NDnano
Notre Dame Nanoscience and Technology

NDnano Summer Undergraduate Research
2022 Project Summary

1. Student name & home university:
   - Edwin X. Velez Ortiz-University of Puerto Rico, Mayaguez

2. ND faculty name & department:
   - Dr. Edward J. Maginn-Chemical and Biomolecular Engineering

3. Summer project title:
   - Molecular Simulation To Enable the Recycling of Hydrofluorocarbon Refrigerants

4. Briefly describe new skills you acquired during your summer research:

Along with my summer research project I learned a variety of new skills. I expanded my programming abilities in Python, learned to use Linux, and the Git/GitHub version control system. I used the Cassandra Monte Carlo molecular simulation engine along with its Python interface MoSDeF Cassandra. Additionally, I leveraged the MoSDeF ecosystem to automate the simulation protocols for the calculations that I performed. In addition to these technical skills, I also learned how to redact and communicate effectively through different reports and presentations.

5. Briefly share a practical application/end use of your research:

The results of this research will serve as a basis for the development of optimized molecular models capable of simulating vapor-liquid equilibrium for a variety of HFCs, which will ultimately aid the design of separation processes that enhance the repurposing of HFCs.

6. 50- to 75-word abstract of your project:

In this work, classical molecular simulations were employed by applying the Gibbs Ensemble Monte Carlo (GEMC) method to compute the phase diagram of pure hydrofluorocarbons. These simulations were performed using model parameters collected from existing literature with the purpose of generating a benchmark of the current available molecular models. The results of this research will contribute to the development of optimized molecular models capable of simulating vapor-liquid equilibrium for a variety of HFCs.

7. References for papers, posters, or presentations of your research:

1. Lísal, M.; Vacek, V. Molecular Dynamics Simulations of Fluorinated Ethanes. Molecular Physics 1996, 87, 167–187.
2. Peguin, R. P.; Kamath, G.; Potoff, J. J.; da Rocha, S. R. All-Atom Force Field for the Prediction of Vapor−Liquid Equilibria and Interfacial Properties of HFA134A. The Journal of Physical Chemistry B 2008, 113, 178–187.
3. Potter, S. C.; Tildesley, D. J.; Burgess ,A.N.; Rogers, S. C. A transferable potential model for the liquid-vapour equilibria of fluoromethanes. Molecular Physics: An International Journal at the Interface Between Chemistry and Physics 1997, 92:5, 825-834.

4. Rai, N.; Rafferty, J. L.; Maiti, A.; Ilja Siepmann, J. Prediction of the Bubble Point Pressure for the Binary Mixture of Ethanol and 1,1,1,2,3,3,3-Heptafluoropropane from Gibbs Ensemble Monte Carlo Simulations Using the Trappe Force Field. Fluid Phase Equilibria 2007, 260, 199–211.
5. Yang, Z.; Gong, M.; Dong, X.; Li, X.; Wu, J. Molecular Modeling and Simulation of Vapor–Liquid Equilibrium of the Refrigerant r152a and Its Mixture R152A+R32. *Fluid Phase Equilibria* **2015**, *394*, 93–100.

One-page project summary that describes problem, project goal and your activities / results:

The Montreal Protocol approved worldwide regulation and phase-down of hydrofluorocarbons (HFCs) due to their Global Warming Potentials (GWPs). This initiative aims to reduce HFC total emissions from 2022 to 2050, this reduction is equivalent to 4.7 billion metric tons of carbon dioxide. The refrigeration systems used today use azeotropic mixtures of HFCs that are challenging to separate with traditional methods such as fractional distillation. To achieve the Montreal Protocol's goals, novel recycling separation strategies need to be developed. These separation techniques require information on HFC vapor-liquid equilibrium, which is not always available from experimental sources. When experimental data is unavailable, molecular simulations can be used to predict equilibrium quantities based on a refrigerant's molecular interactions. A key component in molecular simulations is a model that accurately describes how these molecules behave at a microscopic level. Using these models and statistical mechanics, researchers are able to efficiently simulate these systems in order to predict thermodynamic properties of industrial interest.

