Review

- System in thermal equilibrium with a reservoir at temperature T

- Probability of finding system in a particular microstate, *s*

$$P(s) = \frac{1}{Z} e^{-E(s)/kT} = \frac{1}{Z} \underbrace{e^{-\beta E(s)}}_{\text{Boltzmann factor}}$$

where β=1/kT and

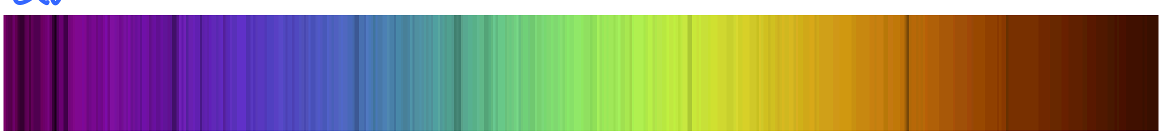
$$Z = \sum_s e^{-\beta E(s)}$$

partition function

Example of the Sun

- Recall the spectrum of the atmosphere of the Sun

uv



darkest lines are absorptions from H atom

→ starting in n=1

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-E_2/kT}}{e^{-E_1/kT}} = e^{-(E_2-E_1)/kT}$$

$$E_2 - E_1 = -3.4\,eV - (-13.6\,eV) = 10.2\,eV$$

Solar spectrum from BASS2000 archive; http://bass2000.obspm.fr/solar_spect.php

$$\frac{P(s_2)}{P(s_1)} = e^{-(10.2\text{eV})/(8.62\times10^{-5}\text{eV/K})(5800\text{K})}$$

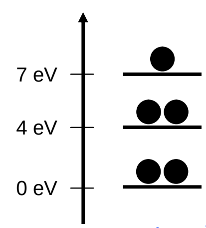
$$\approx e^{-20.4} \approx 1.4\times10^{-9}$$

need to include degeneracy

difference → ~5.6 atom in 1st excited state for every billion in ground state

Calculating Averages

- Using five atom "toy model"



$$\overline{E} = \frac{(0\text{eV})\cdot 2 + (4\text{eV})\cdot 2 + (7\text{eV})\cdot 1}{5} = 3\text{eV}$$

$$\overline{E} = (0\text{eV})\cdot\frac{2}{5} + (4\text{eV})\cdot\frac{2}{5} + (7\text{eV})\cdot\frac{1}{5} = 3\text{eV}$$

probabilities of finding atom in given state

- In general,

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

- For any quantity, X

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

Average Energy

- Average total energy is $U = N\bar{E}$

- A quick trick for calculating average energy

$$\frac{\partial Z}{\partial \beta} = \sum_s e^{-\beta E(s)} \cdot \left[-E(s)\right] = -\sum_s E(s) e^{-\beta E(s)} = -Z\bar{E}$$

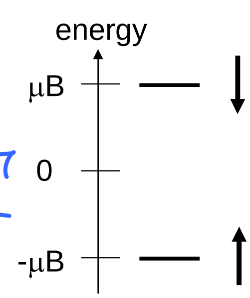
$$\bar{E} = \frac{1}{Z}\sum_s E(s) e^{-\beta E(s)}$$

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln Z$$

Two-state Paramagnet

- Energy levels of a single dipole

$\vec{B}\ \hat{z}$



- Partition function for this dipole:

$$\text{prob}(\downarrow) = \frac{e^{-\mu B/kT}}{Z} \qquad \text{prob}(\uparrow) = \frac{e^{+\mu B/kT}}{Z}$$

$$Z = e^{-\mu B/kT} + e^{+\mu B/kT} = 2\cosh\left(\frac{\mu B}{kT}\right)$$

- Average energy:

$$\bar{E} = \sum_s E(s)P(s) = \frac{1}{Z}\Big[\underbrace{\mu B e^{-\mu B/kT}}_{\text{spin down}} \underbrace{-\mu B e^{+\mu B/kT}}_{\text{spin up}}\Big]$$

$$= \frac{-\mu B}{Z} 2\sinh\left(\frac{\mu B}{kT}\right)$$

$$\bar{E} = -\mu B \tanh\left(\frac{\mu B}{kT}\right)$$

set of N dipoles

$$U = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$$

average magnetic moment along $\vec{B}$

$$\bar{\mu}_z = \sum_s \mu_z(s) P(s) = \mu \tanh\left(\frac{\mu B}{kT}\right)$$

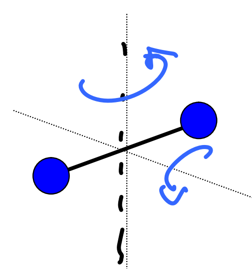
total average magnetization

$$M = N\bar{\mu}_z = N\mu \tanh\left(\frac{\mu B}{kT}\right)$$

Rotation of Diatomic Molecules

- From classical mechanics:
  - Rotational energy $\quad E = \dfrac{L^2}{2I}$
  - Need moment of inertia

