

Lecture 16

05.11.2018

Fermi and Bose Distributions

Reminder:

- To derive the Boltzmann factor, we have considered a system which can exchange the energy with the reservoir, but not particles.
- With this assumption, we found the PROBABILITY of a system in any given microstate.
- We had:

Isolated system

$$P(s) = \frac{1}{\Omega(U)}$$

Ω counts number of equally-likely states

System in a thermal bath

$$P(s) = \frac{1}{Z(T)} e^{-\beta E_s}$$

$Z(T)$ counts microstates when they do not have the same probability at given T

Reminder: Atom in contact with reservoir...

- Temperature of reservoir is fixed.
- Any microstate possible, but some are more probable (energy is the key factor)
- Probability depends on how many possible microstates there are!
- We take two states: $E(s_1)$ and $E(s_2)$. Probabilities: $P(s_1)$ and $P(s_2)$.
- Recall: all accessible microstates in isolated system equally possible.
- But what about reservoir???
- Atom + reservoir = isolated system. Together they are in all microstates.

Reminder: Atom in contact with reservoir...

- $\Omega_R(s_1)$ – Multiplicity of reservoir when atom is in state s_1 .
- $\Omega_R(s_2)$ – Multiplicity of reservoir when atom is in state s_2 .
- They are different. If $E(s_1) < E(s_2)$, then more energy is left for R.
- But all microstates are equally probable.
- Probability of atom in a given state is proportional to number of microstates accessible to the reservoir.

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

Reminder: Atom in contact with reservoir...

- We remember that $S=k \ln\Omega$, then we can write:

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

- So we have probability related to change in the entropy of the reservoir. Change related to one atom – tiny...
- Thermodynamic identity gives:

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

- But we can forget about the two last terms: $dS_R = \frac{1}{T}dU_R$

Reminder: Atom in contact with reservoir...

- And we get:

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

- By putting it back to the equation for probability, we get:

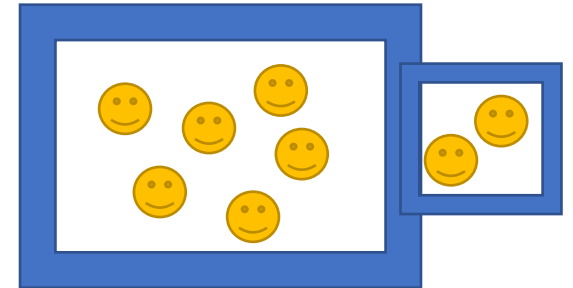
$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = e^{-[E(s_2) - E(s_1)]/kT} = \frac{e^{-E(s_2)/kT}}{e^{-E(s_1)/kT}}$$

- The ratio of probabilities is related to the ratio of exponential factors related to energy of a microstate and temperature of reservoir!
- The exponent is called Boltzmann factor

Let us now allow particles to be exchanged

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

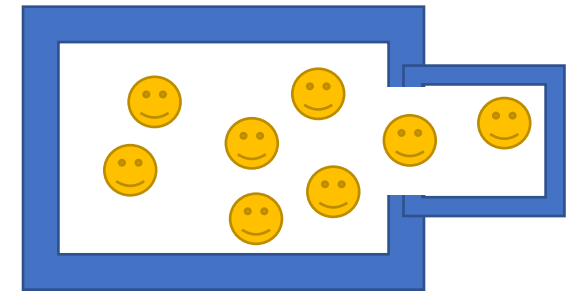
We still neglect PdV term, but need to keep the last term...



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Let us now allow particles to be exchanged

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



We still neglect PdV term, but need to keep the last term...

When considering a small system we will get minus sign :

$$S_R(s_2) - S_R(s_1) = -\frac{1}{T}[E(s_2) - E(s_1) - \mu N(s_2) + \mu N(s_1)]$$

And we end up with the ratio of probabilities:

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = \frac{e^{-[E(s_2) - \mu N(s_2)]/kT}}{e^{-[E(s_1) - \mu N(s_1)]/kT}}$$

GIBBS FACTOR

Z – the grand partition function (Gibbs sum)

- Again – if we want to have the absolute probability we need to find the proportionality constant Z.

$$P(s) = \frac{1}{Z} e^{-[E(s) - \mu N(s)]/kT}$$

- Sum of all probabilities equals 1, so we have:

$$Z = \sum_s e^{-[E(s) - \mu N(s)]/kT}$$

- If there are more types of particles in the system – we need to have a sum over species as well in the Gibbs factor:

