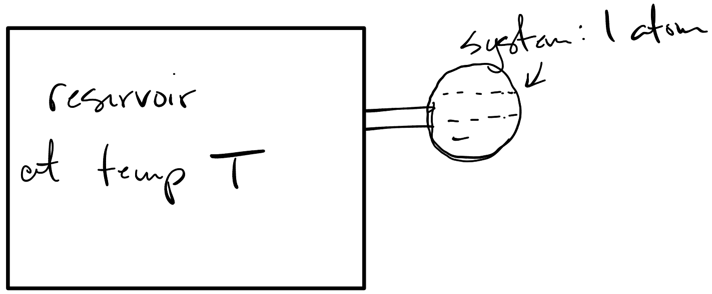
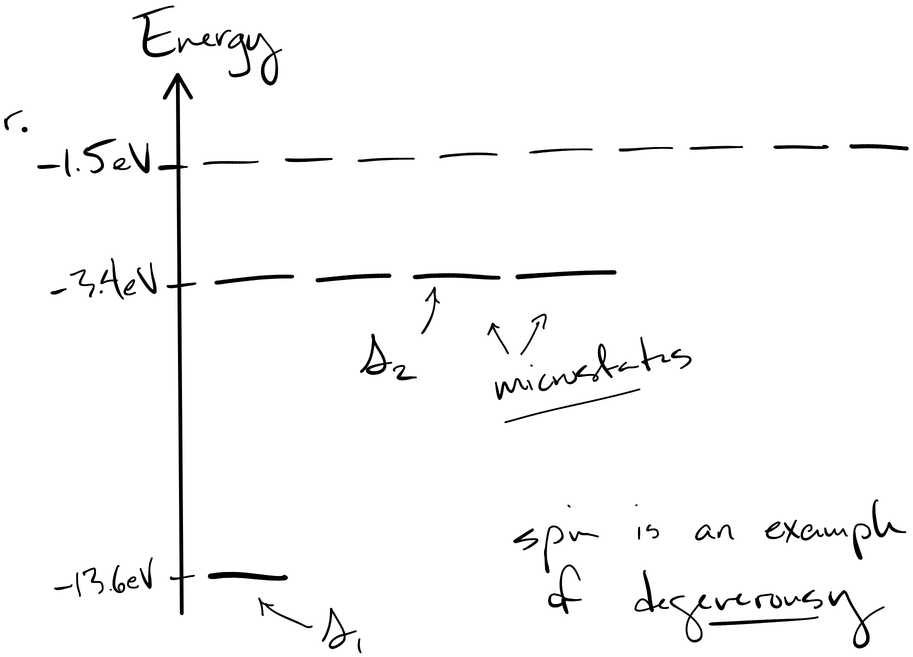
Chapter 6 - Boltzmann Statistics

System of an atom in contact w/ a reservoir.





spin is an example of degeneracy

all of these states are equally probable

states: s_1 + s_2

probabilities: $P(s_1)$ + $P(s_2)$

energies: $E(s_1)$ + $E(s_2)$

multiplicities: $\Omega_R(s_1)$ + $\Omega_R(s_2)$

$$\Omega_R(s_1) > \Omega_R(s_2)$$

$$\frac{P(s_2)}{P(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)}$$

$$\Omega_R(s_1) = e^{\ln(\Omega_R(s_1))} = e^{S_R(s_1)/k_B}$$

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{S_R(s_2)/k_B}}{e^{S_R(s_1)/k_B}}$$

$$\frac{P(s_2)}{P(s_1)} = e^{[S_R(s_2) - S_R(s_1)]/k_B}$$

very small compared to dU

literally 0

$$dS_R = \frac{1}{T}\left(dU_R + \cancel{P\,dV_R} - \cancel{\mu\,dN_R}\right)$$

$$dU_R = T\,dS_R$$

$$S_R(s_2) - S_R(s_1) = \frac{1}{T}\left[U_R(s_2) - U_R(s_1)\right]$$

$$= -\frac{1}{T}\left[E(s_2) - E(s_1)\right]$$

$$dE = -T\,dS_R$$

energy of the system

$$\frac{P(s_2)}{P(s_1)} = e^{-[E(s_2) - E(s_1)]/k_BT} = e^{-E(s_2)/k_BT} \cdot e^{E(s_1)/k_BT} = \frac{e^{-E(s_2)/k_BT}}{e^{-E(s_1)/k_BT}}$$

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-E(s_2)/k_BT}}{e^{-E(s_1)/k_BT}}$$

$$\frac{P(s_2)}{e^{-E(s_2)/k_BT}} = \frac{P(s_1)}{e^{-E(s_1)/k_BT}} = \frac{1}{Z} \Rightarrow \boxed{P(s) = \frac{1}{Z} e^{-E(s)/k_BT}}$$

