Phys 362 2020

Lecture 25

Thurs: Read 6.5, 6.6
Fri: HW by 5pm

Final Exam

Grand canonical ensemble

The grand canonical ensemble considers a system that is in thermal and chemical equilibrium with its environment. The system can exchange both energy and particles. Then if "s" represents a system state, let

N_S = number of particles in state

E_S = energy of the state

The grand partition function is constructed via

$$Z_G = \sum_{\text{all states}} e^{-(E_S - \mu N_S)\beta}$$

and the mean energy and particle number can be determined from this via:

$$\bar{N} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z_G$$

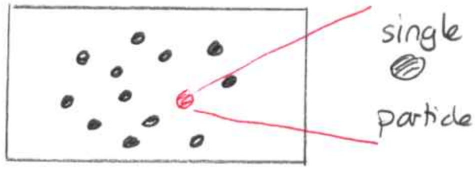
$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z_G + \bar{N}\mu$$

We now reformulate this more conveniently in terms of single particle states. This will be useful since if "k" labels a single particle state with energy ϵ_k then, with n_k = number of particles in this state. (occupation number)

$$\left.\begin{aligned} E_S &= \sum_k n_k \epsilon_k \\ N_S &= \sum n_k \end{aligned}\right\} \Rightarrow \quad Z_G = \sum_{n_1, n_2, \ldots} e^{-(\epsilon_1 n_1 - \mu n_1)\beta} e^{-(\epsilon_2 n_2 - \mu n_2)\beta} \cdots$$

This results in the following scheme:

Ensemble of indistinguishable particles



Describe all single particle states, k

label energy ϵ_k

$k=3$ —— ϵ_3
$k=2$ —— ϵ_2
$k=1$ —— ϵ_1

The grand partition function is

$$Z_G = Z_{G1} Z_{G2} Z_{G3} \cdots$$

where the single level partition function for each state is

$$Z_{Gk} = \sum_{n_k} e^{-(\epsilon_k - \mu) n_k \beta}.$$

Mean occupation number of state k is

$$\bar{n}_k = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z_{Gk}.$$

Mean particle number

$$\bar{N} = \sum_{\substack{\text{single particle} \\ \text{states } k}} \bar{n}_k$$

Mean energy

$$\bar{E} = \sum_{\substack{\text{single particle} \\ \text{states } k}} \epsilon_k \bar{n}_k$$

Proof: In general

$$Z_G = \sum_{n_1, n_2, n_3} e^{-n_1(\epsilon_1 - \mu)\beta} e^{-n_2(\epsilon_2 - \mu)\beta} \cdots$$

$$= Z_{G1} Z_{G2} Z_{G3} \cdots$$

Then we can get mean values via

$$\text{Prob}\left[\text{system state} = (n_1, n_2, n_3 \ldots)\right] = \frac{e^{-n_1(\epsilon_1-\mu)\beta} \, e^{-n_2(\epsilon_2-\mu)\beta} \ldots}{Z_G}$$

$$= \frac{e^{-n_1(\epsilon_1-\mu)\beta}}{Z_{G_1}} \; \frac{e^{-n_2(\epsilon_2-\mu)\beta}}{Z_{G_2}} \ldots$$

Then $N = n_1 + n_2 + \ldots \Rightarrow \bar{N} = \bar{n}_1 + \bar{n}_2 + \ldots$ and thus we need $\bar{n}_1$, etc, ...

$$\bar{n}_1 = \sum_{n_1, n_2, \ldots} n_1 \, \text{Prob}\left[(n_1, n_2, n_3 \ldots)\right]$$

$$= \sum_{n_1, n_2, \ldots} \frac{n_1 e^{-n_1(\epsilon_1-\mu)\beta}}{Z_{G_1}} \; \frac{e^{-n_2(\epsilon_2-\mu)\beta}}{Z_{G_2}} \ldots$$

$$= \underbrace{\sum_{n_1=0}^{\infty} \frac{n_1 e^{-n_1(\epsilon-\mu)\beta}}{Z_{G_1}}}_{\frac{1}{\beta}\frac{\partial}{\partial \mu} \ln Z_{G_1}} \; \underbrace{\sum_{n_2} \frac{e^{-n_2(\epsilon_2-\mu)\beta}}{Z_{G_2}}}_{\underbrace{Z_{G_2}/Z_{G_2}}_{=1}} \ldots$$

$$\bar{n}_1 = \frac{1}{\beta}\frac{\partial}{\partial \mu} \ln Z_{G_1} \ldots$$

Now, for the energy

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln\left[Z_G\right] + \mu \bar{N}$$

$$= -\frac{\partial}{\partial \beta} \ln\left[Z_{G_1} Z_{G_2} \ldots\right] + \mu\left(\bar{n}_1 + \bar{n}_2 + \ldots\right)$$

$$= -\frac{\partial}{\partial \beta} \ln Z_{G_1} - \frac{\partial}{\partial \beta} \ln Z_{G_2} + \ldots + \mu\left(\bar{n}_1 + \bar{n}_2 + \ldots\right)$$

