Nanoscale Material Modelling
Week 6

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Contents

1 Assignment 1: Who needs Atoms?

1.1 All Atom Model Information

Figure 1.1 shows the `Ovito` visualization of the `PLA_CHARMM.data` file. Using the `Expresssion Selection` of the `MoleculeIdentifier` property resulting in a single monomer containing nine atoms: two oxygens, four hydrogens, and three carbon atoms. The polylatic acid was determined to made up of 50 monomers based on the number of carbons bounded to two oxygens. This method also includes the two monomers at the end, which consist of ten atoms each. Therefore, the entire system consists of 452 atoms.
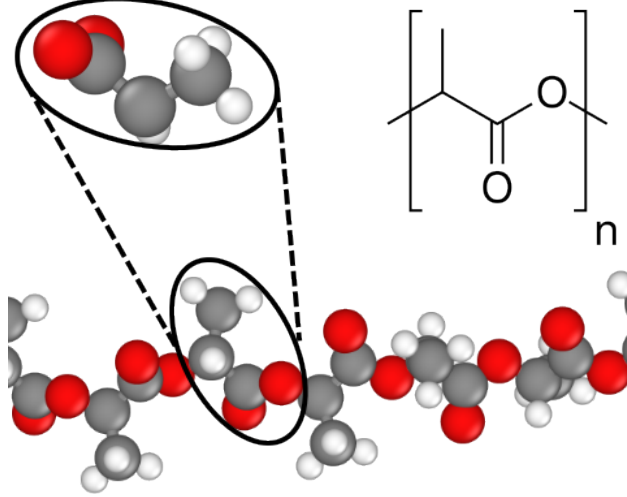

Figure 1.1: An `Ovito` snapshot of the all-atom model of polylatic acid with an isolated monomer in the middle of the chain shown. Hydrogen atoms are white, oxygen atoms red, and carbon atoms grey. The chemical structure is also shown for reference.

1.2 Defining Bonded Interactions of CG Model

To determine the bonded interactions of polylatic acid, the Boltzmann distribution of the energy

$$P(\epsilon_i) \propto \exp\left(-\frac{\epsilon_i}{k_B T}\right) \tag{1.1}$$

for the bond distance, bond angle, and dihedral are fitted against their respective distributions collected during equilibrium. Figure 1.2 demonstrates that equilibrium was reached prior to running the production run from which the bond distance, angle and dihedral distributions were determined.
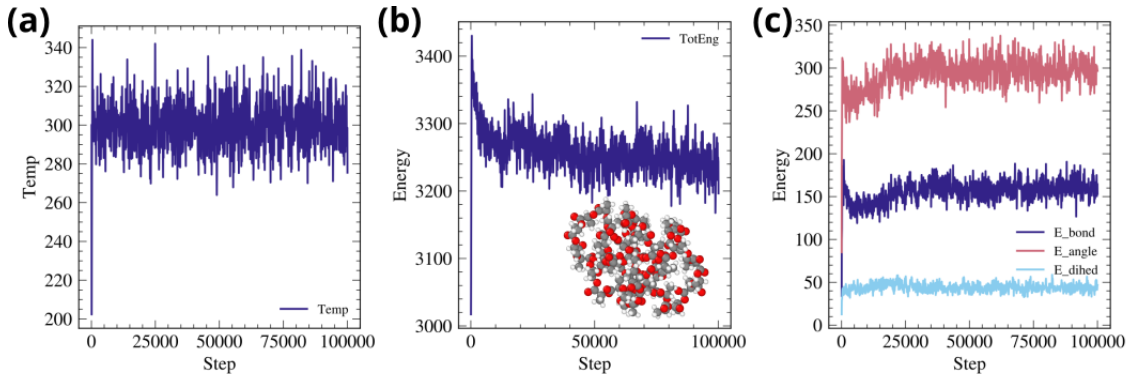

Figure 1.2: The development of several thermodynamic properties during the equilibration run of polylatic acid. (a) shows the temperature, (b) the total energy, and (c) the bond-length, bond-angle, and dihedral energies. The inset in (b) shows an example configuration in equilibrium.

