Problem 1 (30 points). Consider a diatomic molecule, for example, HCl. Here are some data for this molecule that might be useful. The moment of intertia of HCl is I = 2.65×10^{-47} kg m^2; the vibrational wavelength: $\lambda = 3.34 \times 10^{-6}$ m.

(a) (8 pts) Calculate the translational partition function for this molecule confined to a volume of 100 cm^3 at 293 K.

The partition function for a particle in a 3-D box is a product of the partition functions corresponding to translations along x, y, and z,

$$q_{transl}{}^{3D} = \left(\sqrt{2\pi m k_B T}\right)^3 \frac{L_x L_y L_z}{h^3} = \left(\sqrt{2\pi m k_B T}\right)^3 \frac{V}{h^3} = 2.1\times10^{28}$$ -- it is a huge number!

The mass of HCl can be calculated as $m_{HCl} \approx 36.5$ au $\approx 36.5\ m_p$ where m_p=1.67 10^{-27} kg; or from the molecular weight of HCl, if you recall that 1 mole of a substance (in this case 36.5 g of HCl) contains the Avogadro's number of molecules.

(b) (8 pts) Calculate the rotational partition function for this molecule at 293 K.

In the high-temperature approximation, $q_{rot} = 2I\, k_B T / \hbar^2$=19.3

(c) (8 pts) Calculate the vibrational partition function for this molecule at 293 K.

$$q_{vibr} = \frac{1}{1+e^{-\frac{h\nu}{k_B T}}};\quad \frac{h\nu}{k_B T} = \frac{hc}{k_B T\lambda} = 14.7$$, thus $q_{vibr} = \frac{1}{1+e^{-14.7}} \approx 1$

(d) (6 pts) Based on these results, which of these three types of motion has the biggest and which has the smallest number of accessible states at this temperature?

Because *q* characterizes the number of accessible states at a given temperature, translational motion has the largest and vibrational motion the least number of accessible states at these conditions.

Problem 2 (30 points). Consider a system of N distinguishable hypothetical particles, each having four energy levels, with energies 0, ε, 2ε, and 3ε and and the degeneracy numbers 1, 3, 3, and 1, respectively. Let $\varepsilon = 4.5 \times 10^{-21}$ J and $N = N_A$.

(1) (6 pts)What is the temperature of the system if the levels 0 and ε are equally populated?

$P(0) = \frac{1}{q}$; $P(\varepsilon) = \frac{3e^{-\frac{\varepsilon}{kT}}}{q}$ (including the degeneracies). Because $P(0) = P(\varepsilon)$, we get $3e^{-\frac{\varepsilon}{kT}} = 1$, hence $\frac{\varepsilon}{kT} = \ln 3$, and $T = \frac{\varepsilon}{k\ln 3}$=296.8 K.

(2) (6 pts)Write an expression for the molecular partition function and calculate it at this temperature.

$q = 1 + 3e^{-\frac{\varepsilon}{kT}} + 3e^{-\frac{2\varepsilon}{kT}} + e^{-\frac{3\varepsilon}{kT}}$, which can be written in a compact form: $q = \left(1 + e^{-\frac{\varepsilon}{kT}}\right)^3$. From the previous problem, at this temperature we have $e^{-\frac{\varepsilon}{kT}} = 1/3$, hence $q = \left(1 + \frac{1}{3}\right)^3 = 2.37$.

(3) (6 pts)Calculate the total energy of the system at this temperature.

One could use the general equation, $E_{total} = kT^2\left(\frac{\partial}{\partial T}\ln Q\right)_V$, where $Q = q^{N_A}$, but it seems simpler to calculate it as follows: $E_{total} = N_A \times \langle E_{particle}\rangle$, where $\langle E_{particle}\rangle$ is the average energy of one particle: $\langle E_{particle}\rangle = \sum \varepsilon_i P(\varepsilon_i) = \left(0 + \varepsilon 3e^{-\frac{\varepsilon}{kT}} + 2\varepsilon 3e^{-\frac{2\varepsilon}{kT}} + 3\varepsilon e^{-\frac{3\varepsilon}{kT}}\right)/q = 3\varepsilon\, e^{-\frac{\varepsilon}{kT}}\left(1 + e^{-\frac{\varepsilon}{kT}}\right)^2 / q$.