But

$$\frac{\partial}{\partial\beta}\ln Z_{G_1} = \frac{\partial}{\partial\beta}\left[\ln \sum_{n_1} e^{-n_1(\epsilon_1-\mu)\beta}\right]$$

$$= \frac{1}{Z_{G_1}} \sum_{n_1} -n_1(\epsilon_1-\mu)e^{-n_1(\epsilon_1-\mu)\beta}$$

$$= -(\epsilon_1-\mu)\,\bar{n}_1$$

Thus $\bar{E} = (\epsilon_1-\mu)\bar{n}_1 + (\epsilon_2-\mu)\bar{n}_2 + \cdots + \mu(\bar{n}_1+\bar{n}_2+\cdots)$

$$= \epsilon_1\bar{n}_1 + \epsilon_2\bar{n}_2 \ \cdots \quad \Rightarrow \quad \bar{E} = \sum \bar{n}_k\epsilon_k$$

This reduces statistical physics calculations to single particle system calculations. In quantum physics there are generally two types of particles:

1) <u>Bosons</u> - an unlimited number of particles can occupy any single state
   - Bose-Einstein statistics
   - examples: * photons, spin-1 nuclei, paired electrons
     * any particle with spin 0, 1, 2, ..

2) <u>Fermions</u> - at most one part occupies any single state.
   - Fermi-Dirac statistics
   - examples: * electrons, protons
     * spin $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ particles.

<u>Bose-Einstein statistics</u>

In this case for any k

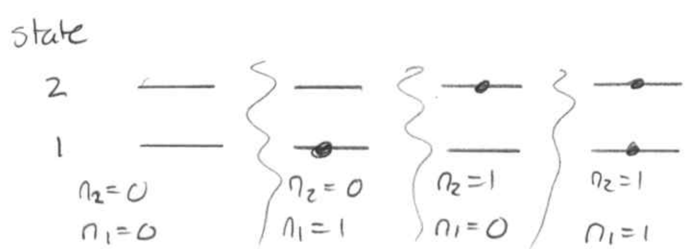
$$n_k = 0, 1, 2, 3 \ldots\ldots \to \infty$$

so

$$Z_{Gk} = \sum_{n_k=0}^{\infty} e^{-n_k(\epsilon_k - \mu)\beta}$$

<u>Fermi-Dirac statistics</u>

Here $n_k = 0, 1$ only. So $Z_{Gk} = \sum_{n_k=0}^{1} e^{-n_k(\epsilon_k-\mu)\beta}$. We can represent system states via occupancy diagrams. Suppose that each particle can be in one of two states. Then the possible system states are



1 Bose-Einstein statistics

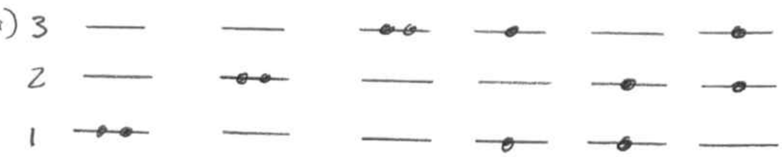
Consider a particle which can be in one of three states, with energies ϵ_1, ϵ_2 and ϵ_3, and suppose that this is a Boson.

a) Given a system of two such particles, use an occupancy diagram to list all microstates.

b) Assuming that $\mu < \epsilon_k$ for each k, determine the single state partition function, Z_{Gk}.

c) Determine the mean occupation number for any state.

