[redacted]

25 points

1. The interaction energy between two atoms of a species is given by the Lennard-Jones potential as follows:

$$U_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

(a) Derive an expression for the force exerted by the two atoms on each other.

$$\cancel{F = -\frac{\partial U_{LJ}(r)}{\partial r} = \frac{\partial}{\partial r}\left[4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \sigma\right.\right.}$$

* Used d not Partial (∂) because we are only considering r & not θ & ϕ

$$F = -\frac{d\,U_{LJ}(r)}{dr} = -\frac{d}{dr}\left[4\epsilon\cdot\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]\right]$$

$$= -\left[-48\cdot\epsilon\cdot\left(\frac{\sigma^{12}}{r^{13}}\right) + 24\epsilon\cdot\left(\frac{\sigma^{6}}{r^{7}}\right)\right]$$

$$F = 48\cdot\epsilon\left(\frac{\sigma^{12}}{r^{13}}\right) - 24\cdot\epsilon\cdot\frac{\sigma^{6}}{r^{7}} \longrightarrow *$$

$\boxed{F = C\,\frac{M_1 M_2}{r^2}} \rightarrow (1)$ ~~F = ma ⇒ F = −∂V/∂r~~

Problem 1 continued …..

(b) What are the ranges of values of the separation distance r for which the force between the atoms is

→ ~~r2 according to~~ r → Atoms have to be close

Repulsive: ~~r is small (atoms are too close each other)~~ ~~$\frac{1}{r^n}$ (Short range)~~

Attractive: r is large ~~$\frac{1}{r}$ (long range)~~

↳ r^2 according to Eq^n (1)

(c) What are the ranges of values of separation distance r for which the interaction energy between the atoms is

Repulsive: $\frac{1}{r^n}$ (Short Range)

Attractive: $\frac{1}{r}$ (long Range)

25 points

2. A molecule of a chemical is known to exist in three conformational states that are denoted by the symbols: $A, B,$ and C. It is further known that:
(1) The states B and C have the same energy i.e., $E_B = E_C$, and $\Rightarrow m_1 = 2$
(2) The state A has the highest energy such that $E_A = 2E_B$ $\Rightarrow m_2 = 1$

In an experiment at a constant temperature T, the conformational states of one million (i.e., 10^6) molecules of this chemical are determined (either spectroscopically or by computer simulation). How many of these molecules are expected to be in State A?

$$P_j = \frac{e^{-\frac{E_j}{k_B \cdot T}}}{\sum e^{-E_j/k_B \cdot T}}$$

~~$P_1 \Rightarrow \sum e^{-\frac{E_A}{kT}}$~~

~~$P_1 = \frac{}{e^{-\frac{E_1}{kT}} + e^{-E_1}}$~~

$$P_1 = \frac{e^{-\frac{E_1}{k_B \cdot T}}}{e^{-\frac{E_1}{k_B T}} + e^{-\frac{E_2}{k_B T}}} \Rightarrow (B \,\&\, C)$$

$$P_2 = \frac{e^{-\frac{E_2}{k_B \cdot T}}}{e^{-\frac{E_1}{k_B \cdot T}} + e^{-\frac{E_2}{k_B \cdot T}}} \Rightarrow (A)$$

Problem 2 continued …..

From $E_B = E_C$

& $E_A = 2E_B$

$$E_1 = \frac{1}{2} E_2$$

$$P_1 = \frac{e^{-\frac{E_1}{k_BT}}}{e^{-\frac{E_1}{k_BT}} + e^{\frac{-E_1}{2k_B T}}} = \frac{e^{\frac{-E_1}{k_BT}}}{e^{\frac{-E_1}{k_BT}}\left[1 + e^{\frac{1}{2}}\right]}$$

$$P_1 = \frac{1}{\left[1 + e^{-\frac{1}{2}}\right]}$$

Probability of system in energy state 1

is $P_1 = \frac{1}{\left[1+e^{\frac{1}{2}}\right]}$

$$M = 10^6 \Rightarrow m_1 = M \cdot P_1$$

$$= 1 \times 10^6 \cdot \frac{1}{\left[1 + e^{\frac{1}{2}}\right]}$$

$\because M = \sum_j m_j$

$$m_2 = 1 \times 10^6 - \frac{10^6}{\left[1+e^{\frac{1}{2}}\right]}$$

(Number of systems in energy state E_B

$$m_2 = \frac{\left[1+e^{\frac{1}{2}}\right] \times 10^6 - 10^6}{\left[1+e^{1/2}\right]}$$

$\therefore$ m_2 ~~System 2~~ consist of systems in E_A

$$m_A = \frac{\left[1+e^{\frac{1}{2}}\right] \times 10^6 - 10^6}{\left[1+e^{1/2}\right]}$$

30 points

3. For the isothermal-isobaric ensemble, it is known that the Gibbs energy is related to the partition function by the expression $G = -kT \ln \Delta(N, P, T)$.

(a) Derive an expression for the entropy in terms of the partition function Δ.

$$dG = V \cdot dp - S \cdot dT + \mu \cdot dN \rightarrow (1)$$

$$\left(\frac{\partial G}{\partial T}\right)_{V,N} = -S \Rightarrow S = -\frac{\partial}{\partial T}\left[-k \cdot T \cdot \ln(\Delta)\right]\Big|_{V,N}$$

$$S = k \cdot \ln(\Delta) + kT \cdot \left[\frac{\partial \ln(\Delta)}{\partial T}\Big|_{V,N}\right] \longrightarrow *$$

(b) Derive an expression for the Helmholtz energy in terms of the partition function Δ.

$$G = U - TS + PV \qquad \because A = U - TS$$

$$(2) \leftarrow G = A + PV \qquad \because P \text{ is constant} \qquad \therefore \text{we need an expression for } V$$

from (1) in previous Question :-

$$\left(\frac{\partial G}{\partial p}\right)_{T,N} = V \Rightarrow V = \frac{\partial}{\partial p}\left[-k \cdot T \cdot \ln(\Delta)\right]\Big|_{T,N}$$

$$V = -k \cdot T \cdot \left[\frac{\partial \ln(\Delta)}{\partial p}\Big|_{T,N}\right] \overset{(2)}{\Rightarrow} A = G - PV \Rightarrow$$

$$\boxed{A = -k \cdot T \cdot \ln(\Delta) + kT \cdot \left[\frac{\partial \ln(\Delta)}{\partial p}\Big|_{T,N}\right] \cdot P}$$

(c) Derive an expression for the internal energy in terms of the partition function Δ.

$* S$ & V from previous questions

$$U = TS - PV$$

$$U = T \cdot \left[k \cdot \ln(\Delta) + kT \cdot \left[\frac{\partial \ln(\Delta)}{\partial T}\Big|_{V,N}\right]\right] - P \cdot \left[-k \cdot T \cdot \left[\frac{\partial \ln(\Delta)}{\partial p}\Big|_{T,N}\right]\right]$$

$$U = E = k \cdot T \cdot \ln(\Delta) + k \cdot T^2 \cdot \left[\frac{\partial \ln(\Delta)}{\partial T}\Big|_{V,N}\right] + p \cdot \left[k \cdot T \cdot \left[\frac{\partial \ln(\Delta)}{\partial p}\Big|_{T,N}\right]\right] \longrightarrow *$$