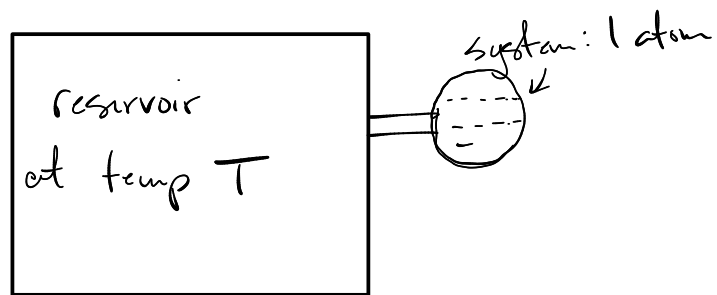


Chapter 6 - Boltzmann Statistics

System of an atom in contact w/ a reservoir.



states: $\delta_1 + \delta_2$

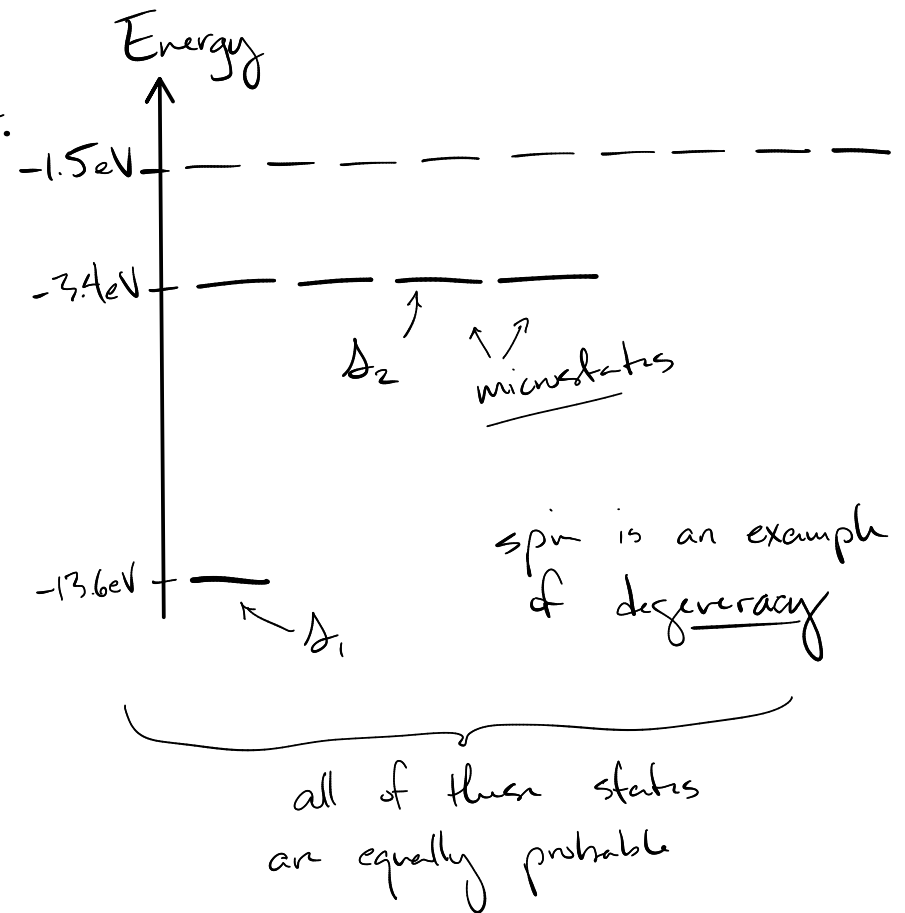
probabilities: $P(\delta_1) + P(\delta_2)$

energies: $E(\delta_1) + E(\delta_2)$

multiplicities: $\Omega_R(\delta_1) + \Omega_R(\delta_2)$

$$\Omega_R(\delta_1) > \Omega_R(\delta_2)$$

$$\frac{P(\delta_2)}{P(\delta_1)} = \frac{\Omega_R(\delta_2)}{\Omega_R(\delta_1)}$$



$$\Omega_R(\delta_1) = e^{\ln(\Omega_R(\delta_1))} = e^{\frac{S_R(\delta_1)}{k_B}}$$

$$\frac{P(\mathcal{A}_2)}{P(\mathcal{A}_1)} = \frac{e^{S_R(\mathcal{A}_2)/k_B}}{e^{S_R(\mathcal{A}_1)/k_B}}$$

$$\frac{P(\mathcal{A}_2)}{P(\mathcal{A}_1)} = e^{\frac{[S_R(\mathcal{A}_2) - S_R(\mathcal{A}_1)]}{k_B}}$$