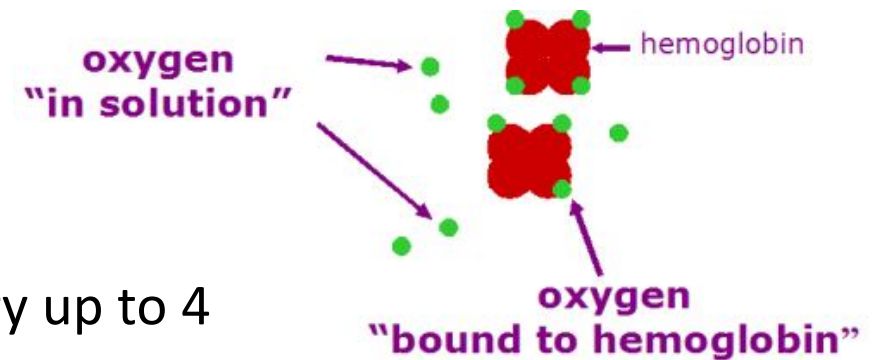
$$\text{Gibbs factor} = e^{-[E(s) - \mu_A N_A(s) - \mu_B N_B(s)]/kT}$$

Example: Oxygen in blood

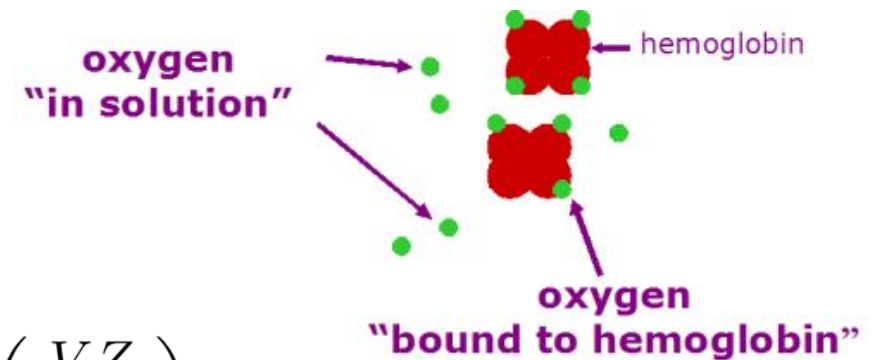
- Each red cell (hemoglobin molecule) can carry up to 4 oxygen atoms – 4 adsorption sites with Fe^{2+} .
- Let us consider 1 site only, for simplicity.
- If there is only O^2 that can take the site, we have two states: unoccupied (energy 0) and occupied ($\epsilon = -0.7 \text{ eV}$).

- Grand partition function: $Z = 1 + e^{-[\epsilon - \mu]/kT}$

- What is the chemical potential for the lungs?



Example: Oxygen in blood



- Recall from last week that:

$$\mu(T, V) = \left(\frac{\partial F}{\partial N} \right)_{T, V} = -kT \ln \left(\frac{VZ}{Nv_Q} \right)$$

- So we have:

$$\mu \approx -0.6\text{eV}$$

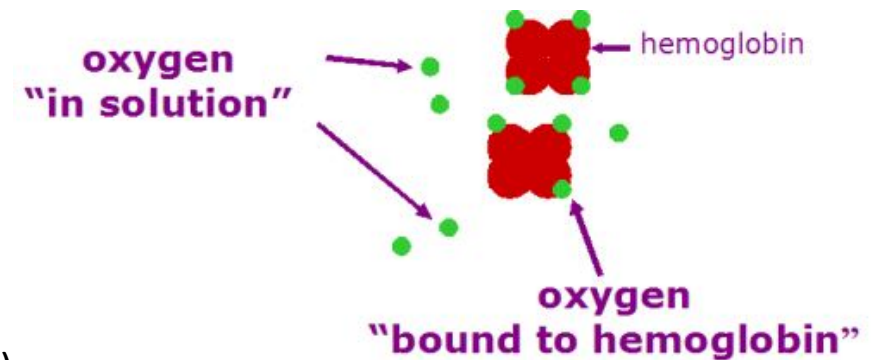
- For the body temperature 310 K we get the value of gibbs factor:

$$e^{-[\epsilon - \mu]/kT} = 40$$

- Finally we get the probability of the site being occupied by oxygen:

$$\mathcal{P} = \frac{40}{40 + 1} = 98\%$$

Example: Oxygen in blood



- But what if we have a CO – carbon monoxide present?
- The grand partition function is then (ϵ' corresponds to CO):

$$Z = 1 + e^{-[\epsilon - \mu]/kT} + e^{-[\epsilon' - \mu']/kT}$$

- CO is less abundant. If it is less by a factor of 100. Then we have: $\mu' \approx -0.72\text{eV}$
- But it more tightly bound than oxygen: $\epsilon' \approx -0.85\text{eV}$
- For the body temperature 310 K we gett the value of gibbs factor: $e^{-[\epsilon' - \mu']/kT} = 120$
- Probability of the site being occupied by oxygen is much lower: $\mathcal{P} = \frac{40}{40 + 1 + 120} = 25\%$

