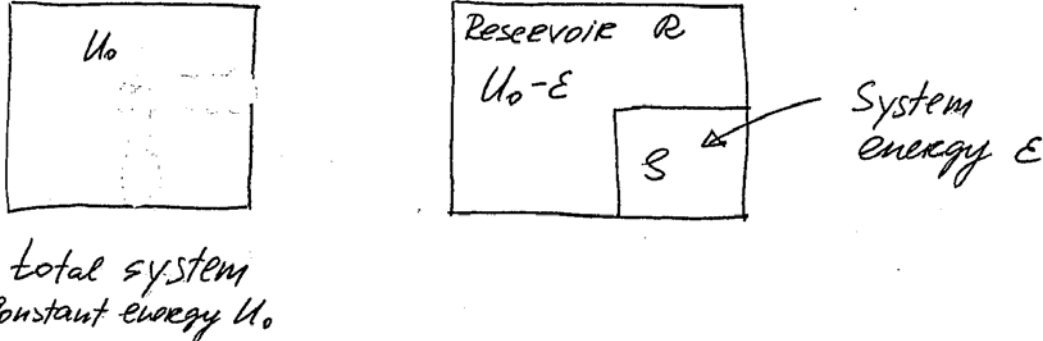


Lecture 13

Quantum Statistics

Reminder: How we got Boltzman distribution from general principles.



1) System is specified to be in some state S with energy E_s . If we the state S the number of accessible state for the total system is the number of accessible state of reservoir at energy $U_0 - E_s$ $g_R \times 1 = g_R$

2) Fundamental assumption: All accessible quantum states are equally probable. (Here accessibility of quantum state is determined by the condition on energy. The energy of the reservoir is fixed)

3) From (2) and (1) we have

$$(3) \frac{P(E_1)}{P(E_2)} = \frac{\text{multiplicity of R at } U_0 - E_1}{\text{multiplicity of R at } U_0 - E_2} = \frac{g_R(U_0 - E_1)}{g_R(U_0 - E_2)}$$

$P(E_1)$ - Probability to find system in quantum state with energy E_1

$S_R = k_B \ln g_R$ - definition of entropy

$$(4) \frac{P(E_1)}{P(E_2)} = \frac{\exp\left(\frac{1}{k} S_R(U_0 - E_1)\right)}{\exp\left(\frac{1}{k} S_R(U_0 - E_2)\right)} = \exp\left[\frac{1}{k} [S(U_0 - E_1) - S(U_0 - E_2)]\right] =$$

$$= S_R(U_0 - E) = S_R(U_0) - \left(\frac{\partial S_R}{\partial U}\right)_{V,N} \cdot E$$

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \text{ definition of temperature in statistical mechanics}$$

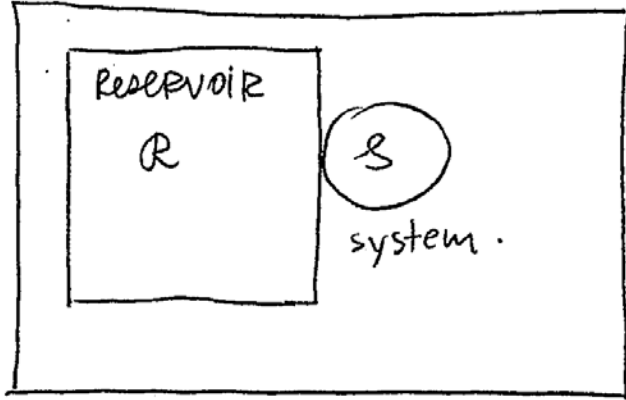
From (4) we thus have

$$\frac{P(E_1)}{P(E_2)} = \frac{\exp\left(-\frac{E_1}{kT}\right)}{\exp\left(-\frac{E_2}{kT}\right)} \quad \text{and} \quad P(E_s) = \frac{\exp\left(-\frac{E_s}{kT}\right)}{Z}, \text{ where}$$

$\exp\left(-\frac{E_s}{kT}\right)$ is the Boltzmann factor

$Z(T) = \sum_s \exp\left(-\frac{E_s}{kT}\right)$ is the partition function

Let's consider now a system in thermal and diffusive contact with large reservoir.



$$T_R = T_S, \quad \mu_R = \mu_S$$

U_0 - total energy, N_0 - total number of particles

$P(N, E_S)$ - Probability that the system has N particles and is in a particles state S .

