1 Quantum Statistics

1.1 Identical particles and symmetry

From Gibbs' paradox

$$Z == \frac{Z_1^N}{N!}$$

where we have indistinguishable particles.

- Classical particles: $A, B, C, \dots$ where we have distinguishable particles
- Quantum particles: $A, A, A, \dots$ which are indistinguishable...but we also have two types of quantum particles
  - Bosons: Integer spin, symmetric total wave function Ψ e.g. photons, gamma rays
  - Fermions: Half-integer spin, antisymmetric total wave function $\Psi \to$ pauli exclusion principle, e.g. electrons

Worksheet

1. Assume 2 partilces and each particle can be in one of three possible staes,

$$r = 1, 2, 3$$

(1) Maxwell-Boltzmann statistics (classical particle) total number of available states

$$\Omega = 3^2 = 9$$

(2) Bose-Einstein statistics (bosons) total number of available states

$$\Omega = 3 + 3 = 6$$

(3) Fermi-Dirac statistics (fermions) we take away the same states occupations

$$\Omega = 6 - 3 = 3$$

1.2 Formulation of quantum statistical problem

Consider a gas of particles in volume V at temperature T.

- ϵ_r: is the energy of a particle in state r
- n_r: # of particles in state r
- R: specify all possible states of the whole system

So the total energy of the system is

$$E_R = n_1\epsilon_1 + n_2\epsilon_2 + \cdots = \sum_r n_r\epsilon_r$$

where $\sum_r n_r = N$. The partition function is

$$Z = \sum_R e^{-\beta E_R} = \sum_R e^{-\beta \sum_r n_r \epsilon_r}$$

Since the probability of having $\{n_1, n_2, \dots, n_r, \dots\}$ state is

$$\frac{e^{-\beta E_R}}{Z}$$

for a state R, the mean number of particles in states S is

$$\bar{n}_S = \frac{\sum_R n_S e^{-\beta E_R}}{Z}$$

or

$$= \frac{1}{Z}\sum_R \left(-\frac{1}{\beta}\frac{\partial Z}{\partial \epsilon_S}\right)$$

- Bose-Einstein Statistics (BE)

$$\sum n_R = N$$

- Photon statistics: no restriction of particle number
- Fermi-Dirac Statistics (FD): for $n_r = 0, 1$

Using the mulitplication math thing

$$e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+\dots)} = e^{-\beta n_s \epsilon_s} e^{-\beta n_1 \epsilon_1 + \dots}$$

where the second term doesn't have a n_s term. So the mean number of particles in state S is

$$\begin{aligned}
\bar{n}_S &= \frac{1}{Z}\sum_R n_S e^{-\beta E_R} \\
&= \frac{1}{Z}\sum_R n_S e^{-\beta n_s \epsilon_s} e^{-\beta n_1 \epsilon_1 + \dots} \\
&= \frac{\sum_R \left(n_s e^{-\beta n_s \epsilon_s} e^{-\beta n_1 \epsilon_1 + \dots}\right)}{\sum_R \left(e^{-\beta n_s \epsilon_s} e^{-\beta n_1 \epsilon_1 + \dots}\right)} \\
&= \frac{\sum_{n_s}\left(n_s e^{-\beta n_s \epsilon_s} \sum_{n_1,n_2,\dots}^{(S)} e^{-\beta n_1 \epsilon_1 + \dots}\right)}{\sum_{n_s}\left(e^{-\beta n_s \epsilon_s} \sum_{n_1,n_2,\dots}^{(S)} e^{-\beta n_1 \epsilon_1 + \dots}\right)}
\end{aligned}$$

Photon statistics No restriction on # of particles $\implies$ the sum $\sum_{n_1,n_2,\dots}$ is always infinite, so the second term cancels out

$$\bar{n}_S = \frac{\sum_{n_s} n_s e^{-\beta n_s \epsilon_s}}{\sum_{n_s} e^{-\beta n_s \epsilon_s}} - \frac{1}{\beta}\frac{\partial}{\partial \epsilon_s}\ln\left(\sum_{n_s=0}^{\infty} e^{-\beta n_s \epsilon_s}\right)$$

and using the geometric series

$$\begin{aligned}
&= -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_s}\ln\frac{1}{1-e^{-\beta\epsilon_s}} \\
&= \frac{1}{\beta}\frac{\partial}{\partial \epsilon_s}\ln\left(1-e^{-\beta\epsilon_s}\right) \\
&= \frac{1}{\beta}\frac{\beta e^{-\beta\epsilon_s}}{1-e^{-\beta\epsilon_s}} \\
&= \frac{1}{e^{\beta\epsilon_s}-1}
\end{aligned}$$