The bonded interactions between monomers were separated into contributions from the bond-length r, bond angle θ and dihedral angle ϕ. The contribution from the bond-length between monomers was fitted against

the `class2` bond style of LAMMPS

$$E_{\text{bond}} = K_{r,2}(r - r_0)^2 + K_{r,3}(r - r_0)^3 + K_{r,4}(r - r_0)^4, \tag{1.2}$$

where $K_{r,i}$ are coefficients describing the strength of each term while r_0 is the minimum engery bond length. Similarly, the bond angle between two CG beads was modelled as the `quartic` angle style:

$$E_{\text{angle}} = K_{\theta,2}(\theta - \theta_0)^2 + K_{\theta,3}(\theta - \theta_0)^3 + K_{\theta,4}(\theta - \theta_0)^4, \tag{1.3}$$

where θ_0 is the bond angle of minimum energy and $K_{\theta,i}$ coefficients describing the contribution of term. Finally, the dihedral interaction between monomers was modelled as a sum of seven harmonics:

$$E_{\text{dihed}} = \sum_{i=1}^{7} A_i \cos^{i-1}(\phi), \tag{1.4}$$

The actual CG beads were defined as the center of masses of each monomer, which was achieved using `residues` of the simulation.

```
bond_lengths = []
residues = u.residues
for ts in u.trajectory[start:end]:
    for i in range(1, len(residues) - 1):
        res1 = residues[i]
        res2 = residues[i + 1]
        com1 = res1.atoms.center_of_mass(unwrap=True)
        com2 = res2.atoms.center_of_mass(unwrap=True)
        bond = calc_bonds(com1[np.newaxis, :], com2[np.newaxis, :],
                          box=u.dimensions)[0]
        bond_lengths.append(bond)
return bond_lengths
```

Listing 1: **An example on how the CG beads are defined from the all-atom simulation. The example is used when determining the bond lengths of the CG model.**

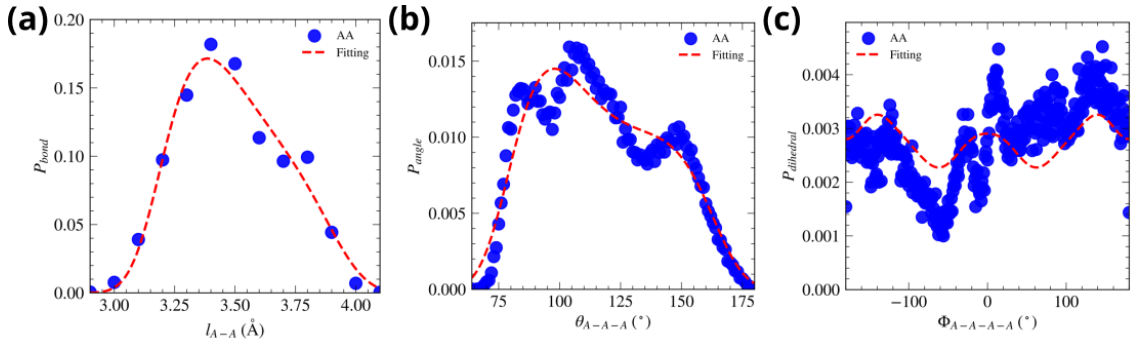## 1.3 Distribution of Bonds, Angles, and Dihedrals

Figure 1.3: **The results of a single iteration of Boltzmann inversion for (a) the bond distance (b) the bond angle and (c) the dihedrals. The resepective fits correspond to the interaction potentials described earlier in the text. The resulting final bonded interaction is given in equation** (1.5).

The single-iteration Boltzmann inversion results in a final bonded interaction between CG beads of

$$\begin{aligned}
E_{\text{bonded}} = \; & K_{r,2}(r - r_0)^2 + K_{r,3}(r - r_0)^3 + K_{r,4}(r - r_0)^4 \\
& + K_{\theta,2}(\theta - \theta_0)^2 + K_{\theta,3}(\theta - \theta_0)^3 + K_{\theta,4}(\theta - \theta_0)^4 \\
& + \sum_{i=1}^{7} A_i \cos^{i-1}(\phi),
\end{aligned} \tag{1.5}$$

with coefficients

$\boldsymbol{E_{\text{bond}}}$: $\quad r_0 = 3.38588\text{Å} \quad K_{r,i} = \{5.99659, -16.18383, 19.99841\}\text{kcal/mol}$

