

## Nanoscale Science and Engineering, 2016

Due: 9/28/2016 @9am

### Assignment #5

**Objective:** In this problem set we will use a molecular mechanics/dynamics code (LAMMPS) to optimize the structure and compute vibrational frequencies of CO<sub>2</sub>, and compare our results to those obtained using QM.

#### Part 1: Setting things up

1. % ssh -Y <username>@hydra.javerianacali.edu.co
2. Create a new directory the new problem set via % mkdir HW2 and entering that directory via % cd HW2
3. Use the CO<sub>2</sub> molecule configuration that you obtained in HW1. Save the molecule in xyz format and copy it under your HW2 directory.
4. Use 'module load lammps' on hydra to setup LAMMPS.
5. Save the attached files under the HW2 directory in hydra (use the 'scp data.co2 in.co2 <username>@hydra.javeriana.cali.edu.co:/users/<username>/HW2/'

#### Part 2: Performing calculations

6. Optimize the geometry using a reax/c potential, per script attached. This should produce a set of .xyz output files with the same name. You can visualize the optimization process by loading the .xyz files in VMD to see how it converges to the stable structure.
7. Run an MD NVE ensemble and Langevin thermostat trajectory at 300K for sufficient time to equilibrate. Use 1fs integration timestep. See attached script.
8. Modify the script to compute the radial distribution function (RDF) for C-O during your NVE run and to dump the velocities from the atoms you're simulating, every 2fs. See <http://lammps.sandia.gov/doc/dump.html> and [http://lammps.sandia.gov/doc/compute\\_rdf.html](http://lammps.sandia.gov/doc/compute_rdf.html) commands in LAMMPS.
9. Build the velocity autocorrelation function (VAC) from the dumped file then compute a Fourier transform of the VAC results; this will give you the power spectrum that you can compare to experiment. As an alternative to step 8 and 9, you can use the "compute VACF" in LAMMPS (see [http://lammps.sandia.gov/doc/compute\\_vacf.html](http://lammps.sandia.gov/doc/compute_vacf.html)) to calculate the VAC. You may want to do 8+9 to compute the VAC and then compare to the results obtained from a LAMMPS run.

NOTE: The vibrational spectrum (or vibrational density of states) can be computed from atomic velocities obtained at fixed time intervals over the duration of an equilibrated simulation, you can then load the data into Matlab (or any of your favorite numerical software, e.g. Scipy), take its discrete FFT and then absolute-

square it. According to the Wiener-Khinchin theorem, this would be equivalent to taking the Fourier transform of the velocity auto-correlation function.

**For extra credit (+25%)**

10. Build the system's  $3N \times 3N$  ( $9 \times 9$ ) Hessian. The Hessian is a matrix whose elements are the 2nd order derivatives of the mass weighted degrees of freedom in the system (9 in the CO<sub>2</sub> case). Mass-weighted means you have to normalize the Hessian entries by the individual atomic masses.
11. Find the eigenvalues and eigenvectors of the Hessian (i.e. solve the secular equation); these are the normal modes and frequencies.
12. Compare to the MD results obtained previously.

**Write up**

1. (10%) Compare the 0K CO<sub>2</sub> geometry (bond length and bond angle) to your QM results obtained in HW1. Explain the origin of any difference.
2. Use the RDF results to deduce the C-O bond length average at the finite equilibration temperature of 300K.
  - a. (10%) Is it different from the 0K one? If so, explain.
  - b. (10%) What does the C-O bond distribution in the RDF mean? Please explain (hint: modify your temperature and see what happens to the RDF).
3. (10%) In the script file included for the CO<sub>2</sub> case, you'll see an explicit command to compute charges using the Charge Equilibration Scheme (fix qeq/reax/c) by Rappe and Goddard. Compare to charges obtained during your HW1 using QM and comment on how accurate is the qeq solver for this molecule.
4. Plot the energy as a function of optimization iteration, and energy of the ground state of CO<sub>2</sub>.
  - a. (10%) Does the 0K equilibrium energy have any meaning or relation to the QM results? Explain your answer.
  - b. (10%) What is the equilibrium (converged) energy of your system at 300K? What does the difference between the 0K energy and the 300K energy mean?
5. (10%) Comment on how much did the original geometry change after optimization with respect to your original coordinates and to the final coordinates obtained from QM. Explain any differences.
6. (30%) Plot the power spectrum obtained from the Fourier transform of the VAC and identify the characteristic vibrational frequencies for each mode.
  - a. What does the power spectrum give you? Explain.
  - b. Please compare and comment on any differences with respect to your QM data.