Fermi-Dirac statistics For $n_r = 0, 1$ (the easier one)

$$\begin{aligned}
\bar{n}_S &= \frac{0 + e^{-\beta\epsilon_s} Z_S(N-1)}{Z_S(N) + e^{-\beta\epsilon_S} Z_S(N-1)} \\
&= \frac{1}{\left(\frac{Z_S(N)}{Z_S(N-1)} e^{-\beta\epsilon_s} + 1\right)}
\end{aligned}$$

where the Z_S ommits the n_s term

$$Z_S(N) \equiv \sum_{n_1,n_2,\dots}^{(S)} e^{-\beta n_1 \epsilon_1 + \dots}$$

To relate $Z_S(N)$ and $Z_S(N-1)$ for large N:

$$\ln Z_S(N-1) = \ln Z_S(N) - \frac{\partial \ln Z_S(N)}{\partial N} \cdot 1$$

where the $\frac{\partial \ln Z_S(N)}{\partial N} = \alpha_S$ so

$$Z_S(N-1) = Z_S(N) e^{-\alpha_S}$$
$$\implies \frac{Z_S(N)}{Z_S(N-1)} = e^{\alpha_S}$$

ASSUMPTION: Since the sum of Z_S includes *many* states, α_S cannot does not depend too much on S, so we assume a constant

$$\alpha_S = \alpha = \frac{\partial \ln Z}{\partial N}$$

So the mean number of particles in state S is

$$\bar{n}_S = \frac{1}{e^{\alpha + \beta\epsilon_s} + 1}$$

Since we know the relation

$$F = -kT \ln Z \implies \frac{\partial F}{\partial N} = -kT \frac{\partial \ln Z}{\partial N} = \mu \implies \alpha = -\beta\mu$$

So we get the Fermi-Dirac distribution

$$\bar{n}_S = \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1}$$

Worksheet Bose-Einstein stats using

$$\frac{Z_S(N)}{Z_S(N-1)} = e^{\alpha}$$

The average number of particles in state S is

$$\bar{n}_S = \frac{0 + e^{-\beta\epsilon_s} Z_S(N-1) + 2e^{-\beta\epsilon_s} Z_S(N-2) + \dots}{Z_S(N) + e^{-\beta\epsilon_s} Z_S(N-1) + e^{-2\beta\epsilon_s} Z_S(N-2) + \dots}$$

taking out a $Z_S(N)$ term for each e.g.

$$e^{-\beta\epsilon_s} Z_S(N-1) = Z_S(N) \left(e^{-\beta\epsilon_s} \frac{Z_S(N-1)}{Z_S(N)} \right) = Z_S(N) e^{-\beta\epsilon_s} e^{-\alpha}$$

and for the next term

$$\begin{aligned} e^{-2\beta\epsilon_s} Z_S(N-2) &= Z_S(N) e^{-2\beta\epsilon_s} \frac{Z_S(N-2)}{Z_S(N)} \\ &= Z_S(N) e^{-2\beta\epsilon_s} \frac{Z(N-2)}{Z(N-1)} e^{-\alpha} \\ &= Z_S(N) e^{-2\beta\epsilon_s} e^{-2\alpha} \end{aligned}$$

So

$$\bar{n}_S = \frac{Z_S(N)\big(0 + e^{-\beta\epsilon_s} e^{-\alpha} + e^{-2\beta\epsilon_s} e^{-2\alpha} + \dots\big)}{Z_S(N)(1 + e^{-\beta\epsilon_s} e^{-\alpha} + e^{-2\beta\epsilon_s} e^{-2\alpha} + \dots)}$$

From last time

- Photon Statistics (Boson):

$$\bar{n}_s = \frac{1}{e^{\beta\epsilon_s} - 1}$$

- Bose-Einstein Statistics:

$$\bar{n}_s = \frac{1}{e^{\beta(\epsilon_s - \mu)} - 1}$$

- Fermi-Dirac Statistics:

$$\bar{n}_s = \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1}$$

Today: Partition function for quantum statistics...

$$Z = \sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}$$

where for BE and FD, $\sum n_r = N$

1.3 Photon statistics

$$\begin{aligned}
Z &= \sum_{n_1, n_2, \dots} e^{-\beta n_1 \epsilon_1 + \dots} \\
&= \underbrace{\sum_{n_1=0}^{\infty} e^{-\beta n_1 \epsilon_1}}_{1 + e^{-\beta\epsilon_1} + e^{-2\beta\epsilon_1} + \dots} \sum_{n_2=0}^{\infty} e^{-\beta n_2 \epsilon_2} \dots \\
&= \frac{1}{1 - e^{-\beta\epsilon_1}} \frac{1}{1 - e^{-\beta\epsilon_2}} \dots
\end{aligned}$$