$$I = \sum mr^2 \qquad L: \text{ angular momentum}$$



Rotation of Diatomic Molecules

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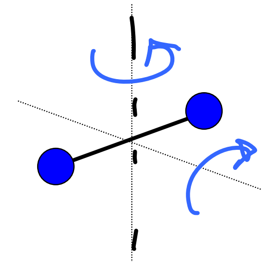
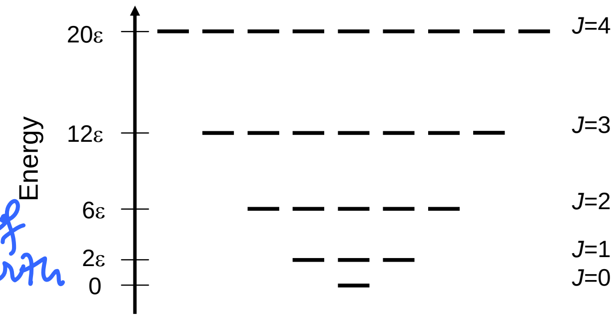


- In quantum mechanics:
  - Angular momentum $L^2 = \hbar^2 J(J+1)$ ← rotational quantum no.
  - Degeneracy: $2J+1$ → number of states with same energy

$$\varepsilon = \frac{\hbar^2}{2I}$$

$\hbar = \frac{h}{2\pi}$



Rotational Energies

- Consider partition function for rotational energy levels

$$Z_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1) e^{-E(J)/kT} = \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)\varepsilon/kT}$$

- For CO, take bond length of 1 Å and masses of 12 M_p and 16 M_p for atoms C and O, respectively

$$I = \sum mr^2 = \left[(12 M_p) \times (0.5 \times 10^{-10}\,m)^2 + (16 M_p) \times (0.5 \times 10^{-10}\,m)^2\right] \times 1.6 \times 10^{-27}\,kg$$

→ assume centre of mass in middle for simple calc.

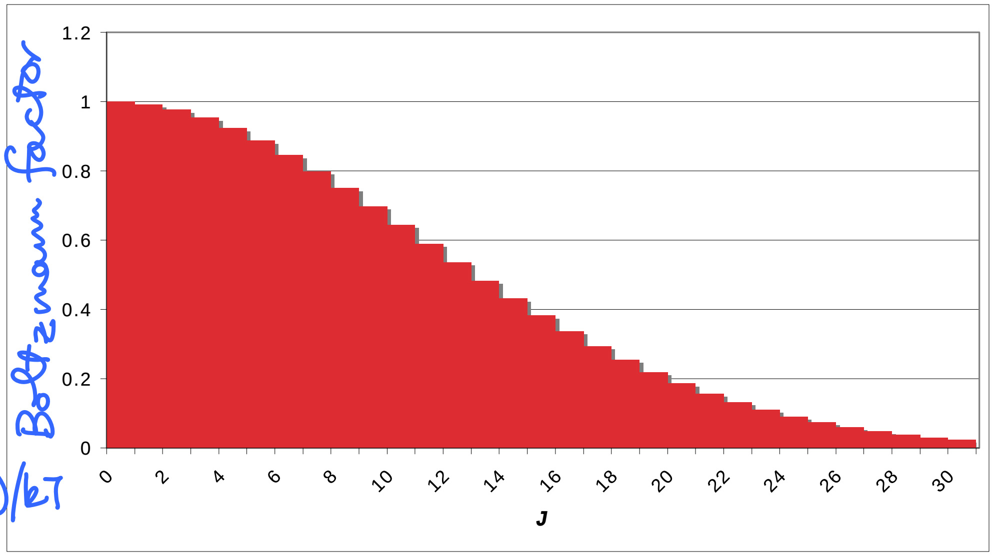
$$\varepsilon = \frac{(6.626 \times 10^{-34})^2}{(2\pi)^2} \times \frac{1}{2I}$$

