10.491 Integrated Chemical Engineering Materials Design Module

Assignment #4: Modeling an Amorphous Polymer Phase
Due Mon, 5/3/99, 10am

In preparation for this assignment, work through the following Polymer Tutorials:

a. Amorphous Cell Module/Lesson 1 “Create an Initial Guess Structure of Polypropylene”
b. Amorphous Cell Module/Lesson 2 “Refining the Initial Guess Structure”
c. Analysis and Property Prediction/Lesson 1 “Display Periodic Structures”
d. Analysis and Property Prediction/Lesson 2 “Compute the Pair Correlations for Polypropylene”

as well as the following General Modeling Tools tutorial:

e. Analysis/Lesson 3 “Analyzing motion, predicting mean square displacement”

When you have completed these, exit InsightII and restart it to initiate a new .log file(s). At the end of this assignment, you will turn in the log(s) of your session(s) *by email*. Do not hand in hard copies of these .log files; email each .log file that results from your work on this assignment to the TA, nwaheed@mit.edu. Each file should be sent as a separate message or attachment, suitably labeled so that the TA knows in what order they were generated (if more than one).

Construct an amorphous cell model of atactic poly(3-hydroxypentanoic acid) (common name: polyhydroxyvalerate, or PHV) with 2% water sorbed into it. Indicate how you chose the chain molecular weight and density for constructing this model, and the size of the model cell which results. Refine this amorphous cell model using the AC_Refine/Refine_Run option as many times as necessary until the energy of the model is relatively stable. Then use Discover_3 to run a short (e.g. 100 fs) simulation, in order to get an idea for how long a simulation takes. (The calculation time will scale linearly with number of time steps and as the square of the number of atoms in the model.) Then run a longer dynamics simulation (e.g. 5000 fs) in order to equilibrate the model fully. Finally, run a long dynamics simulation (e.g. 50000 fs) in order to get the real properties of the water-polymer system. All your simulations can be at constant NVT, if your choice of density is correct. Be sure to use the Analyze/Output option in Discover_3 to save your simulation trajectories to a history file; about 200 saves (“frames”) per simulation should suffice for subsequent analysis.

Important note: This homework involves some long calculations. You will need to allow ample time for the simulations to run. Before starting a long calculation, you can use the “kinit -l” command on Athena to make sure that your kerberos tickets are long enough, and “fsid -a” to update your NFS tokens for chefs. Use the commands “klist” and “tokens” to see what tickets and tokens you have. The 50000 fs simulation should be run on one of the SGI’s in 66-008 (the private Chem. Eng. Athena cluster), where

you can use the unix “xlock” command to lock the machine without it being rebooted.

When you are have completed the simulation, compute the following properties for PHV.

a) potential energy vs. Time. What does this plot tell you about the effectiveness of the equilibration?

b) the carbon-carbon pair distribution function (use the entire trajectory). What does this plot tell you about whether or not your model was large enough?

c) the distribution of the torsion angles (Property_Name “Dihedral_Distribution” in AC_Analyze) for the bonds connecting the ‘2’ carbon and the ‘3’ carbon in the polymer repeat units (use the entire trajectory). You will need to use the Subset/Template option to define the C-C-C-O subset for this calculation. Does this plot appear as you expected? Why or why not?

d) the diffusion coefficient for water in PHV. You will need to use Subset/Define to create a subset of the model which contains only the water oxygens (Subset_Property “Potential” will work for this), and Property_Name “Mean_Square_Displacement” in AC_Analyze to get the necessary data from the simulation. In order to extract a diffusion coefficient, you should plot the mean square displacement of the water molecules, $\langle r^2 \rangle$ (in $Å^2$), vs time (in ps). Use the Equation option to change the axes to log-log form (the syntax to rescale an axis looks something like ln(GRAPH1:1::X)). Use the Linefit option to fit a straight line to a portion of the plot, by clicking on two points which define the range of data to be fitted. The equation for the line will appear in the Message port. Report the diffusion coefficient D for water in PHV in units of cm^2/s and indicate whether you think this is a reasonable estimate. Why or why not?

e) Arrange the amorphous cell model and each of the four graphs created in parts (a)-(d) in the InsightII workspace and export a plot of the screen to turn in with this assignment. Use the Threshhold and Tickmark options under under the Graph menu option to add axis detail to each of your plots before printing them out.