ND*nano* Summer Undergraduate Research
2016 Project Summary

1. Student name: Aristotle Zervoudakis

2. Faculty mentor name: Dr. Jonathan Whitmer

3. Project title: Complex coacervates and the effects of chain length on critical properties

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

This summer, I was apprehensive about working solely on a computer; however, at the end of it all I've gained a greater appreciation for computational research and plan to continue on with the work. Through my work this summer, I have learned to use a Linux operating system; developed skills using LAMMPS Simulation Software, writing input scripts and analyzing the output; and expanded my coding experience, using Python, C++, and MATLAB for data analysis.

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

The research I have been doing this summer is meant to be the basis of many future applications of coacervates. A better understanding of the basic nature of these complexes will prove invaluable when future applications are tested. As of now, coacervates have been used in carbon-less copy paper and are a promising avenue for advances in drug delivery, with the coacervate encapsulating a certain medication and releasing under certain biological conditions, and underwater adhesives, mimicking the secretions of mussels that allow them to cling to surfaces.

Begin two-paragraph project summary here (~ one type-written page) to describe problem and project goal and your activities / results:

This project focused on the behavior of polymer complexes known a complex coacervates. These complexes form when two oppositely charged polymer chains coalesce in a salt solution to form polymer-rich and polymer-poor solutions. The polymer-rich portions have already shown to be useful and provide promise in a variety of fields. They have been used to create carbon-less copy notebooks. The coacervate exhibits the ability to encapsulate ink particles, and when pressure is applied, these capsules burst, creating the copy. This encapsulating ability also provides a new means of drug encapsulation and delivery. In this project, we aimed to better understand the basic nature of the coacervates, studying the critical properties of polyelectrolyte-rich potions, more specifically the critical density, critical temperature, and surface tension. To begin, we wanted to recreate the results of a previous paper published by Chapela et al[1] in order to provide evidence that our simulations were running correctly. The experiments in this paper, and our own following, used a Yukawa potential to model a system of two oppositely charged species with an implicit salt concentration. Our simulations took a molecular dynamics approach, using LAMMPS software. Molecular dynamics uses the Verlet method of integration to calculate the forces between atoms, and using

these forces to predict the movement of each atom throughout the system. After confirming the validity of our process, we shifted our simulations to explore the effects chain length has on the critical properties, testing chain lengths of 2, 4, 5, and 10.

To get results, we set up a simulation box with a slab of dense liquid in the center. We then, allowed the liquid to come to equilibrium with a new vapor phase. We gathered from these simulations a density profile for different temperatures, as seen below in Figure 1. Then, using a Python script that recorded densities greater than 80% of the max density to be liquid and those less than 20% of the max density to be vapor, we gathered the average vapor and liquid densities of the system. Using MATLAB, we plotted these densities and used the Wegner expansion to fit a curve to the data, which provided the critical temperatures and pressures. One of these phase diagrams is shown in Figure 2. In order to gather the surface tension of the liquid phase, we first attempted using standard method, derived from anisotropy of the pressure tensor; however, the fluctuations in these values relative to their actual values were too large to state a meaningful answer. The primary reason for this is that the surface tension in complex coacervate systems is very small, and vanishes in the near-critical region we are studying. We then moved to using the Zwanzig free-energy perturbation equation and test area sampling[2] to calculate the surface tension, which has proved promising, but has not yielded accurate results as of yet. Further areas of exploration include models that do not include implicit salts, with the ultimate aim the development of a course-grained model to explain salt-partitioning within the whole system and the stability of the complex. We plan to publish these results after performing further simulations to improve the accuracy of the critical properties and the near-critical surface tension values; a tentative target for submission is the end of fall semester.

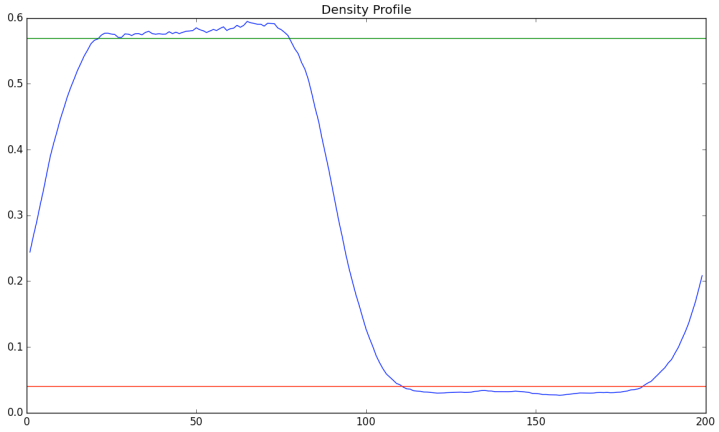

Figure 1: This is a density profile gathered from a simulation, showing the liquid (green) and vapor (red) densities.

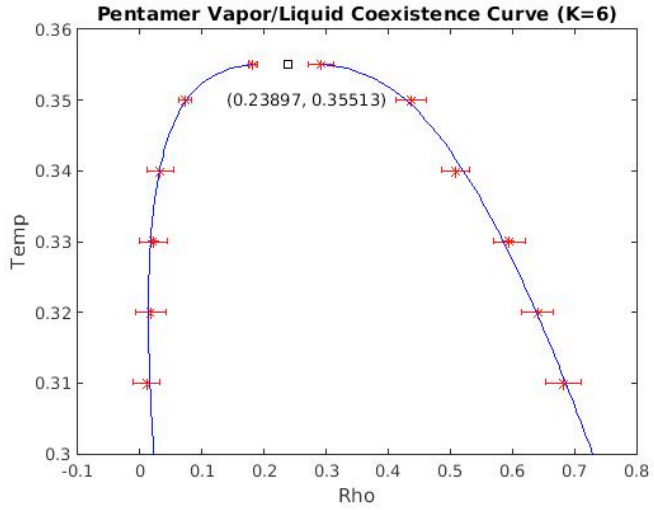

Figure 2: This is a phase diagram for a pentamer modeled with a kappa value of 6. Kappa is the inverse of the Debye length, and determines the range of interactions between atoms.

References:

1. G. A. Chapela, F. del Río, and J. Alejandre. "Liquid-vapor phase diagram and surface properties in oppositely charged colloids represented by a mixture of attractive and repulsive Yukawa potentials." J. Chem. Phys., 138(5):054507, 2013.
2. J. R. Errington, D. A. Kofke. "Calculation of surface tension via area sampling." J. Chem. Phys., 127(17), 2007.