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:

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

Thermodynamic Ensemble

Collection of all possible systems which have different microscopic states but have identical macroscopic (thermodynamic) states

Ergodic Hypothesis

Assumption whereby all accessible microstates are equally probable over a long period of time. $\langle Q \rangle_{ensemble} = \langle Q \rangle_{time}$

Periodic Boundary Condition

Perform simulation with a cut off region where only a relatively small number of particles experience forces as if they were in bulk.

Minimization

Process used to find minimum energy conformations (relieve strain in experimental conformation / find stable states) given a potential energy function.

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.

$$E = \sum_{bonds} K_r (r - r_{eq})^2 + \sum_{angles} K_\theta (\theta - \theta_{eq})^2 + \sum_{dihedral} \frac{V_n}{2} [1 + \cos(n\varphi - \gamma)] + \sum_{non-bonded\ interactions} \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} + \frac{q_i q_j}{\varepsilon R_{ij}} \right]$$

Calculate the *overstretched bond angle* and then the *overstretched force of the angle* with the following data: $K_\theta = 10\ J/degree$ $\theta_{eq} = 180^o$ $V_{angle} = 229\ kJ$

$$V_{angle} = K_\theta (\theta - \theta_{eq})^2$$

$$\theta = \sqrt{\frac{V_{angle}}{K_\theta}} + \theta_{eq} = \sqrt{\frac{229000}{10}} + 180 = 331^o\ or\ 29^o$$

$$F_{angle} = 2K_\theta (\theta - \theta_{eq}) = 3020\ N$$

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.

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.

Steepest Decent – Local minima found by travelling along potential energy surface (PES) by steepest gradients. Trapped in local minima and rare to find global minimum. Depends on starting point.

Constant Energy (NVE) – Can go up and down PES but highest energy contour accessible is E_{total}. Creates PES valleys and barriers which cannot crossed.

Constant Temperature (NVT) – Average KE held constant but PE can vary hence E_{total} can fluctuate. Leads to random crossings of energy barriers in attempt to find global minima.

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$$\Delta G = -RTln\left(\frac{P_2}{P_1}\right)$$

$$T = -\frac{\Delta G}{RlnK} = \frac{1240}{8.314 \; x \ln\left(\frac{15475}{2541}\right)} = 83 \; K$$

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

$$\vec{K} + Br_2 \rightarrow KBr + \overrightarrow{Br}$$
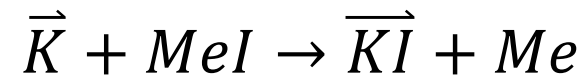$$\vec{K} + MeI \rightarrow KI + \overrightarrow{Me}$$
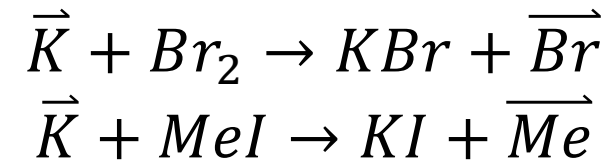
b) We would like to see transition states as they are made, however the concentration of the activated species is very low and their lifetime is very short. How does ultrafast spectroscopy overcome this in pump-probe spectroscopy?

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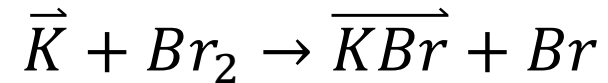
Reaction very likely and product moves in same direction as product (0 º).
Has larger cross collision section wtr MeI. Br_2 electronegative and favourable to transfer electron at a distance by reeling in bromine as potassium cation flies past it.

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

Reaction improbable and product scattered back to source (180 º). Low cross section as no reaction if hits methyl. No electronegativity difference so harpooning not observed.

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?

- Creates high concentration by putting many molecules at TS with an ultrashort intense pulse of light (PUMP)
- Measure spectrum with another sport pulse of light just after initial pulse with an adjustable precise time difference (PROBE)

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.

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$$Z = \sigma \bar{c}_{rel} N \qquad \sigma = \pi r^2 \qquad \bar{c}_{rel} = \left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}} \qquad N = \frac{liquid\ density\ x\ N_A}{atomic\ mass}$$

$$Z = (\pi(10^{-10})^2)\ x\ \left(\frac{8\ x\ 1.38\ x\ 10^{-23}\ x\ 300}{\pi\ x\ 18\ x\ 1.67\ x\ 10^{-27}}\right)^{\frac{1}{2}}\ x\ \left(\frac{10^3\ x\ 6.03\ x\ 10^{23}}{18\ x\ 10^{-3}}\right)$$

$$= 6.3\ x\ 10^{11}\ s^{-1}$$

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

Expect that high solvent friction (or viscosity) should slow the reaction as collisions push molecules heading towards TS back into reactant well.

However at low friction this is not observed and there is an increase in rate with increasing friction. Some friction is required in order for reactants to acquire enough energy to reach TS.

At high friction the expected theory is put in place where rate decreases with increasing friction. Hence there is a friction where there is a turnover (Kramer's turnover)

Theory predicts that the barrier shape influences reaction rates, whereby higher frequencies react faster (barrier recrossing less frequent with sharp barrier)

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.

Reorganisation energy: Amount of energy required to reorganise equilibrium geometry of reactant (DA) to product (D^+A^-) with same geometry.

$$\lambda = \lambda_i + \lambda_o$$

λ_i = INTERNAL (molecular structure of D^+A^- pair)
λ_o = OUTER (solvation of D^+A^- pair)

Small molecules:
Both important

Large molecules:
Molecular ion structure similar to neutral structure, therefore dominant contribution from outer factor.