$\boldsymbol{E_{\text{angle}}}$: $\quad \theta_0 = 97.910908° \quad K_{\theta,i} = \{2.02467, -3.79927, 2.17714\}\text{kcal/mol}$

$\boldsymbol{E_{\text{dihed}}}$: $\qquad\qquad\qquad\qquad A_i = \{3.55479, 0.22113, 0.01174, -0.15241, -0.37184, -0.07968, 0.29841\}\text{kcal/mol}$

2 Assignment 2: Walking Randomly

2.1 Theoretical Scaling Law

One of the fundamental concepts of polymer physics is that of scaling laws, which aim to describe interactions in the context of different length scales. The key length scale is that at which the interaction energy is comparable to that of the thermal energy $k_B T$. For scales smaller than this, the interactions of the polymer are dominated by the thermal energy and thus behave according to unperturbed statistics, while for larger length scales the polymer conformations are dominated by the interactions.

In the case of single chain conformations in solvents, the interaction of interest is that of the excluded volume interaction. For good solvents, the excluded volume interaction is positive, i.e., interaction with the solvent is more favorable than with itself, allowing for the chain to be more extended. On the other hand, poor solvents are described by a negative excluded volume interaction in which the polymer tends to collapse in on itself due to the unfavorable interactions with the solvent. The dependence of the size of a polymer chain on the number of monomers $N \gg 1$ can be described for both good and poor solvents by a power law:

$$R \approx bN^\nu, \tag{2.1}$$

where $\nu \approx 3/5$ for good solvents and $\nu = 1/3$ in poor solvents [**?**].

2.2 Model and Results

The environment of a good and poor solvents was implemented implicitly through the use of a modified Lennord-Jones potential between monomer beads:

$$E_{\mathrm{LJ}} = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma^6}{r}\right) \right], \quad r < r_c, \tag{2.2}$$

where ε represents the strength of the interaction, σ the zero-crossing distance, and r_c the cut-off distance. Following Chang and Yethiraj [**?**], both solvents had the same strength of $\varepsilon = 1$ and zero-crossing of $\sigma = 1.0$ while the quality of solvent was induced through the cut-off of the potential. The good solvent was implemented through a purely repulsive potential with $r_c = 1.12246 \approx 2^{1/6}$ while a "full" LJ potential was used for the poor solvent with $r_c = 2.5$.

Figure 2.1 shows that this implementation is in good agreement with the theoretical scaling arguments. The relatively large error bars are due to the value of R_g being taken as the average throughout the entire simulation of the single chain.
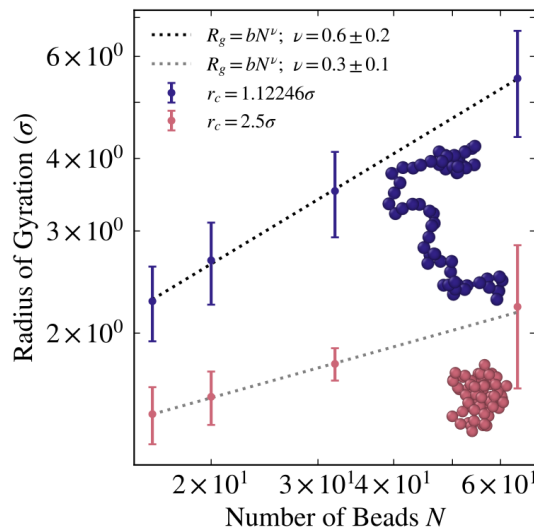

Figure 2.1: The radius of gyration R_g of a single polymer chain with $N = \{16, 20, 32, 64\}$ monomers in both good (blue) and poor (red) solvent conditions. The values of R_g and the error were determined by taking average standard deviation, respectively, over the entire trajectory. The insets show the final conformation of a $N = 64$ chain in good (blue) and poor (red) solvent conditions.

3 Assignment 3: Digital Breaking Bad

4 Assignment 4: Opposites Attract

4.1 Model Information at equilibration

4.2