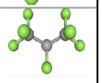
Refrigerant name	IUPAC name	SMILES	Molecule
HFC-32	difluoromethane	C(F)F	
HFC-23	trifluoromethane	C(F)(F)F	
HFC-14	Tetrafluoromethane	C(F)(F)(F)F	
HFC-161	Fluoroethane	CCF	
HFC-152a	1,1-difluoroethane	CC(F)F	
HFC-134a	1,1,1,2-tetrafluoroethane	C(C(F)(F)F)F	
HFC-227ea	1,1,1,2,3,3,3-heptafluoropropane	C(C(F)(F)F)(C(F)(F)F)F	

Figure 1. List of refrigerants simulated.

In this work, classical molecular simulations were employed by applying the Gibbs Ensemble Monte Carlo (GEMC) method to compute the phase diagram of pure hydrofluorocarbons. These simulations were performed using model parameters collected from existing literature with the purpose of generating a benchmark of the current available molecular models.

$$E = \sum_{bonds} k_r(r - r_0)^2 + \sum_{angles} k_\theta(\theta - \theta_0)^2 + \sum_{torsions} k_\phi \times [(1 + cos(n\phi - \gamma)] + \sum_{i=1}^{N-1} \cdot \sum_{j>i}^{N} \left\{ 4 \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\}$$

Figure 2. An example of a functional form used, in which the first three terms represent the intramolecular potential energy, while the last two terms represent the intermolecular potential energy

In order to perform the molecular simulation, we used Cassandra software package to simulate all molecules listed in **Figure 1**, using GEMC simulations to reproduce the vapor-liquid equilibrium properties of several models applying parameters collected from literature specific for each molecule.

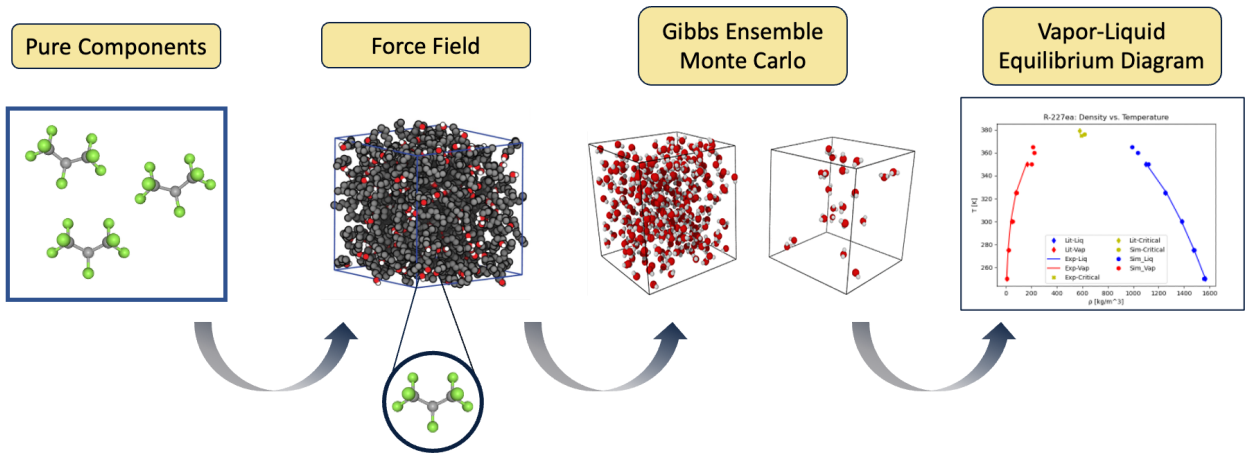


Figure 3. Schematic representation for the simulation process.

Our simulations were able to reproduce the VLE for R161, R152a, R134a, and R227ea.