Example: Saha equation

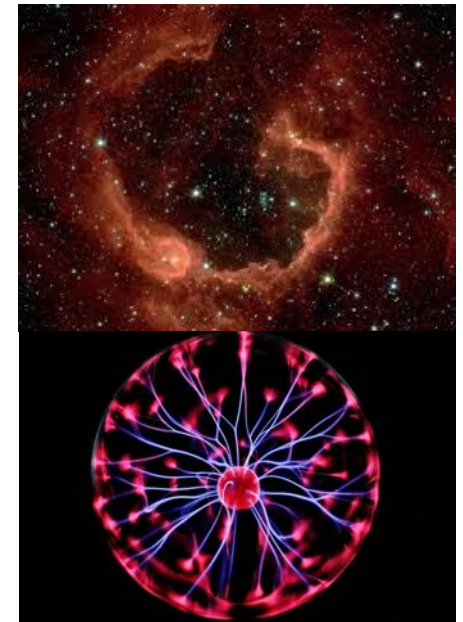
- How much can a gas be ionised if it is in thermal equilibrium?
- Neglect spin and excited states. Consider a system with single hydrogen atom/ion, which has two possible states:

Unoccupied (no electron present – ionised):

$E=0$, $N=0$, Gibbs factor: $e^0 = 1$

Occupied (electron present – neutral atom):

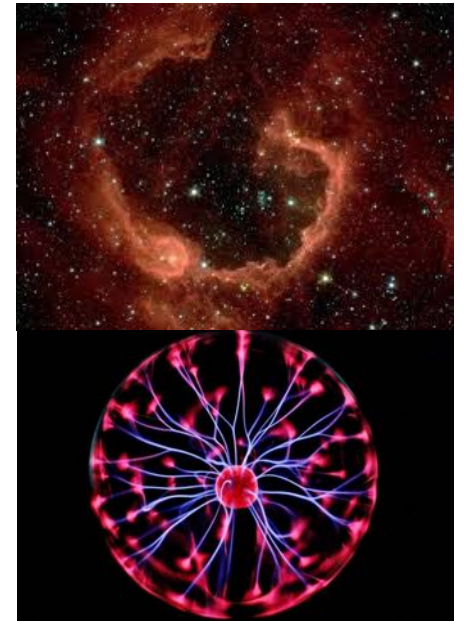
$E=-I$, $N=1$, Gibbs factor: $e^{-(-I-\mu)/kT}$



Example: Saha equation

- Ratio of probabilities equals the ratio of pressures of ionised and neutral states.

$$\frac{P_i}{P_n} = \frac{\mathcal{P}_i}{\mathcal{P}_n} = \frac{1}{e^{-(-I-\mu)/kT}} = \frac{e^{-I/kT}}{e^{\mu/kT}}$$



Example: Saha equation

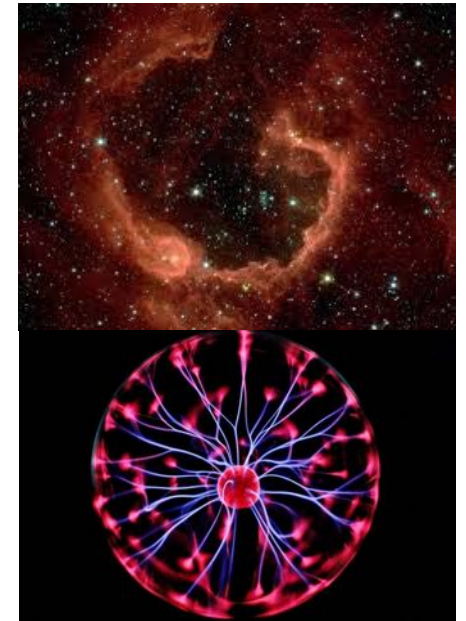
- Chemical potential for electrons (treated as ideal gas):

$$\mu = -kT \ln \left(\frac{VZ}{Nv_Q} \right) = -kT \ln \left(\frac{kT}{P_e v_Q} \right)$$

- This gives us Saha equation, where I is the ionisation potential:

$$\frac{P_i}{P_n} = \frac{kT}{P_e v_Q} e^{-I/kT} = \frac{1}{n_e} \left(\frac{2\pi kTm}{h^3} \right)^{3/2} e^{-I/kT}$$

- Surface of the Sun – less than 1 in 10000 atoms are ionised...

