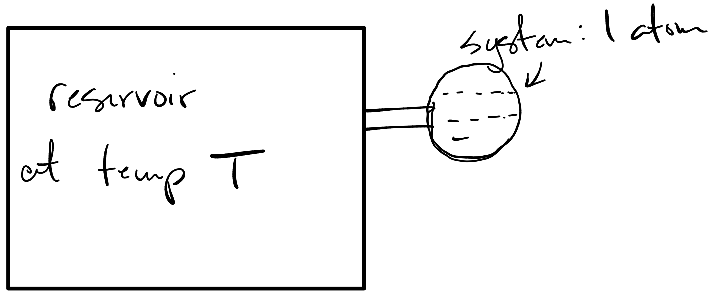
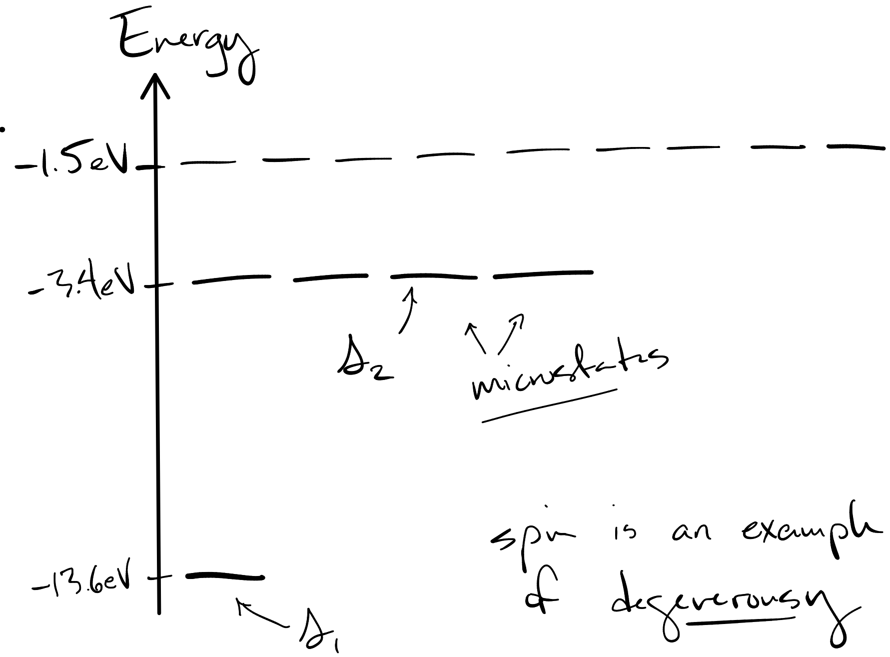
Chapter 6 - Boltzmann Statistics

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

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

$$dU_R = T\,dS_R$$

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

$$dE = -T\,dS_R$$

energy of the system

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

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

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

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

$Z \rightarrow$ partition function

How do we calculate Z?

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

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

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

Sun's atmosphere

from the ground state to the first excited state 10.2 eV

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

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

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

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

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

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

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

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

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

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

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

$\times 4$ ← 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 <u>many</u> state we can integrate!

energy function

probability density

small space between states

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

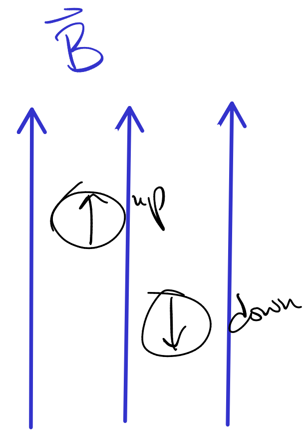
Go back to the total energy of a system

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

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

Let's try this w/ an <u>unusual system</u>

↳ <u>two state</u> 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 derivative 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

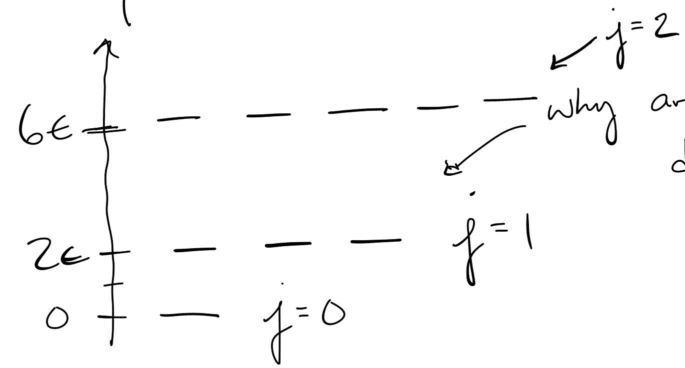
Now, lets consider diatomic gases + rotational energy

- just like energy levels of hydrogen → quantized (discret) energy levels

$$E(j) = j(j+1)\cdot\epsilon$$

↳ constant

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



why are the three?

degeneracy

$2j+1$

Molecules w/ distinguishable atoms (CO, CN)

Z