in the bulk material and to adjust the system to a set volume. Much time was spent considering the best ways to initialize the molecular system. I changed the time increment of simulation and how symmetrically the bulk forces were applied to the system to see if a more stable bulk conformation could be achieved.

The Slatt Research Fellowship concluded with attempts to run a temperature ramp on the bulk material and to study the physical structure of the liquid crystal electrolyte. First, a temperature ramp was run in which the CnTFSI- system was simulated at incrementally increasing temperatures. At each temperature, the bulk material was given time to stabilize to a new low-energy conformation. Through this process, energy data was developed for the bulk material at each temperature. Any significant change in energy in the system indicated that a phase change had occurred. Several temperature ramps were performed on the C10TFSI- system, and each time the simulation became unstable at relatively low temperatures. This instability indicates that the bulk material was no longer ordered and thus an isotropic liquid. However, the simulation yielded melting points that were consistently lower than experiment results measured in Professor Schaefer's lab. These results indicated that the simulation contained inaccuracies. These inaccuracies persisted through several iterations of the simulating process.

Finally, the research project concluded with an analysis of material structure. The nematic order parameter is one measure of material order. The parameter, bounded between a pure liquid value (0) and a crystalline solid value (1), indicates the bulk order in a system. The nematic order parameter for the C10TFSI is plotted as a function of simulation time below:

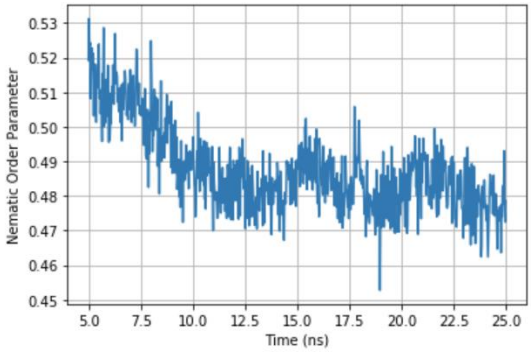

Figure 3. The nematic order parameter is around 0.49.

The nematic order parameter settled at approximately 0.49 for the molecular system, indicating an intermediate degree of order. This intermediate value may correspond to the desired smectic phase of the system, although more research is required to confirm this result.

These results were presented at the Summer Undergraduate Research Symposium on July 14, 2021 at the University of Notre Dame. I presented this project remotely from the event. At the end of the Slatt Fellowship, the molecular system had been fully modeled, and substantial work had been performed with temperature ramps. In addition, early work was completed on identifying the structure of the bulk material.

After the Slatt Fellowship ended, I continue to work this research project as paid position in Fall 2021. In the Fall, I mostly implemented the work from the summer to a more complex molecular system, [Li+][C18TFSI-]. Again, the temperature ramps yielded low melting points, suggesting that GAFF may be a poor force field to use for liquid crystal electrolytes.