Define the following terms with respect to molecular dynamic simulations:

- Thermodynamic Ensemble
- Ergodic Hypothesis
- Periodic Boundary Condition
- Minimization

Give a general force field expression for the interactions among atoms in the molecular dynamics simulation for calculating the total energy of a real structure.

Calculate the *overstretched bond angle* and then the *overstretched force of the bond angle* with the following data:

$$K_\theta = 10\ J/degree$$
$$\theta_{eq} = 180^o$$
$$V_{angle} = 229\ kJ$$

There are many different types of energy minimisation techniques in molecular dynamics simulations. Give a brief description of **THREE** and explain what kind of results to expect.

Work out the temperature of a molecular dynamic simulation for the eclipsed / staggered conformation of ^{n}butane when the counts of each were 2541 : 15475 respectively and the gibbs free energy difference between the two respectively was determined to be -1240 J.

a) Describe observations made from the following two reactions with respect to ‘harpooning’.

$$\vec{K} + Br_2 \rightarrow KBr + \overrightarrow{Br}$$
$$\vec{K} + MeI \rightarrow KI + \overrightarrow{Me}$$

b) We would like to see transition states as they are made, however the concentration of the activated species is very low and their lifetime is very short. How does ultrafast spectroscopy overcome this in pump-probe spectroscopy?

a) Calculate the frequency of collisions in solution with the following data:

Liquid density: 1 g cm^{-3}
Atomic mass: 18 x 10^{-3} kg mol^{-1}
Molecular radius: 0.1 nm
Temperature: 300 K

b) Describe what is meant by Kramer's Turnover.

What is the reorganisation energy? What are the two factors that comprise the reorganisation energy? What factors play an important part for small and for large molecules.