PHYS 3014: Statistical Mechanics

Lecture Notes
Part 13

Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac Statistics 2

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Distribution Laws (M-B, B-E and F-D statistics)

For finding the statistical distribution laws, we have to obtain most probable distribution of particles among the energy levels for which entropy must be maximum.

$$S(N, V, E) \simeq k \ln W\{n_i^*\} \quad \text{--- (1)}$$

Where $\{n_i^*\}$ is the distribution set which maximizes the number $W\{n_i\}$. n_i^* are the most probable values of the distribution numbers n_i. So $\ln W\{n_i\}$ have the maximum value for most probable distribution set $\{n_i^*\}$ subjected to the restriction that N and E remain Constant.

For maximum value of $\ln W\{n_i\}$,

$$\delta \ln W\{n_i\} = 0 \quad \text{-- (2)}$$

and $$\sum_i \delta n_i = 0 \quad \text{and} \quad \sum_i \epsilon_i \delta n_i = 0 \quad \text{-- (3)}$$

For most probable distribution set $\{n_i^*\}$, using method of Lagrange's undetermined multipliers, we have

$$\delta \ln W\{n_i\} - \left[\alpha \sum_i \delta n_i + \beta \sum_i \epsilon_i \cdot \delta n_i\right] = 0 \quad \text{--- (4)}$$

For finding $\ln W\{n_i\}$, all $g_i >> 1$ and $n_i >> 1$ so that stirling approximation could be used.

Now.

$$\ln W\{n_i\} = \sum_i \ln w(i) \quad \text{--- (5)}$$

(a)

$$\ln W_{MB}\{n_i\} = \sum_i (n_i \ln g_i - n_i \ln n_i + n_i)$$

$$= \sum_i \left[n_i \ln\left(\frac{g_i}{n_i}\right) + n_i\right]$$

$$= \sum_i \left[n_i \ln\left(\frac{g_i}{n_i} - a\right) - \frac{g_i}{a} \ln\left(1 - a\frac{n_i}{g_i}\right)\right]$$

where $a = 0$

--- (6)

(b) $\ln W_{BE}\{n_i\} \simeq \sum_i \Big[(n_i+g_i-1)\ln(n_i+g_i-1) - (n_i+g_i-1)$
$- n_i \ln n_i + n_i - (g_i-1)\ln(g_i-1) + (g_i-1)\Big]$

$$\simeq \sum_i \Big[(n_i+g_i)\ln(n_i+g_i) - (n_i+g_i) - n_i \ln n_i + n_i - g_i \ln g_i + g_i\Big]$$

$$= \sum_i \Big[n_i \ln\left(\frac{g_i}{n_i}+1\right) + g_i \ln\left(1+\frac{n_i}{g_i}\right)\Big]$$

$$= \sum_i \Big[n_i \ln\left(\frac{g_i}{n_i}-a\right) - \frac{g_i}{a}\ln\left(1-a\frac{n_i}{g_i}\right)\Big]$$

where $a=-1$ --- (7)

(c) $\ln W_{FD}\{n_i\} \simeq \sum_i \Big[g_i \ln g_i - g_i - n_i \ln n_i + n_i - (g_i-n_i)\ln(g_i-n_i)$
$+ (g_i-n_i)\Big]$

$$= \sum_i \Big[n_i \ln\left(\frac{g_i}{n_i}-1\right) - g_i \ln\left(1-\frac{n_i}{g_i}\right)\Big]$$

$$= \sum_i \Big[n_i \ln\left(\frac{g_i}{n_i}-a\right) - \frac{g_i}{a}\ln\left(1-\frac{a n_i}{g_i}\right)\Big]$$

where $a=+1$ --- (8)

$$\therefore \ln W\{n_i\} = \sum_i \left[n_i \ln\left(\frac{g_i}{n_i} - a\right) - \frac{g_i}{a} \ln\left(1 - a\frac{n_i}{g_i}\right)\right] \quad --- (9)$$