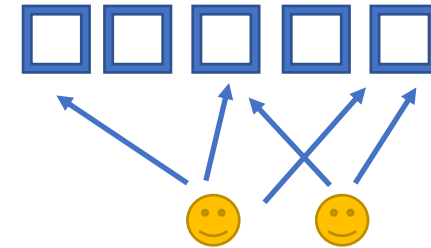


Bosons vs. Fermions

- Gibbs factor applicable to quantum statistics...
- Many identical particles want to occupy single particle state.

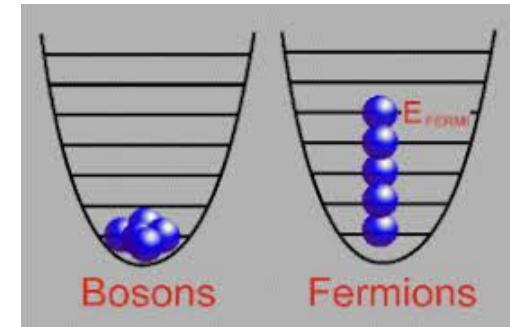
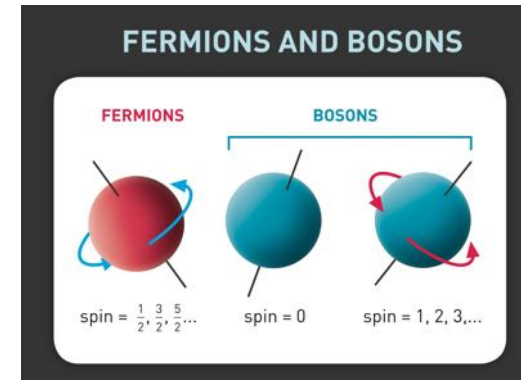
- We had for indistinguishable, noninteracting particles: $Z = \frac{1}{N!} Z_1^N$
- But this breaks down – particles can have the same states...

- Particles distinguishable: 25 states
- Particles indistinguishable: 25/2 states ? But Z must be integer.
- In fact we have 15 states: 10 where particles are in different states (20 if particles are distinguishable), and 5 when they occupy the same state.



Bosons vs. Fermions

- Bosons: particles can occupy the same state (can share the state).
 - Photons, pions, helium-4 atoms etc.
- Fermions: particles can NOT share a state with another particle of the same type.
 - Electrons, protons, neutrons, neutrinos, helium-3 atoms etc.
- **Bosons are social**
- **Fermions are antisocial**
- Bosons -> integer spin
- Fermions -> half-integer spin



Bosons vs. Fermions

- If $Z_1 \gg N$; the number of available single particle states is much greater than the number of particles, boson-fermion differences are not crucial

- Ideal gas: single particle partition function is:

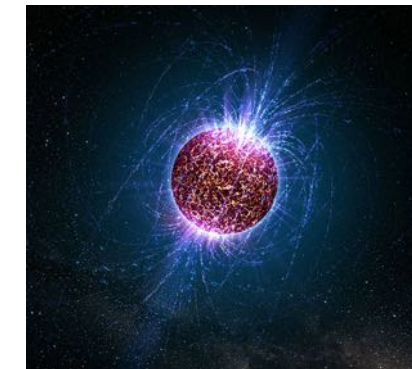
$$Z_1 = \frac{V Z_{int}}{v_Q}$$

- Where the quantum volume is ca. the cube of de Broglie wavelength.

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

- Then the condition $Z_1 \gg N$ for many particles $Z = Z_1^N / N!$ is $V/N \gg v_Q$. So the average distance must be greater than de Broglie length.

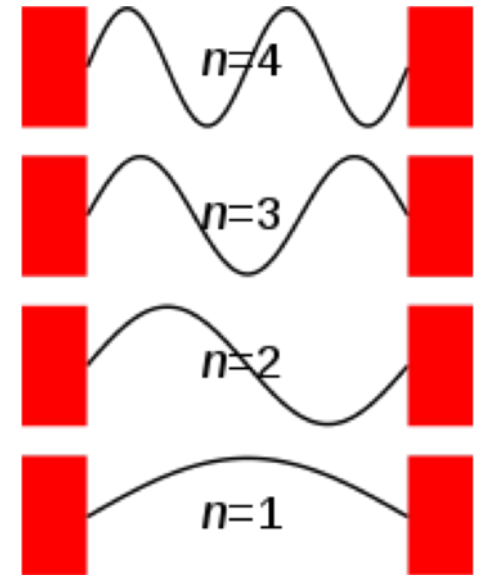
- But the condition broken in very dense or very cold environments (e.g., neutron star, liquid helium)