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

very small compared to dU

literally 0

$$dU_R = T dS_R$$

$$S_R(\mathcal{A}_2) - S_R(\mathcal{A}_1) = \frac{1}{T} [U_R(\mathcal{A}_2) - U_R(\mathcal{A}_1)]$$

$$= -\frac{1}{T} [E(\mathcal{A}_2) - E(\mathcal{A}_1)]$$

$$dE = -T dS_R$$

energy of the system

$$\frac{P(\mathcal{A}_2)}{P(\mathcal{A}_1)} = e^{-[E(\mathcal{A}_2) - E(\mathcal{A}_1)]/k_B T}$$

$$= e^{-E(\mathcal{A}_2)/k_B T} \cdot e^{E(\mathcal{A}_1)/k_B T} = \frac{e^{-E(\mathcal{A}_2)/k_B T}}{e^{-E(\mathcal{A}_1)/k_B T}}$$

$$\frac{P(\Delta_2)}{P(\Delta_1)} = \frac{e^{-E(\Delta_2)/k_B T}}{e^{-E(\Delta_1)/k_B T}}$$

$$\frac{P(\Delta_2)}{e^{-E(\Delta_2)/k_B T}} = \frac{P(\Delta_1)}{e^{-E(\Delta_1)/k_B T}} = \frac{1}{Z}$$

$$\Rightarrow P(\Delta) = \frac{1}{Z} e^{-E(\Delta)/k_B T}$$

$Z \rightarrow$ partition function

How do we calculate Z ?

$$\sum_{\Delta} P(\Delta) = 1 = \sum_{\Delta} \frac{1}{Z} e^{-E(\Delta)/k_B T} = \frac{1}{Z} \sum_{\Delta} e^{-E(\Delta)/k_B T} = 1$$

how probability works!

$$Z = \sum_{\Delta} e^{-E(\Delta)/k_B T}$$

An example: probability of finding a H in its first excited state $T = 5800\text{K}$
from the ground state to the first excited state 10.2eV

↑
Sun's atmosphere

$\text{eV} \rightarrow$ energy of one electron accelerated from rest by a potential of 1V .

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

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

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

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

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

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

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

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

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

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

$\times 4 \rightarrow$ degenerate states

$$\underline{\underline{5.5 \cdot 10^9}}$$

Problem 6.6 + 6.12

6.2 Average Values

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

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

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

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 states
we can
integrate!

energy function

probability density

small space
between states

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

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

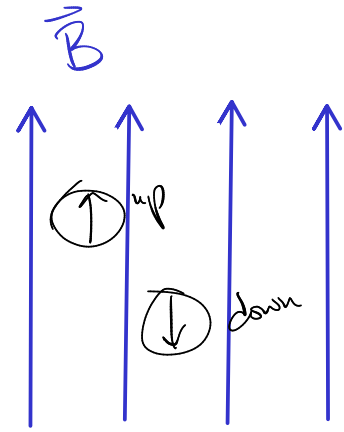
$$E_{\uparrow} = -\mu B$$

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

↳ magnetic dipole moment

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

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



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

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

$$P_{\uparrow} = \frac{e^{\beta\mu B}}{2\cosh(\beta\mu B)}$$

$$P_{\downarrow} = \frac{e^{-\beta\mu B}}{2\cosh(\beta\mu B)}$$

$$P_{\uparrow} + P_{\downarrow} = 1$$

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

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

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

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

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

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

$$\langle E \rangle = \sum_s E(s) P(s)$$

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

$$\langle E \rangle = \frac{\sum_{\lambda} E(\lambda) e^{-\beta E(\lambda)}}{\sum_{\lambda} e^{-\beta E(\lambda)}}$$

← this looks like the
derivative of the
denominator wrt β
 $\frac{\partial}{\partial \beta} \sum_{\lambda} e^{-\beta E(\lambda)} = -\sum_{\lambda} E(\lambda) e^{-\beta E(\lambda)}$

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

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

← apply to the
paramagnet

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

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

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

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

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

Problems: 6.15, 6.20

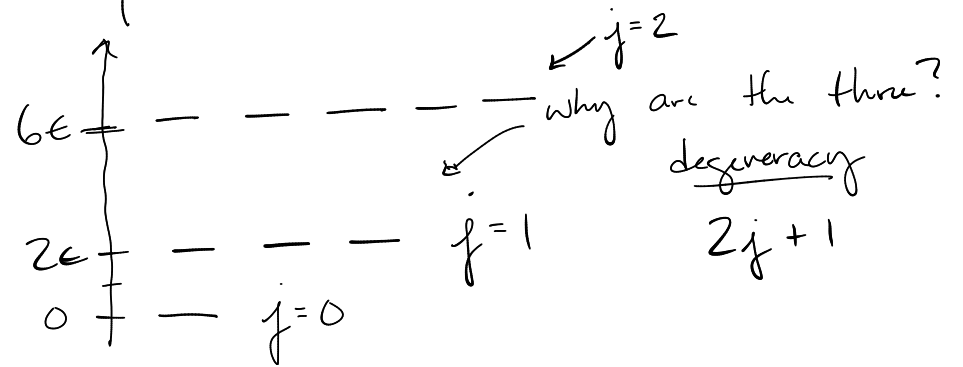
Now, let's consider diatomic gases + rotational energy

