

From Clusters to Chains: Lennard Jones A-B dimers with a variable repulsive A-B interaction.

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Diblock copolymers are very important in polymer processing because of their ability to form long range structures. Here a simple model of two particles denoted A and B are bound together by a simple harmonic potential to form dimers. Both the A-A and B-B interactions are governed by a standard LJ potential. The A-B interactions are modeled by a potential consisting of the repulsive part of the LJ interaction plus a softer, longer ranged (r^4) repulsion. The strength and range of the additional repulsive interaction is varied by changing a multiplicative factor λ from 0 to 10. By varying λ , aggregate structures can be varied from clusters to chains.

Introduction and Methods

Polymers are widely used in the manufacturing of packaging, consumer goods, and everyday products like computers, cars, and shoes. The properties of these products like strength, flexibility, and electrical conductivity are often controlled by making polymer blends. Because most polymers are immiscible, copolymers are usually added to provide compatibility between the phases. Copolymer architecture and intermolecular interaction potentials govern the types of polymer blends that can be formed and what, in any, long range structure will be present in the resulting blend.

In this study I have chosen to study a copolymer fluid of the simplest possible copolymer architecture, an A-B dimer, and examine the effects of changing the interaction potential on structure formation. The potential energy of the system is described in equations (0.1) - (0.4). Like-particles (AA and BB) interact via a standard Lennard-Jones (LJ) interaction. Bonded particles (A-B) interact through a standard harmonic potential with a spring constant k of 3000 at a bond distance of 1.0 in dimensionless units. Finally, dissimilar non-bonded particles (AB) interact through a purely repulsive interaction consisting of a LJ repulsive term plus an additional repulsive term λr^{-4} , where λ is varied from 0 to 10 to increase the strength and range of the repulsion. It is expected that as λ is increased at temperatures that allow aggregate formation that the aggregates will shift from clusters to chains. In equations (0.1) - (0.4) U is the potential energy, r_{ij} is the center-to-center distance between the i^{th} and j^{th} particles, r_c is the cutoff distance after which the potentials are zero, AA/BB denotes an interaction of similar particles, A-B denotes an interaction between bonded particles, and A B denotes the interaction between dissimilar non-bonded particles.

$$U = U_{AA/BB} + U_{A-B} + U_{AB} \quad (0.1)$$

$$U_{AA/BB} = \sum_{i < j, ij=AA/BB} 4 \left[r_{ij}^{-12} - r_{ij}^{-6} \right] - 4 \left[r_c^{-12} - r_c^{-6} \right] \rightarrow r_{ij} < r_c \quad (0.2)$$

$$U_{A-B} = \sum_{i < j, ij=A-B} \frac{k}{2} (r_{ij} - r_0)^2 \quad (0.3)$$

$$U_{AB} = \sum_{i < j, ij=AB} 4 \left[r_{ij}^{-12} + \lambda r_{ij}^{-4} \right] - 4 \left[r_c^{-12} + \lambda r_c^{-4} \right] \rightarrow r_{ij} < r_c \quad (0.4)$$

The system is studied using molecular dynamics with a simple velocity rescaling thermostat to simulate an NVT ensemble. The simulation parameters used in this study such as time step, rescaling frequency, and number of particles can be found in the code which is included in the supporting material. Initially all of the atoms were placed at random in a cube with density of 1.0. The actual density of the system was varied from 0.01 to 0.5, but in all cases the initial local density was 1.0 to reduce aggregation time at the lower densities. Next, a conjugate gradient search was performed to relax the system to a local minimum in energy. Then, the simulation was run until the potential energy had met the equilibration criteria or a maximum number of equilibration steps (3×10^6) was reached. The potential energy was considered equilibrated if the percent difference in the average over the two previous checkpoint times was less than 0.1%.

After equilibration a production run of a minimum number of steps (2×10^4) plus additional steps proportional to how many steps were required for equilibration (up to 1.536×10^6) was performed. Using the data from the production run, the radial distribution function and the coordination number of the particles was calculated. The cutoff distance for the coordination number was defined to be 1.25.

Results

In order to analyze the formation of aggregates and aggregate structure the radial distribution function was computed and the coordination number of the individual particles. The radial distribution function is computed in all simulations for the AA, AB, and overall (all A and B particles included separately rather than by center of mass) distributions of particles as shown in Figure 1. It is clear from the Figure 1 that the overall radial distribution function is the average of the AA and AB distributions. I will only plot the overall radial distribution function for different parameters in Figure 2 to show how the structure changes with temperature, density, and λ . In all plots of the radial distribution function there is a very sharp peak at $r = 1.0$ due to the bond between the individual dimers.

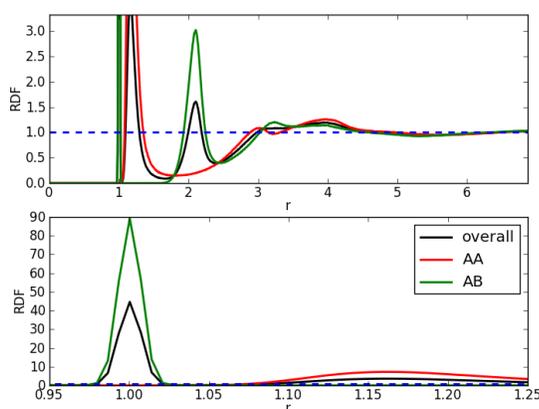


Figure 1. Radial Distribution Function. The upper graph shows the radial distribution function for the different particle-particle pairs in the system at a density of 0.1, a temperature of 0.1, a λ value of 2.0 which corresponds to a set of parameters that form mostly chain aggregates. The lower graph shows in detail the portion of the upper graph corresponding to the bonded particle and coordination shell.