$$\varepsilon = \frac{\hbar^2}{2I} \approx 2.5 \times 10^{-4}\,eV$$

at room T $kT \approx 250 \times 10^{-4}\,eV$

High Temperature Limit

- Boltzmann factors for room temperature ~ 300 K



Boltzmann factor

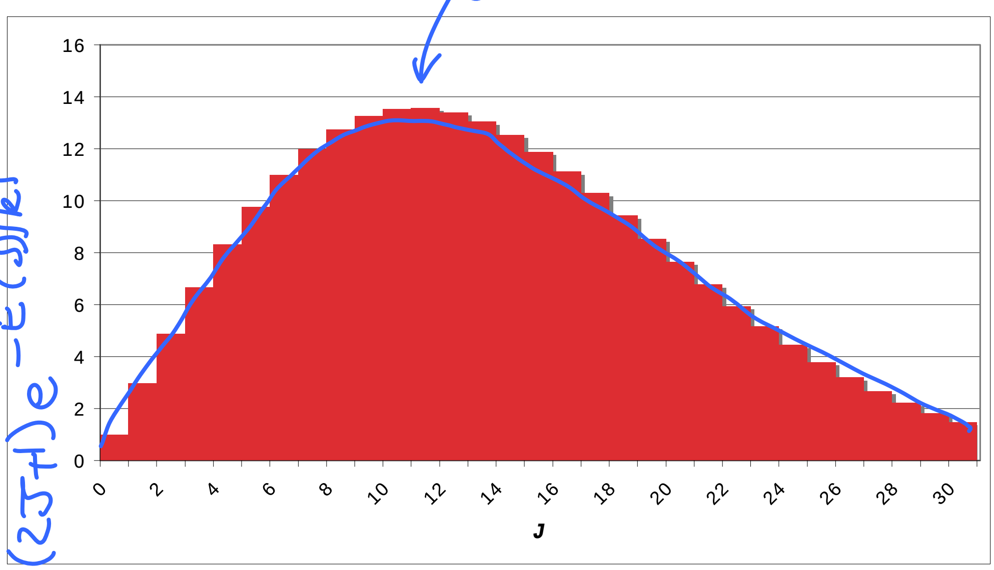
$e^{-E(J)/kT}$

$\frac{kT}{\varepsilon} \approx 250$

High Temperature Limit

- Number of terms contributing to Z at room temperature is quite large

J=11



$(2J+1)e^{-E(J)/kT}$

$$Z = \sum e^{-E(J)/kT}$$

$$\Rightarrow \sum_J (2J+1) e^{-J(J+1)\varepsilon/kT}$$

$$\simeq \int_0^\infty (2J+1) e^{-J(J+1)\varepsilon/kT} dJ$$

sub in $x \equiv J(J+1)\varepsilon/kT$

$$\frac{dx}{dJ} = (2J+1)\frac{\varepsilon}{kT}$$

sub $Z = \int_0^\infty e^{-x} \frac{kT}{\varepsilon} dx = \frac{kT}{\varepsilon}\left[-e^{-x}\right]_0^\infty = \frac{kT}{\varepsilon}$

high T limit
$kT \gg \varepsilon$

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high T approx. $\longrightarrow$ average energy per molecule

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\varepsilon\beta \cdot \frac{\partial}{\partial \beta}\left(\frac{1}{\varepsilon\beta}\right)$$

$$= -\beta \cdot -\left(\frac{1}{\beta}\right)^2$$

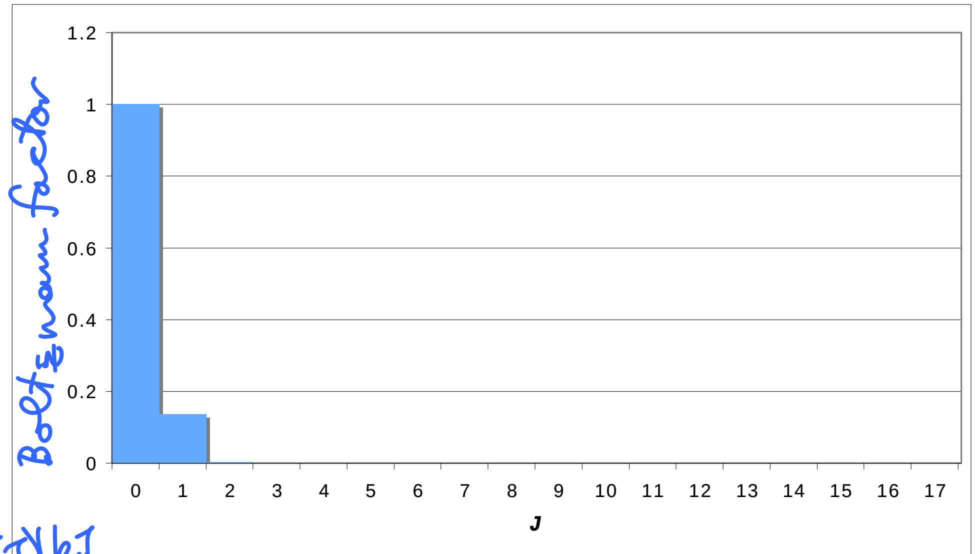
$$= \frac{1}{\beta} = kT$$

2 degrees of freedom in rot.
same answer as equipartition

$$\left(\frac{\partial \bar{E}}{\partial T}\right) = C = k$$

Low Temperature Limit

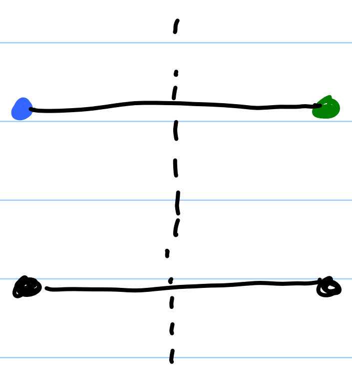
- Higher J values can be ignored since population is negligible



$e^{-E(J)/kT}$

indistinguishable atoms → O_2, N_2

distinguishable atoms → HCl, CO



180° rotation gives different spatial configuration

→ $\frac{1}{2}$ as many rotational states as distinguishable atom molecules

in high T limit

$$Z_{rot} \approx \frac{kT}{2\varepsilon} \quad kT \gg \varepsilon$$

midterm

→ covers up to today → lec 10

→ similar form as example
but not exactly the same

→ you will get same
equation sheet as given
for example midterm

→ ROOM EX200