$P(N, E_S) \propto$ Number of accessible state for the reservoir

$g(R+S) = g(R) \times 1 \leftarrow$ Multiplicity of quantum state of the system

Then,

$$\frac{P(N_1, E_1)}{P(N_2, E_2)} = \frac{g(N_0 - N_1, U_0 - E_1)}{g(N_0 - N_2, U_0 - E_2)}$$

Using definition of entropy we have,

$$\frac{P(N_1, E_1)}{P(N_2, E_2)} = \exp\left[\frac{1}{k} \left(S(N_0 - N_1, U_0 - E_1) - S(N_0 - N_2, U_0 - E_2) \right)\right]$$

Entropy expression

$$S(N_0 - N, U_0 - E) = S(N_0, U_0) - N \left(\frac{\partial S}{\partial N} \right)_{U,V} - E \left(\frac{\partial S}{\partial U} \right)_{N,V}$$

Using the definition of the chemical potential and temperature

$$\left(\frac{\partial S}{\partial N} \right)_{U,V} \equiv -\frac{\mu}{T} \quad \text{and} \quad \frac{1}{T} \equiv \left(\frac{\partial S}{\partial U} \right)_{N,V} \quad \text{we have}$$

$$\frac{P(N_1, E_1)}{P(N_2, E_2)} = \frac{\exp\left[\frac{(N_1 \mu - E_1)}{kT}\right]}{\exp\left[\frac{(N_2 \mu - E_2)}{kT}\right]}$$

The factor $\exp\left[\frac{N\mu - E}{kT}\right]$ is called the Gibbs factor.

The sum of Gibbs factors over all states of the system for all number of particles is the normalizing factor that convert relative probabilities to absolute probabilities:

$$Z(\mu, T) = \sum_{N=0}^{\infty} \sum_{s(N)} \exp \left[\frac{(N\mu - E_{s(N)})}{kT} \right] = \sum_{ASN} \exp \left[\frac{(N\mu - E_{s(N)})}{kT} \right]$$

ASN – all states of the system over all number of particles.

$Z(\mu, T)$ is called the Grand partition function or the Gibbs sum. (I use the same letter Z for the grand partition function and the partition function $Z(T)$ because of the limited typesetting. They are different quantities)

$$P(N_1, E_1) = \frac{\exp \left[\frac{(N_1\mu - E_1)}{kT} \right]}{Z}$$

$$\langle X \rangle = \sum_{ASN} X(N, S) P(N_1 E_s) - \text{average value}$$

Now number of particles in the system is not fixed we can always get some from reservoir.

The average of N

$$\langle N \rangle = \frac{1}{Z} \sum_{ASN} N \exp \left[\frac{(N\mu - E)}{kT} \right]$$

$$\frac{\partial Z}{\partial \mu} = \frac{1}{kT} \sum_{ASN} N \exp \left[\frac{(N\mu - E)}{kT} \right] = \frac{1}{kT} Z \langle N \rangle$$

$$\langle N \rangle = \frac{kT}{z} \frac{\partial Z}{\partial \mu} = kT \frac{\partial \ln Z}{\partial \mu}$$

Bosons and Fermions

The most important application of Gibbs factor is in quantum statistics that consider dense system with small interparticle separation. The peculiar properties of such systems come (among the other stuff) from the fact that we should take into account indistinguishability of particles. (One electron cannot be distinguished from the other)

Entropy of the system depends on multiplicity – number of possible different arrangements of the particles corresponding to given energy.

Say we have 5 boxes and 2 balls

If balls are different then we have 25 possible arrangements

If balls are the same we have 15 possible arrangements

11000	01010	20000
10100	01001	02000
10010	00110	00200
10001	00101	00020
01100	00011	00002

Notice that total number of combinations is different from binomial $\frac{5!}{2!3!}=10$ - that counts states only in first two columns (because we have 0 and 1 two options). Third columns - two balls in the same basket.

Bosons - Particles that can share a state with another of the same species. (Photons, pion, He-4 atoms) (Spin in integer 0,1,2...)

Fermions - Particles that cannot share the same quantum state with each other.

Examples - electron, protons, neutrons....

(Spin is half-integer (1/2, 3/2...))

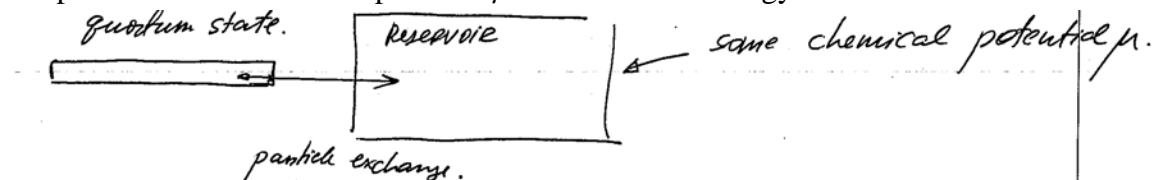
Example, any atom

F $1s^2 2s^2 2p^5$ each quantum is filled with one electron due to Pauli exclusive principle.

When number of available single-particles state is much large than the number of particles - we have dilute gas - classical statistics.