$Z \rightarrow$ partition function

How do we calculate Z?

$$\underbrace{\sum_s P(s) = 1}_{\text{now probability works!}} = \sum_s \frac{1}{Z} e^{-E(s)/k_BT} = \frac{1}{Z} \sum_s e^{-E(s)/k_BT} = 1$$

$$Z = \sum_s e^{-E(s)/k_BT}$$

An example: probability of finding a H in its first excited state $T = 5800K$

Sun's atmosphere

from the ground state to the first excited state 10.2eV

eV → energy of one electron accelerated from rest by a potential of 1V.

$$\Delta K = q\Delta V = 1.6 \cdot 10^{-19} C \cdot 1V = 1.6 \cdot 10^{-19} J$$

$$1 eV = 1.6 \cdot 10^{-19} J$$

$$\frac{P(s_2)}{P(s_1)} = e^{-[E_2 - E_1]/k_B T}$$

$$k_B T = 1.38 \cdot 10^{-23} \frac{J}{K} \cdot 5800 K$$

$$k_B = \left[\frac{eV}{K}\right] = 1.38 \cdot 10^{-23} \frac{\cancel{J}}{K} \cdot \frac{1 \, eV}{1.6 \cdot 10^{-19} \cancel{J}}$$

$$= 0.8625 \cdot 10^{-4}$$

$$= 8.625 \cdot 10^{-5} \, eV/K$$

$$k_B T = 8.625 \cdot 10^{-5} \frac{eV}{K} \cdot 5800K = 0.5 eV$$

$$\frac{P(s_2)}{P(s_1)} = e^{-10.2eV/0.5eV} = e^{-20.4}$$

$$= 1.4 \cdot 10^{-9}$$

$\times 4$ ← degenerate states

$5.5 \cdot 10^9$

Problem 6.6 + 6.12

6.2 Average Values

$$P(s) = \frac{1}{Z} e^{-E(s)/k_B T} \rightarrow P(s) = \frac{1}{Z} e^{-\beta E(s)}$$

$$\beta = \frac{1}{k_B T}$$

$$Z = \sum_s e^{-E(s)/k_B T} \longrightarrow Z = \sum_s e^{-\beta E(s)}$$

What is the average energy?

$$\langle E \rangle = \sum_s E(s) P(s) = \frac{1}{Z} \sum_s E(s) e^{-\beta E(s)}$$

"average"

"expectation value"

if there are many state we can integrate!

energy function

probability density

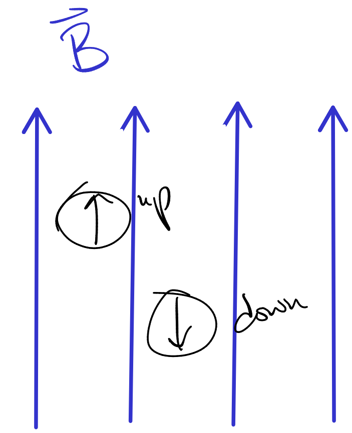
small space between states

$$\langle E \rangle = \int E(s) \cdot \rho(s)\, ds$$

Go back to the total energy of a system

$$U = N \cdot \langle E \rangle$$

average is per particle so multiply by the number of particles to get total energy



Let's try this w/ an unusual system

↳ two state paramagnet

$$E_\uparrow = -\mu B$$

$$E_\downarrow = +\mu B$$

↳ magnetic dipole moment

$$Z = \sum_s e^{-\beta E(s)} = e^{-\beta(-\mu B)} + e^{-\beta(+\mu B)}$$

$$Z = e^{\beta \mu B} + e^{-\beta \mu B} = 2\cosh(\beta \mu B)$$

$$\cosh(x) = \frac{e^x + e^{-x}}{2}$$

$$\sinh(x) = \frac{e^x - e^{-x}}{2}$$

$$P_\uparrow = \frac{e^{\beta\mu B}}{2\cosh(\beta\mu B)} \qquad P_\downarrow = \frac{e^{-\beta\mu B}}{2\cosh(\beta\mu B)} \qquad P_\uparrow + P_\downarrow = \underline{1}$$

$$\langle E\rangle = \sum_s E(s)\,P(s) = \frac{-\mu B\cdot e^{\beta\mu B}}{2\cosh(\beta\mu B)} + \frac{\mu B\, e^{-\beta\mu B}}{2\cosh(\beta\mu B)}$$

$$= \frac{-\mu B}{2\cosh(\beta\mu B)} \underbrace{\left(e^{\beta\mu B} - e^{-\beta\mu B}\right)}_{2\sinh\beta\mu B}$$

$$= -\mu B \tanh(\beta\mu B)$$

total energy $\rightarrow$ $U = N\cdot\langle E\rangle = -N\mu B\tanh(\beta\mu B)$