For M-B $\quad a = 0$

B-E $\quad a = -1$

F-D $\quad a = +1$

Now
$$\delta \ln W\{n_i\} = \sum_i \left\{ \ln\left(\frac{g_i}{n_i} - a\right) + \frac{n_i\left(-\frac{g_i}{n_i^2}\right)}{\left(\frac{g_i}{n_i} - a\right)} - \frac{g_i}{a} \frac{1\left(-\frac{a}{g_i}\right)}{\left(1 - a\frac{n_i}{g_i}\right)} \right\} \delta n_i$$
$$--- (10)$$

By equations (4) and (10) we have

$$\sum_i \left[\ln\left(\frac{g_i}{n_i} - a\right) - \alpha - \beta \epsilon_i \right]_{n_i = n_i^*} \delta n_i = 0 \quad --- (11)$$

Since δn_i is arbitrary, so for all i, we must have

$$\ln\left(\frac{g_i}{n_i^*} - a\right) - \alpha - \beta \epsilon_i = 0$$

or,
$$n_i^* = \frac{g_i}{e^{\alpha + \beta\epsilon_i} + a} \quad --- (12)$$

or, $$\frac{n_i^*}{g_i} = \frac{1}{e^{\alpha+\beta\epsilon_i} + a} \quad \text{--- (13)}$$

$\frac{n_i^*}{g_i}$ is the most probable number of particles per energy level in the i^{th} cell. It is the most probable number of particle in a single level of energy ϵ_i.

$$n_i^* = g_i e^{-(\alpha+\beta\epsilon_i)} \qquad \text{M-B.}$$

$$= \frac{g_i}{e^{\alpha+\beta\epsilon_i} - 1} \qquad \text{B-E} \quad \text{--- (14)}$$

$$= \frac{g_i}{e^{\alpha+\beta\epsilon_i} + 1} \qquad \text{F-D}$$

$\frac{n_i^*}{g_i}$ is the fraction of the g_i states that are occupied. $f(\epsilon_i) = \frac{n_i^*}{g_i}$ is called the occupation index for the states ϵ_i.

Value of α and β

Now

$$N = \sum_i g_i e^{-\alpha-\beta\epsilon_i}$$

$$N e^{\alpha} = \sum_i g_i e^{-\beta\epsilon_i} = Z \quad \text{partition function}$$

$$\therefore \; e^{\alpha} = \frac{Z}{N} \implies n_i^* = \frac{N}{Z} g_i e^{-\beta\epsilon_i}$$

$$N = e^{-\alpha} \sum_i g_i e^{-\beta \epsilon_i}$$

$$= e^{-\alpha} \int_0^\infty g(\epsilon)\, e^{-\beta\epsilon} d\epsilon$$

$$= e^{-\alpha} \frac{2\pi V}{h^3} \int_0^\infty (2m)^{3/2} \epsilon^{1/2} e^{-\beta\epsilon} d\epsilon$$

$$= e^{-\alpha} \frac{2\pi V (2m)^{3/2}}{h^3} \int_0^\infty \epsilon^{1/2} e^{-\beta\epsilon} d\epsilon$$

$\beta\epsilon = y$

$d\epsilon = \frac{dy}{\beta}$.

$$= e^{-\alpha} \frac{2\pi V}{h^3} (2m)^{3/2} \beta^{-3/2} \int_0^\infty y^{3/2-1} e^{-y} dy$$

$$= e^{-\alpha} \frac{2\pi V}{h^3} \left(\frac{2m}{\beta}\right)^{3/2} \cdot \frac{\sqrt{\pi}}{2}$$

$$N = e^{-\alpha} V \left(\frac{2\pi m}{h^2 \beta}\right)^{3/2}$$

$$\Rightarrow e^{-\alpha} = \frac{N}{V} \left(\frac{h^2\beta}{2\pi m}\right)^{3/2} = \frac{N}{V} \lambda^3$$

$$e^{\alpha} = \frac{V}{N} \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} = \frac{V}{N} \frac{1}{\lambda^3}, \quad \lambda = \left(\frac{\beta h^2}{2\pi m}\right)^{1/2}$$