Occupation numbers for fermions and bosons

Let us consider a quantum State that is in equilibrium with large particle reservoir with temperature T and chemical potential μ . Let E be the energy of the state.



If the state is unoccupied, its energy $E_s = 0$

If the state is occupied by n particles its energy is $E_s = nE$

Probability of the state to be occupied by n particle is

$$P(n) = \frac{1}{Z} \exp\left(-\frac{1}{kT}(nE - \mu n)\right)$$

Fermi-Dirac distribution

For fermions

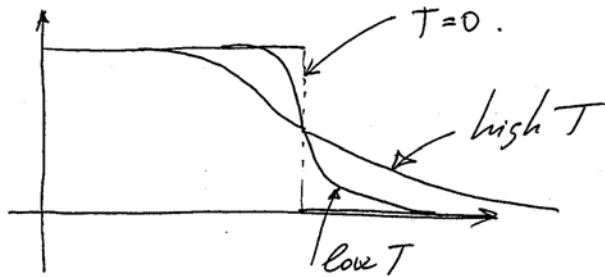
$$Z = 1 + \exp\left[-\frac{1}{kT}(E - \mu)\right]$$

Average number of particles in the state occupancy

$$\langle \bar{n} \rangle = \sum n P(n) = 0 \times P(0) + 1 \times P(1) = \frac{\exp\left[-\frac{1}{kT}(E - \mu)\right]}{1 + \exp\left[-\frac{1}{kT}(E - \mu)\right]} = \frac{1}{\exp\left(\frac{(E - \mu)}{kT}\right) + 1}$$

Figure

If particles are bosons, then n can be any non-negative integer $\left(\frac{1}{kT} - \beta\right)$



Bose-Einstein distribution

For bosons

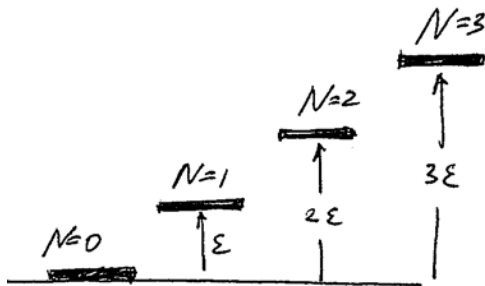
$$Z = 1 + \exp(-\beta(E - \mu)) + \exp(-2\beta(E - \mu)) + \dots = \frac{1}{1 - \exp(-\beta(E - \mu))}, \text{ where}$$

$$\beta = 1/kT.$$

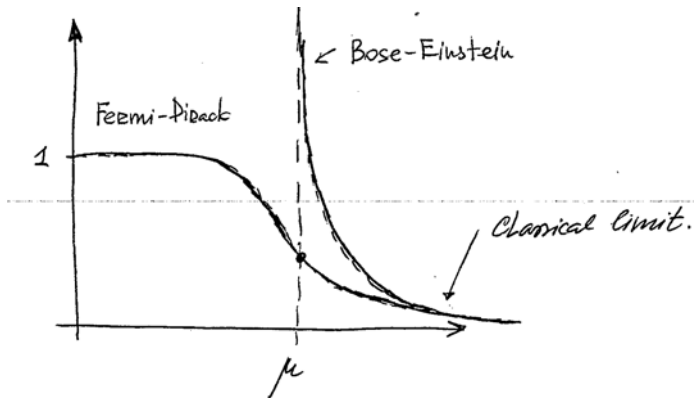
$$\langle \bar{n} \rangle = \sum_n n P(n) = \sum_n n \frac{e^{-nx}}{Z}, \text{ where } x = (-\beta(E - \mu))$$

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

Example of entropy levels of non-interacting bosons. Here E is energy of an orbital when it is energy of the same orbital when it is occupied by 1 particle. N_E is the energy of the same orbital when occupied by N particle. Any number of bosons can occupy the same orbit.



A gas is classical when the average number of atoms in each orbital is much less than one. The average orbital occupancy for a gas at room temperature and atmospheric pressure is only 10^{-6} . (We will define in following lecture what are the orbital of a gas). The differences between BE and FD distributions arises only when occupancy is close to 1.



$$n(E) = \frac{1}{\exp[\beta(E - \mu)] \pm 1} \quad +1 \text{ FD, } - \text{BE}$$

In order for $n(E)$ to be small $\exp[\beta(E - \mu)] \gg 1$ for all E . When this identity is satisfied we may neglect the term ± 1 in the denominator of $n(E)$. Then for either fermions or bosons we have.

$$n(E) = \exp\left(\frac{\mu}{kT}\right) \times \exp\left(-\frac{E}{kT}\right). \text{ We see that this equation contains the Boltzmann factor.}$$

Even though the above equation describes classical statistical distribution, it still comes from quantum mechanics: expression for μ involves the Planck constant \hbar .