<u>Problem 6.16</u> Show $\langle E\rangle = -\frac{1}{Z}\cdot\frac{\partial Z}{\partial\beta} = -\frac{\partial(\ln Z)}{\partial\beta}$

$$Z = \sum_s e^{-\beta E(s)} \qquad \langle E\rangle = \sum_s E(s)\,P(s)$$

$$= \frac{1}{Z}\sum_s E(s)\,e^{-\beta E(s)}$$

$$\langle E\rangle = \frac{\sum_s E(s)e^{-\beta E(s)}}{\sum_s e^{-\beta E(s)}}$$

this looks like the derivation of the denominator wrt β

$$\frac{\partial}{\partial\beta}\sum e^{-\beta E(s)} = -\sum E(s)\, e^{-\beta E(s)}$$

$$\langle E\rangle = -\frac{\frac{\partial Z}{\partial\beta}}{Z}$$

$$\langle E\rangle = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{\partial \ln(Z)}{\partial\beta}$$

apply to the paramagnet

$$\frac{d\cosh(x)}{dx} = \sinh(x)$$

$$\frac{d\sinh(x)}{dx} = \cosh(x)$$

$$\langle E\rangle = -\frac{1}{Z}\cdot\frac{\partial Z}{\partial\beta} = -\frac{1}{\cancel{2}\cosh(\beta\mu B)}\cdot\frac{\partial(\cancel{2}\cosh\beta\mu B)}{\partial\beta}$$

$$= -\mu B\cdot\frac{\sinh\beta\mu B}{\cosh\beta\mu B}$$

$$= -\mu B\tanh\beta\mu B$$

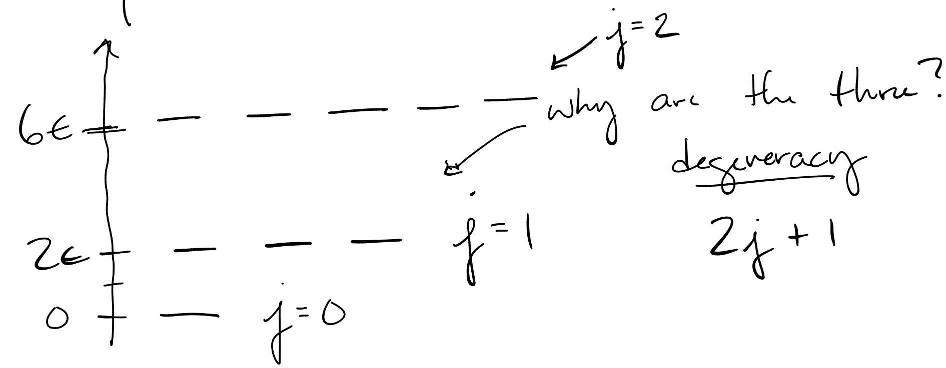
Problems: 6.15, 6.20

Now, lets consider diatomic gases + rotational energy

- just like energy levels of hydrogen $\rightarrow$ quantized (discret) energy levels

$$E(j) = j(j+1)\cdot \underbrace{\epsilon}_{\text{constant}}$$

$$j = 0, 1, 2 \dots$$



- Molecules w/ distinguishable atoms (CO, CN)

$$Z = \sum_{j=0}^{\infty} \underbrace{(2j+1)}_{\substack{\text{need to multiply}\\ \text{by the degeneracy}\\ \text{to count all of the}\\ \text{boltzman factors}}} e^{-j(j+1)\epsilon/k_BT}$$

convert to integral

$$Z = \int_0^{\infty} (2j+1)\, e^{-j(j+1)\epsilon/k_BT}\, dj$$ $\leftarrow$ hard math $\rightarrow$ use mathematica

this integral can be used b/c $k_BT \gg \epsilon$

$$Z = \frac{kT}{\epsilon} = \frac{1}{\epsilon\beta}$$

so now, what about average rotational energy

$$\langle E_{rot} \rangle = \frac{-1}{Z} \cdot \frac{\partial Z}{\partial \beta} = -\epsilon\beta \cdot \left(\frac{-1}{\epsilon\beta^2}\right) = k_B T$$

total $\rightarrow$ $U = N k_B T$ $\quad f = ?\quad$ equipartition theorem $\rightarrow U = \frac{f}{2} N k_B T$