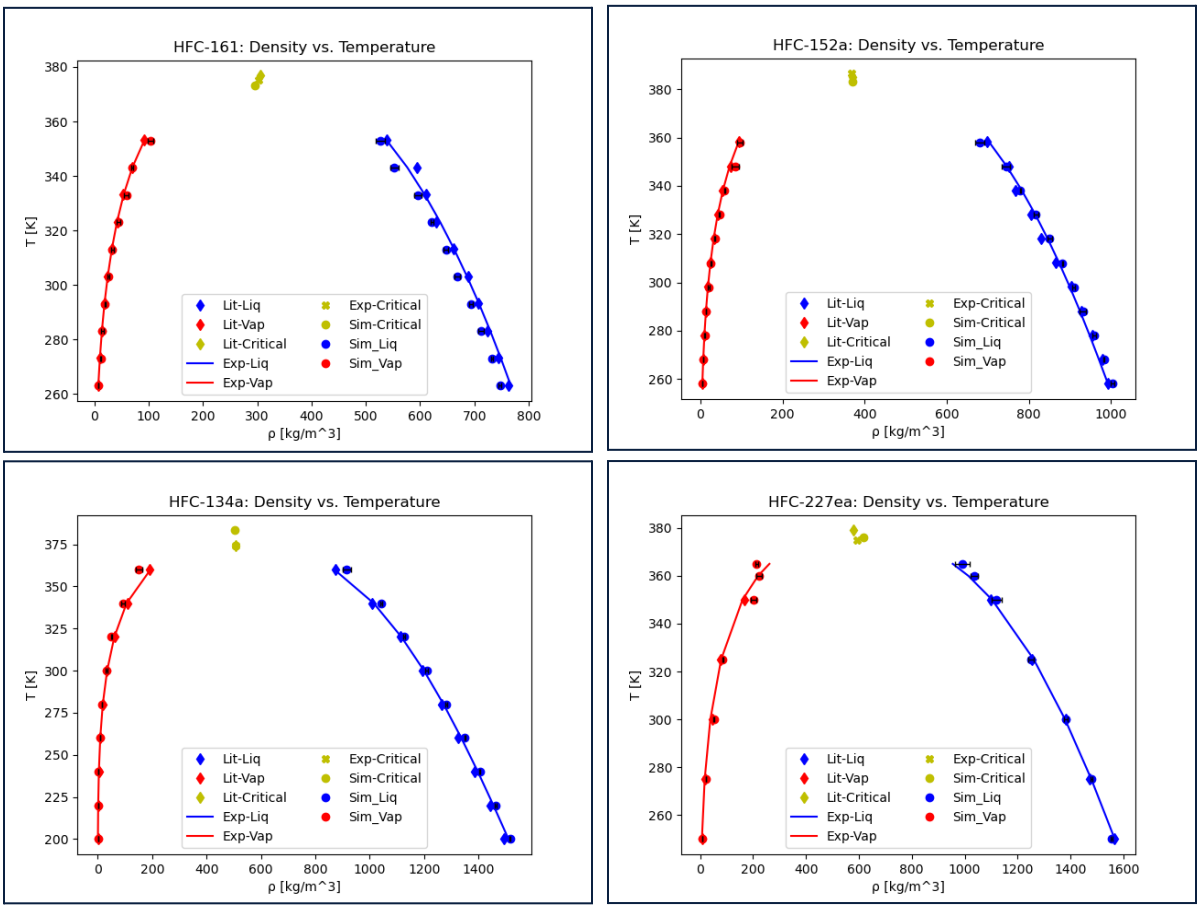


Figure 4. Plots for vapor-liquid coexistence curves for R-161, R-152a, R-134a, and R-227ea.

However, we could not match the published results for R32, R23, R14. Possible reasons could be that our simulations are not yet fully equilibrated, errors in the parameters in the publication, errors in conversion of functional forms, errors in original simulation setup, etc.