Substituting the expression for q from the previous problem, $\langle E_{particle}\rangle = 3\varepsilon\, e^{-\frac{\varepsilon}{kT}} / \left(1 + e^{-\frac{\varepsilon}{kT}}\right) = 3\varepsilon/4$, thus $E_{total} = 3\varepsilon N_A/4 = 2.03\times10^3$ J/mol.

(4) (6 pts)Calculate the entropy of the system at this temperature.

$S = \frac{E_{total}}{T} + k\ln q^{N_A} = \frac{E_{total}}{T} + R\ln q =$ 14 J/(mol K)

(5) (6 pts)What are the values of the molecular partition function at T = 0 and at T → ∞ ?

when T → 0, $q = \left(1 + e^{-\frac{\varepsilon}{kT}}\right)^3 \to \left(1 + e^{-\frac{\varepsilon}{0}}\right)^3 = 1$; when T → ∞, $q \to \left(1 + e^{-\frac{\varepsilon}{\infty}}\right)^3 \to (1+1)^3 = 8$.

Problem 3. (20 points) The highest magnetic field currently available in NMR spectrometers is B_o = 22.3 T ("T" stands for "Tesla", the unit of measurement of magnetic field). Proton's magnetogyric ratio is $\gamma = 26.75 \times 10^7\ T^{-1}\ s^{-1}$

1. (5 pts) Calculate the energy that corresponds to a transition between the two proton spin states at this magnetic field.

$\varepsilon = -\gamma\hbar\, B_o\, m_I$; where $m_I = \pm 1/2$. $\Delta\varepsilon = \gamma\hbar\, B_o\, \Delta m_I = \gamma\hbar B_o = 6.285\times10^{-25}$ J.

2. (5 pts) Compare this energy with the thermal energy (k_BT) at 293 K. (Calculate the ratio of the two energies). This will tell you whether molecular motions are affected by the magnetic field.

$\Delta\varepsilon/k_BT = 1.55\times10^{-4}$
the energy of a transition is much smaller than k_BT, therefore the effect on molecular motions is negligible.

3. (5 pts) Compare the populations of the two spin states of the proton at these conditions. (For example, calculate their ratio)

$\frac{P(m_I = -1/2)}{P(m_I = +1/2)} = e^{-\Delta\varepsilon/k_BT} = 0.9998$ -- the populations are almost equal

4. (5 pts) At what temperature will the population of the upper level be **half** of the population of the lower level?

From the equation $\frac{P(m_I = -1/2)}{P(m_I = +1/2)} = e^{-\Delta\varepsilon/k_BT} = \frac{1}{2}$ we get $T = \frac{\Delta\varepsilon}{k \ln 2}$=0.0657 K. (should be pretty cold…)

Problem 4 (20 points). You use fluorescence resonant energy transfer (FRET) to measure the distance between two domains in a protein, in order to monitor conformational transition in the protein induced by pH. You discovered that a change in pH from pH7.0 to pH4.5 caused a decrease in the efficiency of FRET from 0.5 at pH6.8 to 0.25 at pH4.5. In a control (calibration) experiment, when the same donor and acceptor were 3.5 nm apart, the efficiency of transfer was 0.4. (Assume that the spectroscopic parameters of the fluorophores that you used do not depend on pH). Determine the donor-acceptor distance at both pH values.

FRET efficiency: $E = \frac{1}{1+(r/R_o)^6}$. In the control experiment, $E = \frac{1}{1+(r/R_o)^6} = 0.4$, hence $(r/R_o)^6 = 3/2$, and $R_o = r\,(2/3)^{1/6}$= 3.27 nm.

At pH=6.8, *E*=0.5, hence $r = R_0$ = 3.27 nm. At pH 4.5, *E* = 0.25, therefore $(r/R_o)^6 = 3$ and $r = 3^{1/6} R_o = 3.93$ nm.

Bonus Problem (10 points) Which of the following molecules has the largest translational partition function: H_2, HD, D_2? Which has the largest rotational partition function. Explain your reasoning. Assume that the conditions (temperature, volume) and the bond lengths are identical.

The translational partition function is proportional to $m^{3/2}$, where m is the molecular mass (not the reduced mass!). Of these molecules, D_2 has the largest m, hence it should have the largest translational partition function (assuming the bond lengths and all conditions are equal).

The rotational partition function is proportional to the moment of inertia I, and therefore is propotional to μ (the reduced mass): $q \propto I \propto \mu$. Of these molecules, D_2 has the largest reduced mass ($\mu = m_p$), hence the largest rotational partition function.