1. This system consists of block copolymers made up 'A' particles and 'B' particles, totaling 4000 particles in a $10 \times 10 \times 10$ simulation box. These polymers all have a fixed length of N = 10, with varying fractions of B particles. Within these polymers the like particles have attractive forces comparative to the repulsion forces. These forces are dependent on attractive, a_{AA} & a_{BB}, and repulsion parameters, a_{AA}. Simulations were performed using dissipative particle dynamics, which utilizes the bead-spring model of a polymer fluid. This method applies a pair force between every particle which includes a interaction force, friction force and a random force. This simulation is given a temperature for a thermostat to maintain and a cut-off distance for the interaction parameters to act. From an initialized starting point, the system is allowed to equilibriate for 10,000 time steps, a snapshot of that system is taken and is given another 10,000 time steps to reach equilibrium where analysis of the system can be performed.

2. This system is used to explore the interactions of block copolymers and the morphologies they resolve into. DeHoff explores the application of statistical thermodynamics in characterizing solution behavior and Flory-Huggins theory provides an extension of that study. This theory shows how adding constraints to a system will influence its phase behavior and can be applied to microphase separation, electronics processing, DNA and in this case, polymers. This theory presumes molecules confined to a lattice where internal energy is equal to the deviations from ideal mixing. Free energy with respect to lattice site is expressed as such:

$$\Delta G_{mix} = RT\left[n_A \ln \phi_A + n_B \ln \phi_B + \chi \phi_A \phi_B\right]$$

where n_i is the moles per component i, ϕ_i is the volume fraction of i, and χ is the Flory-Huggins interaction parameter. This parameter can be further defined as:

$$\chi = \frac{2\alpha(a_{AB} - a_{AA})(\rho_A + \rho_B)}{k_B T}$$

Where α is a constant derived in Groot & Warren through determining the compressability of a system. Using this definition, Gavrilov, Kudryavsev, and Chertovich were

Thermodynamics in Materials Science, 2nd Edition, DeHoff, 2006, *CRC Press*. **Phase diagrams of block copolymer melts by dissipative particle dynamics simulations**, Gavrilov, Kudryavtsev Chertovich, 1979, *J. Chem. Phys.*. **Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation**, Groot, Warren, 1997, *J.* 1

able to produce a phase diagram through plotting χN with respect to composition, ϕ_i. In a range of $\phi_B = 0.1 - 0.5$, and increasing the repulsion parameter, a_{AB}, a variety of morphologies result. In analyzing the morphologies, Gavrilov *et al.* used static structure factors to decipher which morphology is present in a system in addition to visual inspection. In the instance of this specific system, a combination of static structure factor, grazing-incidence small-angle scattering generated through a program created by the computational materials engineering lab, and visual inspection of the equilibriated simulation box will be used to evaluate the morphologies for a given χN & ϕ_B.

3. Your predominance diagram(s), and answers to these questions:

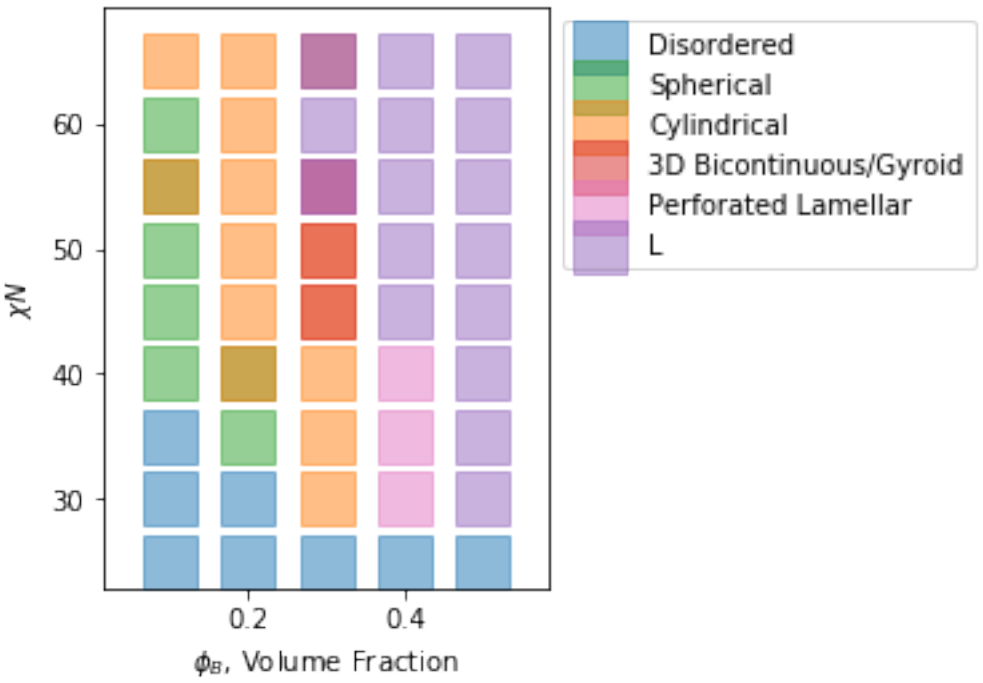

Figure 1: DPD Phase Diagram for block copolymer

(3.1.) In replicating the DPD Phase Diagram from Gavrilov *et al.*, the first task was to explore how to mimic their system in a reasonable time frame, so that simulation time was manageable. Adjusting this system took a few tries before the system

behaved correctly and yielded comparable results. Once a system was found, a spread of simulations with varying volume fractions and interaction parameters was performed so that the resulting data could be stored and accessed with ease. The large amounts of data within these files meant that creating them and moving them around took some time and coaxing. With the data sets available, analysis could begin. First, exploring the static structure factor plots proved to be tricky, where peak detection for a specific morphology did not follow a robust pattern and required visual verification. Identifying the morphologies visually was also difficult as the system are dense and smaller features may hide within the system. Alternatively, the smaller volume fractions yielded small differences between the two major morphologies, Spherical and Cylindrical. Visual inspection was made slightly easier through using grazing-incidence small-angle scattering, but of course may be subject to human error.

(3.2.) Incorporating grazing-incidence small-angle scattering analysis aided in morphology identification the most, though seeing the patterns within systems of similar morphologies deepened my understanding of the interaction within that system.

4. In order to complete the phase diagram, the three analysis techniques were combined to best represent this replication of the DPD phase diagram. This was difficult as the visual inspection techniques may yield incorrect assessments and conflict with the numerical results provided by the structure factor analysis. So the structure factor results seemed to hold more weight compared to the system and grazing-incidence small-angle scattering analysis. Another minor challenge was finding a way to properly plot the phase diagram, as the uncertainty between morphologies seemed to be worth including, rather than choosing a single morphology to represent a given value.

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