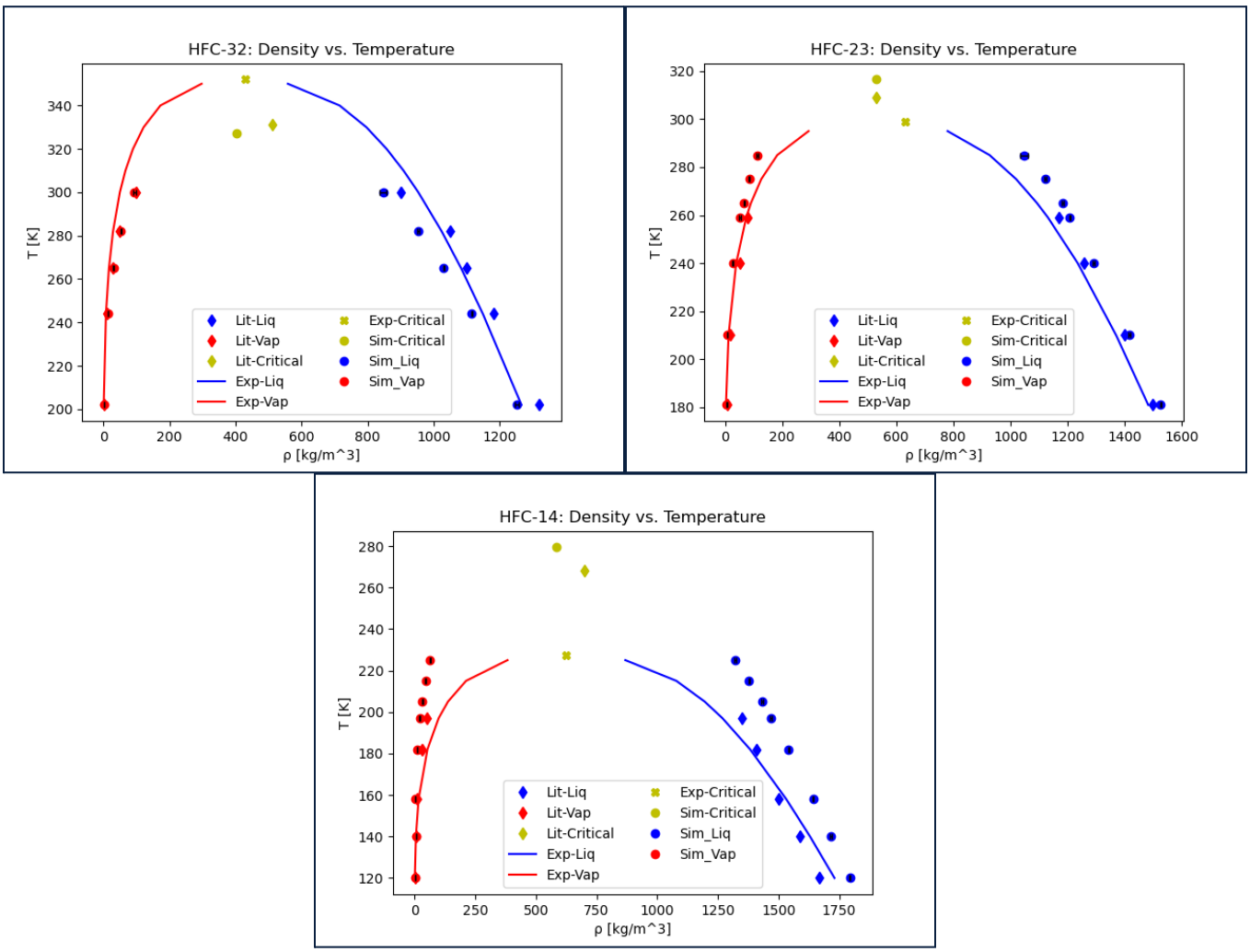


Figure 5. Plots for vapor-liquid coexistence curves for R-32, R-23, and R-14.

The results of this research will serve as a basis for the development of optimized molecular models capable of simulating vapor-liquid equilibrium for a variety of HFCs, which ultimately aid the design of separation processes that enhance the repurposing of HFCs.