Answer: a)



b)
$$Z_{Gk} = \sum_{n_k=0}^{\infty} e^{-n_k(\epsilon_k-\mu)\beta}$$

$$= 1 + e^{-(\epsilon_k-\mu)\beta} + e^{-2(\epsilon_k-\mu)\beta} + \dots$$

geometric series with $e^{-(\epsilon_k-\mu)\beta} < 1$

$$= \frac{1}{1-e^{-(\epsilon_k-\mu)\beta}}$$

c)
$$\bar{n}_k = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\left[Z_{Gk}\right]$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\left[1-e^{-(\epsilon_k-\mu)\beta}\right]$$

$$= \cancel{-}\frac{1}{\cancel{\beta}}\,\frac{\cancel{-}e^{-(\epsilon_k-\mu)\beta}\cancel{\beta}}{1-e^{-(\epsilon_k-\mu)\beta}} = \frac{e^{-(\epsilon_k-\mu)\beta}}{1-e^{-(\epsilon_k-\mu)\beta}}$$

$$\Rightarrow \quad \bar{n}_k = \frac{1}{e^{(\epsilon_k-\mu)\beta}-1}$$

2 Fermi-Dirac statistics

Consider a particle which can be in one of three states, with energies ϵ_1, ϵ_2 and ϵ_3, and suppose that this is a Fermion.

a) Given a system of two such particles, use an occupancy diagram to list all microstates.

b) Determine the single state partition function, Z_{Gk}.

c) Determine the mean occupation number for any state.

Answer: a)

b)

$$Z_{Gk} = \sum_{n_k=0}^{1} e^{-n_k(\epsilon_k - \mu)\beta}$$

$$= 1 + e^{-(\epsilon_k - \mu)\beta}$$

c)

$$\bar{n}_k = \frac{1}{\beta}\frac{\partial}{\partial\mu} \ln Z_G$$

$$= \frac{1}{\beta}\frac{\partial}{\partial\mu} \ln\left[1 + e^{-(\epsilon_k-\mu)\beta}\right]$$

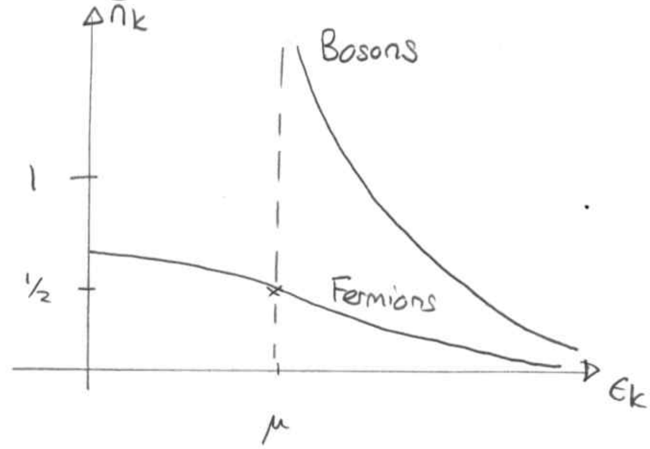
$$= \frac{1}{\cancel{\beta}} \frac{e^{-(\epsilon_k-\mu)\beta}\cancel{\beta}}{1+e^{-(\epsilon_k-\mu)\beta}}$$

$$\Rightarrow \bar{n}_k = \frac{1}{e^{(\epsilon_k-\mu)\beta}+1}$$

Thus:

Bosons	$\bar{n}(\epsilon_k) = \dfrac{1}{e^{(\epsilon_k-\mu)\beta}-1}$	if $\epsilon_k > \mu$
Fermions	$\bar{n}(\epsilon_k) = \dfrac{1}{e^{(\epsilon_k-\mu)\beta}+1}$	all ϵ_k, μ.

Note that the mean occupation number depends on the energy and temperature. In general the mean occupation number is larger for Bosons than it is for Fermions



Maxwell-Boltzmann distribution

Suppose that $e^{(\epsilon_k-\mu)\beta} \gg 1$, i.e. $(\epsilon_k-\mu)\beta \gg 0$. Then

$$\bar{n}_k(\epsilon_k) \approx e^{-(\epsilon_k-\mu)\beta} \qquad \text{if} \quad (\epsilon_k-\mu)\beta \gg 0$$

This is the Maxwell-Boltzmann distribution. This can occur in various ways

If $\epsilon_k \gg \mu$ then adding a single particle requires much less energy than changing particle energy level. The particle energy level structure is much more important

Grand Canonical Ensemble and Entropy

The grand canonical ensemble requires /provides

Single particle partition functions

Z_{Gk}

$\longrightarrow$

Grand partition function

$Z = Z_{G_1} Z_{G_2} \dots$

Mean energy $\bar{E}$

Mean particle number $\bar{N}$

We can possibly obtain the energy equation of state from this. What about pressure equation of state? This requires an expression for entropy in terms of mean energy and particle number. We show that.

