Week 4 – Homework Assignment 3
Statistical Mechanics and MD simulations

Problem 1. Analysis of NVE (microcanonical) simulations. Using the nanoMATERIALS simulation tool in nanoHUB (https://nanohub.org/tools/matsimtk) perform the following simulations. Select a NiAl unit cell (this is a B2 cubic cell 2-atom unit cell in bcc positions), replicate the cell 7x7x7 times along x, y, and z and run in the NVE ensemble, with a timestep of 0.001 ps and 10,000 MD steps. Write to the energy file every step to have a good temporal resolution. Repeat a similar calculation for Al, but use 5x5x5 (4-atom fcc) unit cells.

Question 1.1. How many atoms do you have in the NiAl and Al simulations?
   a) 686 and 500, respectively
   b) 343 and 125, respectively
   c) can not be calculated with the information provided

These simulations are in the microcanonical ensemble and the first thing you should check is that total energy is relatively constant. You will notice that kinetic and potential energies evolve quite a bit early in the simulation before reaching equilibrium and fluctuating around a constant value. The kinetic energy converts into potential and vice versa and total energy remains constant. If the total energy is not constant you are using the wrong ensemble, a timestep that is too large or found a bug in the code.

We will now analyze the kinetic energy in the runs. The code gives the total kinetic energy in kcal/mol, download the data to your computer for analysis. You will calculate the average kinetic energy in both runs from time 1ps to time 10ps. We will ignore the 1st picosecond of simulation while the system is equilibrating.
Question 1.2. The average kinetic energy per atom in the NiAl and Al systems are?
   a) Both approximately 0.9 kcal/mol
   b) The NiAl value about twice the Al one
   c) Both approximately 0.45 kcal/mol

It is very interesting that these two different systems exhibit the same average kinetic energy. Remember the principle of equipartition of energy that states that, regardless of mass, each atom will contribute $\frac{3}{2}kT$ to the total kinetic energy. To check this further, you can run a simulation using a 5x5x5 Si unit cell and check the kinetic energy per atom.

Question 1.3. These simulations contain N atoms in 3D periodic boundary conditions and the c.m. momentum is zeroed at the beginning of the run. What is the most appropriate expression relating total kinetic energy and temperature:

   a) $\langle K \rangle = \frac{3}{2} (N - 6) kT$
   b) $\langle K \rangle = \frac{3}{2} (N - 3) kT$
   c) $\langle K \rangle = \frac{3}{2} NkT$

Interestingly, these two simulations that start with a kinetic energy corresponding the T=300 K and a potential energy of the ground state

$V_0 = V\left(\left\{ R_i^0 \right\}\right)$ (since the initial structure is the perfect crystal)

end up with approximately 150K (i.e. one half of what they started with). To understand this we will analyze the potential energy. The average potential energy of a system at temperature T can be written as the sum of the zero temperature value plus a thermal potential
energy: \[ \langle V(T) \rangle = V \left( \{ R_i^0 \} \right) + V_{th}(T) \]. The term \( V_{th} \) the increase in potential energy because atoms moving away from their equilibrium positions and was analyzed, within the harmonic approximation, during the lectures. For both simulations, compute the average potential energy during the last 9 ps of simulation and subtract the initial value (0.001 ps is close enough) to obtain the thermal potential energy.

**Question 1.4.** The average thermal energy of the NiAl and Al systems are:

a) Both approximately 0.45 kcal/mol  
b) Very different from one another  
c) Both approximately 0.9 kcal/mol

The temperature of our systems is low enough that the harmonic approximation works reasonably well. Thus, the potential energy can be described as a set of 3N harmonic oscillators and their thermal energy will be approximately \( 3/2 kT \) per degree of freedom.

**Problem 2. Analysis of NVT (canonical) simulations.** Before running the simulations.

**Question 2.1.** What is the average kinetic energy (total, not per atom) you expect to obtain for the NiAl and Al systems at \( T=300K? \) \( (k_B=0.0019872041 \text{ kcal/mol/K}) \)

a) 611 kcal/mol for NiAl and 444 kcal/mol for Al  
b) Cannot be estimated with the information we have  
c) 203 kcal/mol for NiAl and 148 kcal/mol for Al
Now repeat the same simulations but this time perform the simulations under NVT conditions at $T=300K$ and confirm your expectations. In these simulations the initial conditions are the same as the NVE above but a thermostat is used to add or remove energy to the system as needed to achieve the desired temperature. You can check the total energy evolution and see what the thermostat is doing.

**Question 2.2.** What is the net effect of the thermostat in this case?

- a) In average, the thermostat removes energy from the system
- b) In average, the thermostat does not remove or add energy
- c) In average, the thermostat adds energy to the system