For M-B system

$$\frac{S}{k} = \sum_i n_i \ln g_i - n_i \ln n_i + n_i$$

$$= \sum_i n_i \ln\left(\frac{g_i}{n_i}\right) + n_i$$

$$= \sum_i \left(n_i(\alpha + \beta\epsilon_i) + n_i\right)$$

$$= N\alpha + \beta E + N$$

$$= N\ln Z - N\ln N + \beta E + N \qquad \because e^{\alpha} = \frac{Z}{N}$$

Now

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \left(\frac{\partial S}{\partial E}\right)_{N,Z} = k\beta$$

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = \left(\frac{\partial S}{\partial N}\right)_{E,Z} = k\ln Z - k\ln N = k\ln\frac{Z}{N} = \alpha k$$

But

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T} \Rightarrow k\beta = \frac{1}{T}$$

or, $\beta = \frac{1}{KT}$

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T} \Rightarrow \alpha K = -\frac{\mu}{T}$$

or, $\alpha = -\frac{\mu}{KT}$

We know that

$$\frac{S}{K} + \frac{\mu N}{KT} - \frac{E}{KT} = \frac{G - (E - TS)}{KT} = \frac{PV}{KT}$$

Now

$$\frac{S}{k} = \ln W \{n_i^*\}$$

$$= \sum_i \left[n_i^* \ln\left(\frac{g_i}{n_i^*} - a\right) - \frac{g_i}{a} \ln\left(1 - a\frac{n_i^*}{g_i}\right)\right]$$

$$= \sum_i \left[n_i^* (\alpha + \beta \epsilon_i) + \frac{g_i}{a} \ln\left(1 + a\frac{n_i^*}{g_i}\right)\right]$$

$$= \sum_i \left[(n_i^* \alpha + n_i^* \epsilon_i \beta) + \frac{g_i}{a} \ln\{1 + a e^{-\alpha - \beta \epsilon_i}\}\right]$$

$$= N\alpha + \beta E + \frac{1}{a}\sum_i g_i \ln\{1 + a e^{-\alpha - \beta \epsilon_i}\}$$

or,

$$\frac{S}{k} + \frac{\mu N}{KT} - \frac{E}{KT} = \frac{1}{a}\sum_i g_i \ln(1 + a e^{-\alpha - \beta \epsilon_i})$$

or,

$$\frac{PV}{KT} = \frac{1}{a}\sum_i g_i \ln(1 + a e^{-\alpha - \beta \epsilon_i})$$

It gives the thermodynamic pressure of the system.

In the M-B case

$$a \to 0$$

$$\therefore \quad PV = \frac{KT}{a} \sum_i g_i a\, e^{-\alpha - \beta \epsilon_i}$$

$$= KT \sum_i g_i e^{-\alpha - \beta \epsilon_i}$$

$$= KT \sum_i n_i^*$$

or, $$\boxed{PV = NKT}$$

Quantum-classical Transition; classical or Boltzmann limit of Bosons and Fermions

The mean occupation number of a single particle state with energy ϵ_i is given by

$$\bar{n}_i = f(\epsilon_i) = \frac{n_i}{g_i} = \frac{1}{e^{\beta(\epsilon_i - \mu)} + a}, \quad a = 1 \quad \text{F-D}$$

$$= -1 \quad \text{B-E}$$

In F-D statistics, mean occupation number cannot exceed unity as variable n_i cannot take a value other than 0 or 1.

When $\epsilon_i < \mu$ and $|\epsilon_i - \mu| >> KT$, then $\bar{n}_i$ tends to get its maximum probable value 1.

In B-E statistics, more than one particle can occupy the same single particle state. The mean occupation number $\bar{n}_i$ is always non-singular and positive. It means μ must be smaller than lowest value of ϵ_i i.e ϵ_0. So we must have $\mu <$ all ϵ_i. When μ becomes equal to smallest value of ϵ_i i.e ϵ_0, the occupancy of that particular energy level becomes infinitely high which leads to the phenomenon of Bose-Einstein Condensation.

In the classical limit, either density or Concentration is very low or temperature is very high. When N is small, $n_i << g_i$ i.e $f(\epsilon_i) << 1$ or $\bar{n}_i << 1$ at fixed T.

or $e^{\beta(\epsilon_i - \mu)} >> 1$ for all states.