> For the grand canonical ensemble the entropy is:
>
> $$S = k \ln Z_G + \frac{1}{T}\left(\bar{E} - \mu \bar{N}\right) = k \ln Z_G - \frac{1}{T}\frac{\partial}{\partial \beta} \ln Z_G$$
>
> where
>
> $$\bar{N} = \frac{1}{\beta}\frac{\partial}{\partial \mu} \ln Z_G \qquad \bar{E} = \mu \bar{N} - \frac{\partial}{\partial \beta} \ln Z_G$$

Proof: Let s be a state of the system. Then

$$S = -k \sum_s p_s \ln p_s$$

where

$$p_s = \frac{1}{Z_G} e^{-(E_s - \mu N_s)\beta}$$

is the probability with which the particle is in state s

Thus $$S = -k \sum p_s \ln\left[\frac{1}{Z_G} e^{-(E_s-\mu N_s)\beta}\right]$$

$$= -k \sum p_s \left[-\ln Z_G - (E_s-\mu N_s)\beta\right]$$

$$= k \ln Z_G \sum p_s + k \sum p_s (E_s-\mu N_s)\beta$$

$$= k \ln Z_G \times 1 + k(\bar{E} - \mu\bar{N})\beta \quad \text{and } k\beta = \frac{1}{T}$$

$$S = k \ln Z_G + (\bar{E} - \mu\bar{N})/T$$

Now $$\bar{E} = \mu\bar{N} - \frac{\partial}{\partial\beta} \ln Z_G$$

$$\Rightarrow S = k \ln Z_G - \frac{1}{T}\frac{\partial}{\partial\beta} \ln Z_G \qquad \boxtimes$$

We can rewrite the entropy in terms of single state partition functions. The result is that

$$S = k \sum_j \ln\left[Z_{G_j}\right] + \frac{1}{T}(\bar{E} - \mu\bar{N})$$

all single states

where

$$\bar{N} = \sum \bar{n}_j$$

$$\bar{E} = \sum \epsilon_j \bar{n}_j$$

and

$$\bar{n}_j = \sum_{n_j} e^{-n_j(\epsilon_j-\mu)\beta}$$

We rewrite this in terms of mean occupation numbers for states:

1) Bose - Einstein statistics : $\bar{n}_j = \dfrac{1}{e^{(\epsilon_j - \mu)\beta} - 1}$

2) Fermi - Dirac " : $\bar{n}_j = \dfrac{1}{e^{(\epsilon_j - \mu)\beta} + 1}$

3) Maxwell - Boltzmann " $\bar{n}_j = e^{-(\epsilon_j - \mu)\beta}$

Then for Bose - Einstein statistics:

$$\bar{n}_j = \frac{1}{e^{(\epsilon_j - \mu)\beta} - 1} \Rightarrow e^{(\epsilon_j - \mu)\beta} = \frac{1}{\bar{n}_j} + 1 = \frac{\bar{n}_j + 1}{\bar{n}_j}$$

and

$$Z_{G_j} = \frac{1}{1 - e^{-(\epsilon_j - \mu)\beta}} = \frac{1}{1 - \frac{\bar{n}_j}{\bar{n}_j + 1}} = \frac{\bar{n}_j + 1}{1} = \bar{n}_j + 1$$

$\Rightarrow$ Bosons: $S = k \sum_j \ln(1 + \bar{n}_j) + \frac{1}{T}(\bar{E} - \mu \bar{N})$

For Fermi - Dirac

$$\bar{n}_j = \frac{1}{e^{(\epsilon_j - \mu)\beta} + 1} \Rightarrow e^{(\epsilon_j - \mu)\beta} = \frac{1 - \bar{n}_j}{\bar{n}_j}$$

$$Z_{G_j} = 1 + e^{-(\epsilon_j - \mu)\beta} = \frac{1}{1 - \bar{n}_j}$$

$\Rightarrow$ Fermions $S = -k \sum_j \ln(1 - \bar{n}_j) + \frac{1}{T}(\bar{E} - \mu \bar{N})$

For Maxwell - Boltzmann $(\epsilon_j - \mu)\beta \gg 0$. So $\bar{n}_j \ll 1$ and

$$\ln(1+\bar{n}_j) \approx \bar{n}_j$$

$$\ln(1-\bar{n}_j) \approx -\bar{n}_j$$

This gives

$$S = k \sum_j \bar{n}_j + \frac{1}{T}(\bar{E} - \mu\bar{N})$$

$$\Rightarrow \quad S = k\bar{N} + \frac{1}{T}(\bar{E} - \mu\bar{N})$$

Note that in general $T = T(\bar{E}, \bar{N})$

$\mu = \mu(\bar{E}, \bar{N})$

and we need to ascertain these before proceeding...