So the log of the partition function is

$$\begin{aligned}
\ln Z &= \sum_r \ln \frac{1}{1 - e^{-\beta\epsilon_r}} \\
&= -\sum_r \ln\left(1 - e^{-\beta\epsilon_r}\right)
\end{aligned}$$

The mean number of particles in one state ϵ_S is

$$\begin{aligned}
\bar{n}_S &= -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_S} \\
&= \frac{1}{\beta} \frac{-(-\beta) e^{-\beta\epsilon_S}}{1 - e^{-\beta\epsilon_S}} \\
&= \frac{e^{-\beta\epsilon_S}}{1 - e^{-\beta\epsilon_S}} \\
&= \frac{1}{e^{\beta\epsilon_S} - 1}
\end{aligned}$$

1.4 Bose-Einstein statistics

The partition function for BE:

$$Z = \sum_R = e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}$$

where $\sum_r n_r = N$ so $Z(N')$ has a rapidly increasing with N' which is a variable.

$Z(N')e^{-\alpha N'}$ has a sharp maximum, so if we choose α, this maximum happens at $N = N'$. First we define a Grand Partition function

$$\mathcal{Z} \equiv \sum_{N'} Z(N')e^{-\alpha N'}$$

so

$$\begin{aligned}
\mathcal{Z} &= \sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)} e^{-\alpha(n_1 + n_2 + \dots)} \\
&= \sum_{n_1=0}^{\infty} e^{-\beta(n_1\epsilon_1) - \alpha n_1} \sum_{n_2=0}^{\infty} e^{-\beta(n_2\epsilon_2) - \alpha n_2} \dots \\
&= \frac{1}{1 - e^{-\beta\epsilon_1}e^{-\alpha}} \frac{1}{1 - e^{-\beta\epsilon_2}e^{-\alpha}} \dots
\end{aligned}$$

where

$$\ln \mathcal{Z} = -\sum_r \ln\left(1 - e^{-(\alpha + \beta e_r)}\right)$$

And using the taylor series approximation $\ln Z = \alpha N + \ln \mathcal{Z}$, and the maximum condition

$$\left.\frac{\partial \ln\left(Z(N')e^{-\alpha N'}\right)}{\partial N'}\right|_{N'=N} = 0$$

and

$$\frac{\partial}{\partial N} \ln Z - \alpha = 0 \implies \alpha = \alpha(N)$$

So we get

$$N + \frac{\partial \ln \mathcal{Z}}{\partial \alpha} = 0 \implies \frac{\partial \ln Z(N)}{\partial \alpha} = 0$$

Worksheet From BE

$$\ln(Z) = -\beta\mu N - \sum_R \ln\left(1 - e^{-\beta(\epsilon_r - \mu)}\right)$$

1. Determine $\bar{n}_S$ for BE

$$\begin{aligned}
\bar{n}_S &= \frac{1}{e^{\beta(\epsilon_S - \mu)} - 1} \\
&= \frac{1}{\beta} \frac{-\beta e^{-\beta(\epsilon_S - \mu)}}{1 - e^{-\beta(\epsilon_S - \mu)}} \\
&= \frac{e^{-\beta(\epsilon_S - \mu)}}{1 - e^{-\beta(\epsilon_S - \mu)}} \\
&= \frac{1}{e^{\beta(\epsilon_S - \mu)} - 1}
\end{aligned}$$

2. Partition function for Fermions (Fermi-Dirac statistics): Since each n_r can be 0 or 1, the partition function is

$$\begin{aligned}\mathcal{Z} &= \sum_{n_1=0}^{1} e^{-\beta n_1 \epsilon_1 - \alpha n_1} \sum_{n_2=0}^{1} e^{-\beta n_2 \epsilon_2 - \alpha n_2} \dots \\ &= \left(1 + e^{-\beta\epsilon_1 - \alpha}\right)\left(1 + e^{-\beta\epsilon_2 - \alpha}\right) \dots\end{aligned}$$

so

$$\ln \mathcal{Z} = \sum_r \ln\left(1 + e^{-\beta\epsilon_r - \alpha}\right)$$

Thus the partition function is

$$\begin{aligned}\ln Z &= \alpha N + \ln \mathcal{Z} \\ &= \alpha N + \sum_r \ln\left(1 + e^{-\beta\epsilon_r - \alpha}\right)\end{aligned}$$