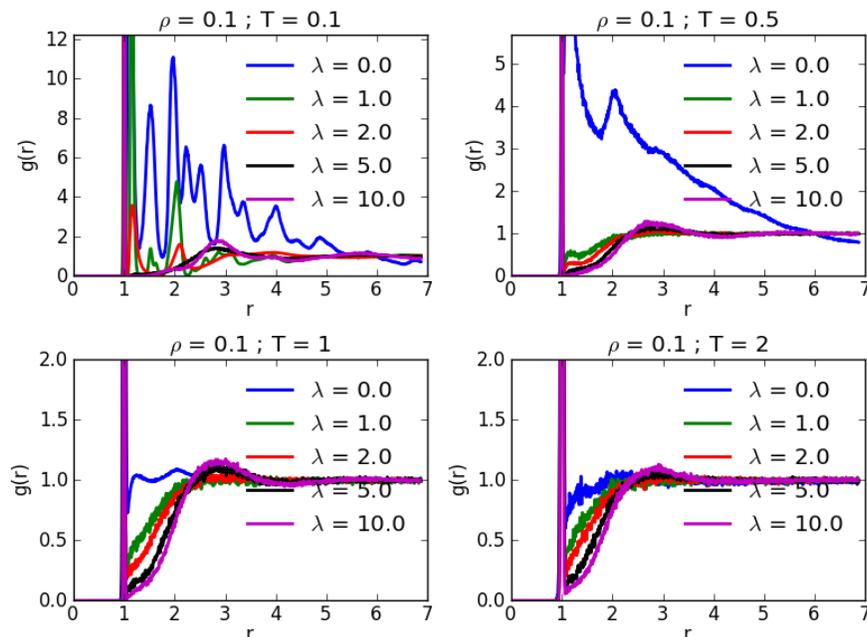


Figure 2. Overall Radial Distribution Function. The four graphs above show how the overall radial distribution function changes with temperature and λ for a density value of 0.1. Radial distributions with a peak at 1.25 and 2.0 is suggestive of chain formation, see ($T = 0.1, \lambda = 2.0$) and ($T = 1.0, \lambda = 0.0$).

At the highest temperature studied ($T = 2.0$) aggregate formation is not possible, due to the high kinetic energy, and the coordination number at this temperature represents the coordination number corresponding to a disordered fluid at each density studied. Figure 3 shows the average coordination number per particle as a function of λ for different densities and temperatures.

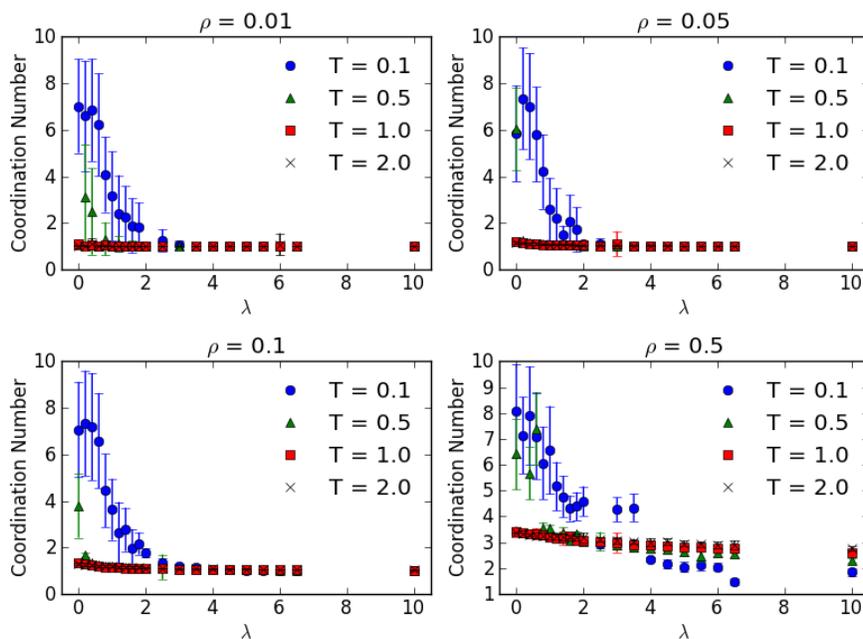


Figure 3. Average Coordination Number. The four graphs above show how the coordination number (averaged over all of the molecules during the production run) varies as a function of density, temperature and λ . Note the maximum in coordination number as a function of λ for $\rho = 0.1$ and $T = 0.1$.

There is some interesting information in the data. If the goal is to form chains I would choose the conditions that produced a coordination number of 2. Interestingly, for the highest density studied (0.5) chains can be achieved over a wide range of λ , while for lower densities chains can only be formed for a very small range of λ at a given temperature. On the other hand, if the goal is to maximize the packing of the particles in most cases this simply requires setting λ equal to 0. In some cases however the maximum packing is achieved at a finite value of λ because the additional repulsion prevents the formation of clumps with less order and forces the aggregates to form crystalline structures. This can clearly be seen in the video in the supporting material.

Conclusion

Although this is a very simple model when compared to real copolymers, it lends some useful insight into how the architecture of copolymer aggregates can be controlled by choosing polymers with different repulsive potentials to form the copolymers. For example, very small molecular weight copolymers in a solvent could be designed to mix very easily, but self assemble into chains after being injected into a mold and provide extra the strength or increase the electrical conductivity of the final product. A more realistic simulation would include the effects of solvent and use a more advanced thermostat. A better model could also be designed that is a good representation of experimentally available interactions like electrostatics or steric effects due to polymer compressibility.