$f = 2 \leftarrow$ two rotational degrees of freedom

- Molecules w/ indistinguishable atoms (H_2, O_2, N_2)

$$Z = \frac{kT}{2\epsilon} \rightarrow \text{proceed from here....}$$

Revisit the Equipartition theorem.

$$U = \frac{f}{2} N k_B T$$ true for all quadratic forms of energy

$$\frac{1}{2} m v_x^2 , \quad \frac{1}{2} I \omega_x^2 , \quad \frac{1}{2} k x^2$$

Proof: $E(q) = c q^2$ ← some variable

$$Z = \sum_q e^{-\beta E(q)} = \sum_q e^{-\beta c q^2}$$

$$Z = \sum_q \frac{1}{\Delta q} e^{-\beta c q^2} \Delta q$$ as $\Delta q \to dq$

$$Z = \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta c q^2} dq$$ ← change of variable to evaluate

$$x^2 = \beta c q^2$$

$$x = q \sqrt{\beta c}$$

$$dx = dq \sqrt{\beta c}$$

$$Z = \frac{1}{\Delta q \sqrt{\beta c}} \underbrace{\int_{-\infty}^{\infty} e^{-x^2}\, dx}_{\text{Gaussian integral}}$$

$\hookrightarrow \sqrt{\pi}$

$$Z = \frac{\sqrt{\pi}}{\Delta q \sqrt{\beta c}}$$

$$\langle E \rangle = -\frac{1}{Z} \cdot \frac{\partial Z}{\partial \beta} = -\frac{\Delta q \sqrt{\beta c}}{\sqrt{\pi}} \cdot \frac{\partial}{\partial \beta}\left(\frac{\sqrt{\pi}}{\Delta q \sqrt{\beta c}}\right) = -\frac{\cancel{\Delta q} \sqrt{\beta \cancel{c}}}{\cancel{\sqrt{\pi}}} \cdot \frac{\cancel{\sqrt{\pi}}}{\cancel{\Delta q} \sqrt{\cancel{c}}} \cdot \left(-\frac{1}{2}\right) \cdot \frac{1}{\beta^{3/2}}$$

$$\langle E \rangle = \frac{1}{2} \beta^{-1} = \underbrace{\frac{1}{2} kT}_{c,\ \Delta q,\ \sqrt{\pi}}$$

all constants cancelled out

6.5) Partition function & Free Energies

Isolated system of fixed energy → Ω is fundamental

$$S = k_B \ln \Omega$$

For a system held a constant T w/ a reservoir

Z is fundamental → analogous to Ω

Z equalish to the number of microstates available to the system at some T.

$$Z = \sum_s e^{-\beta E(s)} \quad \leftarrow \text{sum of Boltzmann factors}$$

Helmholtz Free Energy → $-F \stackrel{?}{=} k_B \ln Z$

incorrect units

$$-\frac{F}{T} = k_B \ln Z$$

$F = -k_B T \ln Z$?? → YES, it is true

Recall, why is F useful?

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = +\left(\frac{\partial F}{\partial N}\right)_{T,V}$$

So how can we scale up the partition function?

$$Z_{total} = \sum_s e^{-\beta[\underbrace{E_1(s)}_{\text{particle 1 energy}} + \underbrace{E_2(s)}_{\text{particle 2 energy}}]}$$

distinguishability matters

for indistinguishable particles

$$Z_{total} = \frac{1}{N!} Z_1^N$$

$$Z_1 = \sum_s e^{-\beta E(s)} = \underbrace{\sum_s e^{-\beta E_{tr}(s)}}_{\text{focus on this}} \underbrace{e^{-\beta E_{rot/vib}(s)}}_{\text{not present in an "ideal gas"}}$$

What can we say about $E(s)$?

$$E(p) = \frac{p^2}{2m}$$

momentum

$$p_n = \frac{h}{\lambda_n}$$ de Broglie wavelengths

$$\lambda_n = \frac{2L}{n}$$

$$p_n = \frac{nh}{2L}$$

$$E_n = \frac{n^2h^2}{8L^2m}$$

$$Z_{1D} = \sum_n e^{-\frac{n^2h^2}{8L^2mk_BT}}$$

↳ becomes an integral for large L + T

$$Z_{1D} = L\sqrt{\frac{2\pi mk_BT}{h^2}}$$

$$Z_{trans} = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-h^2 n_x^2 / 8mL^2 k_B T}$$

3D

$$Z_{trans} = \frac{L_x L_y L_z}{(\qquad)} = \frac{V}{v_Q}$$

"quantum volume"

not velocity

$$v_Q = \left(\frac{h}{\sqrt{2\pi m k_B T}}\right)^3$$