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

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

\hookrightarrow constant

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



- Molecules w/ distinguishable atoms (CO, CN)

$$Z = \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\epsilon/k_B T}$$

need to multiply
by the degeneracy
to count all of the
Boltzmann factors

convert
to
integral \int

$$Z = \int_0^{\infty} (2j+1) e^{-j(j+1)\epsilon/k_B T} dj$$

\leftarrow hard math \rightarrow use mathematics
this integral can be used b/c $k_B T \gg \epsilon$

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

so now, what about average rotational energy

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

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

$$f = 2 \leftarrow \text{two rotational degrees of freedom}$$

• Molecules w/ indistinguishable atoms ($\text{H}_2, \text{O}_2, \text{N}_2$)

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

Revisit the Equipartition theorem.

$$U = \frac{f}{2} N k_B T \quad \text{true for all quadratic forms of energy}$$
$$\frac{1}{2} m v_x^2, \quad \frac{1}{2} I \omega_x^2, \quad \frac{1}{2} k x^2$$

Proof: $E(q) = C q^2$ ← some variable

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

$$Z = \sum_q \frac{1}{\Delta q} e^{-\beta C q^2} \Delta q \quad \text{as } \Delta q \rightarrow dq$$

$$Z = \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta C q^2} dq \quad \leftarrow \text{change of variable to evaluate}$$
$$\left\{ \begin{array}{l} x^2 = \beta C q^2 \\ x = q \sqrt{\beta C} \\ dx = dq \sqrt{\beta C} \end{array} \right.$$

$$Z = \frac{1}{\Delta q \sqrt{\beta c}} \int_{-\infty}^{\infty} e^{-x^2} dx$$

$\underbrace{\hspace{10em}}_{\text{Gaussian integral}}$
 $\hookrightarrow \sqrt{\pi}$

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

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

$$\langle E \rangle = \frac{1}{2} \beta^{-1} = \frac{1}{2} kT$$

$\underbrace{c, \Delta q, \sqrt{\pi}}_{\text{all constants cancelled out}}$

6.5) Partition function & Free Energies

Isolated system of fixed energy $\rightarrow \Omega$ is fundamental

$$S = k_B \ln \Omega$$

For a system held a constant T w/ a reservoir

Z is fundamental \rightarrow 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

$$\rightarrow -F \stackrel{?}{=} k_B \ln Z$$

\uparrow incorrect units

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

$$F = -k_B T \ln Z \quad ?? \rightarrow \text{YES, it is true}$$

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?

$$Z_{\text{total}} = \sum_{\lambda} e^{-\beta [E_1(\lambda) + E_2(\lambda)]}$$

particle 1 energy particle 2 energy

distinguishability matters

for indistinguishable particles

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

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

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

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

↑
momentum

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

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

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

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

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

↳ becomes an integral
for large L & T

$$Z_{1D} = L \int \sqrt{\frac{2\pi m k_B T}{h^2}}$$

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

3D →

$$Z_{\text{trans}} = \frac{L_x L_y L_z}{(\quad)} = \frac{\Delta V}{v_Q}$$

"quantum volume"
not velocity

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

so what can we do w/ this partition function?

Use it to find any of these quantities

Problems: 6.6, 12, 15, 20

6.6) I thought we did this one, but not quite. We worked on the ratio of these things in the sun's atmosphere. But this is different

- from the ground state to the first excited state $\frac{10.2 \text{ eV}}{E_2}$
 $\hookrightarrow 10 \text{ eV} = E_1$

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

$$k_B T = 8.625 \cdot 10^5 \frac{\text{eV}}{\text{K}} \cdot 298 \text{ K} = 0.0257 \text{ eV}$$

$$\frac{P(s_2)}{P(s_1)} = e^{-10.2 \text{ eV} / 0.0257} = 4.3 \cdot 10^{-173}$$

$\times 4$
 doesn't matter

\swarrow very few ionized hydrogen at room temp.

But what about at 9500 K? $k_B T = 8.625 \cdot 10^5 \cdot 9500 \text{ K} = 0.819 \text{ eV}$

$$\frac{P(s_2)}{P(s_1)} = e^{-10.2 \text{ eV} / 0.819} = 3.9 \cdot 10^{-6}$$

$\times 4$ ← degeneracy
 $\frac{1.5 \cdot 10^{-5}}{1.5 \cdot 10^{-5}}$ ←

still small, but
 in comparison to
 Avogadro's number
 there will be a
 good number of
 1st ionized H⁺

6.12 CN $0\text{ eV} \leftarrow$ ground state
 $4.7 \cdot 10^{-4} \text{ eV} \leftarrow$ 1st excited state

3 \leftarrow degeneracy \leftarrow accounting for

$$\frac{3}{10} = \frac{p(\psi_2)}{p(\psi_1)}$$

$$\rightarrow \frac{1}{10}$$

$$0.1 = e^{-4.7 \cdot 10^{-4} \text{ eV} / k_B T} \leftarrow \text{solve for } T$$

$$\ln(0.1) = \frac{-4.7 \cdot 10^{-4}}{k_B T}$$

$$T = \frac{-4.7 \cdot 10^{-4} \text{ eV}}{\ln(0.1) (8.625 \cdot 10^{-5} \text{ eV/K})}$$

$$\boxed{T = 2.36 \text{ K}}$$