Distribution function

- Let us now take a system where $Z_1 \gg N$ is not fulfilled - we need to use Gibbs factors instead of the Boltzmann factor.
- Consider a system of 1 single-particle state. System consists of a spatial wavefunction.
- Particle in a box: system and reservoir have the same physical space. Only one wavefunction is the system (particle).
- Probability of a state being occupied by n particles is:

$$\mathcal{P}(n) = \frac{1}{Z} e^{-(n\epsilon - \mu n)/kT} = \frac{1}{Z} e^{-n(\epsilon - \mu)/kT}$$



Particle in a box

Distribution function - Fermions

- For fermions: $n=0$ or $n=1$.
- The grand partition function:

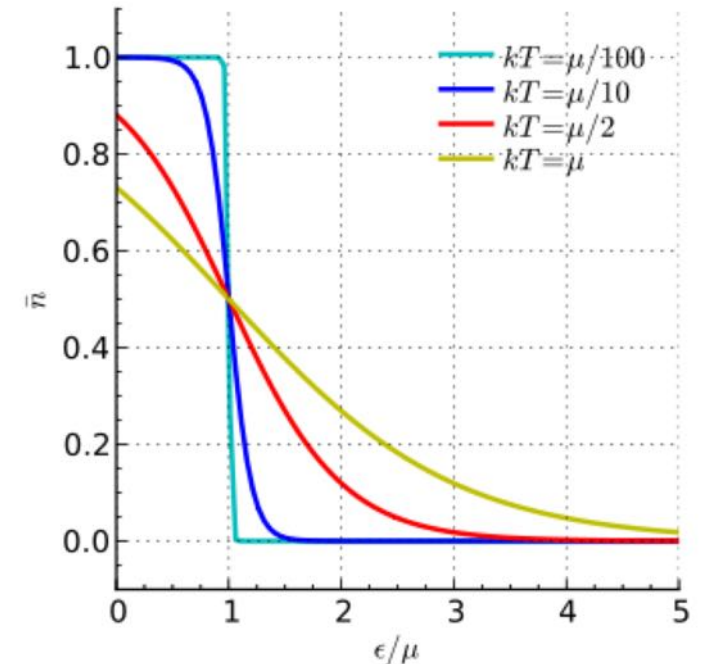
$$Z = 1 + e^{-(\epsilon - \mu)/kT}$$

- Occupancy – probability:

$$\bar{n} = \sum_n n \mathcal{P}(n) = 0 \cdot \mathcal{P}(0) + 1 \cdot \mathcal{P}(1) = \frac{e^{-(\epsilon - \mu)/kT}}{1 + e^{-(\epsilon - \mu)/kT}}$$

- **Fermi-Dirac distribution:**

$$\bar{n}_{FD} = \frac{1}{e^{(\epsilon - \mu)/kT} + 1}$$



Distribution function - Bosons

- For bosons: $n=0,1,2 \dots$
- The grand partition function ($\mu < \epsilon$):

$$Z = 1 + e^{-(\epsilon-\mu)/kT} + e^{-2(\epsilon-\mu)/kT} + e^{-3(\epsilon-\mu)/kT} + \dots$$

$$= \frac{1}{1 - e^{-(\epsilon-\mu)/kT}}$$

- Occupancy – probability:

$$\bar{n} = \sum_n n \mathcal{P}(n) = 0 \cdot \mathcal{P}(0) + 1 \cdot \mathcal{P}(1) + 2 \cdot \mathcal{P}(2) \dots$$

$$= \sum_n \frac{n}{Z} e^{-n(\epsilon-\mu)/kT} = -\frac{1}{Z} \sum_s \frac{\partial}{\partial x} e^{-nx}$$

where we used:

$$x = (\epsilon - \mu)/kT$$

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$$= -\frac{1}{Z} \frac{\partial Z}{\partial x}$$

Bose-Einstein distribution

$$\bar{n}_{BE} = \frac{1}{e^{(\epsilon-\mu)/kT} - 1}$$

Distribution functions - comparison

- For Boltzmann distribution

$$\bar{n}_{Bol} = e^{(\epsilon - \mu)/kT}$$

- Fermi-Dirac distribution

$$\bar{n}_{FD} = \frac{1}{e^{(\epsilon - \mu)/kT} + 1}$$

- **Bose-Einstein distribution**

$$\bar{n}_{BE} = \frac{1}{e^{(\epsilon - \mu)/kT} - 1}$$