For T is very high, then at fixed N, β is small and to keep N constant we must have $\exp \beta(\epsilon_i - \mu) >> 1$ or $e^{-\beta\mu} >> 1$. So we have $\bar{n}_i << 1$. To keep $\beta(\epsilon_i - \mu)$ to be large, μ must be negative and large in magnitude. Fugacity $e^{\mu/kT}$ (absolute activity) must be smaller than unity.

Therefore, classical limit is reached when either concentration is made sufficiently low or temperature is made sufficiently high so that $e^{\beta(\epsilon_i - \mu)} >> 1 \Rightarrow \bar{n}_i << 1$

In the Classical limit both F-D and B-E statistics reduced to M-B statistics.

$$\text{i.e} \quad \bar{n}_i = e^{-\beta(\epsilon_i - \mu)}$$

$$\text{or,} \quad n_i = g_i \, e^{-\beta(\epsilon_i - \mu)}$$

$$N = \sum_i n_i$$

$$= e^{\beta\mu} \sum_i g_i \exp(-\beta\epsilon_i)$$

$$= e^{\beta\mu} \int_0^\infty g(\epsilon)\, d\epsilon \exp(-\beta\epsilon) = e^{\beta\mu} . V \left(\frac{2\pi m k T}{h^2}\right)^{3/2}$$

or, $$e^{\beta\mu} = \frac{N}{Z} \quad , \text{where } Z = \sum_i g_i \exp(-\beta\epsilon_i)$$

$$\therefore \quad \bar{n}_i = \frac{N}{Z} e^{-\beta\epsilon_i} \quad \text{M-B statistics.}$$

A system follows the classical limit is said to be non-degenerate and if the concentration and temperature are such that the actual F-D or B-E statistics is used, the system is said to be degenerate.

strongly degenerate $\frac{n_i}{g_i} >> 1$
weakly degenerate $\frac{n_i}{g_i} > 1$
non-degenerate $\frac{n_i}{g_i} << 1$

The quantum statistics converts to the classical statistics in the limiting case when

$$e^{\beta(\epsilon_i - \mu)} >> 1$$

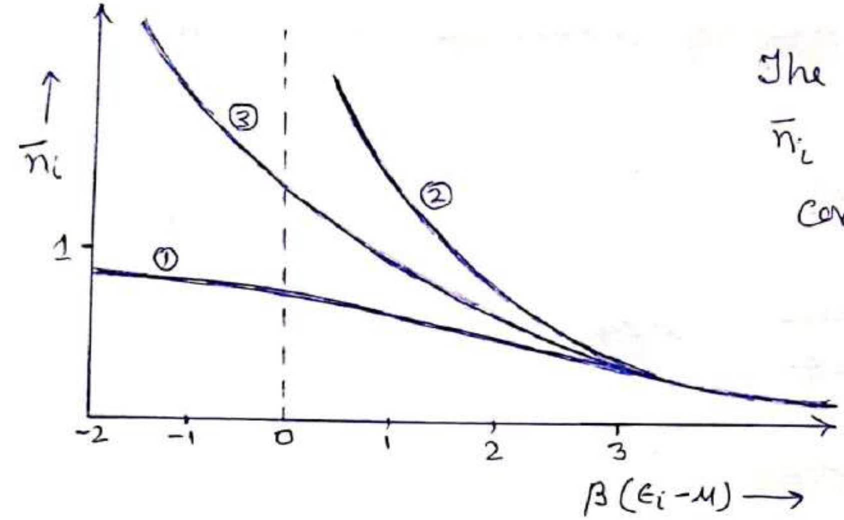
or $$e^{-\beta\mu} >> 1$$

i.e $$\left(\frac{2\pi mKT}{h^2}\right)^{3/2} \frac{V}{N} >> 1$$

or, $$\frac{N}{V} \lambda^3 << 1 \quad , \quad \lambda = \frac{h}{\sqrt{2\pi mKT}}$$

λ is the mean thermal wavelength. It is a measure of the wavefunction of the particle. As long as λ is much smaller than the average particle separation, statistics will be classical. Thus when

$$\left(\frac{h^2}{2\pi mKT}\right)^{3/2} \frac{N}{V} >> 1 \ ,$$ the system is degenerate and this condition is known as degeneracy criterion.



The variation of occupation number $\bar{n}_i$ with $\beta(\epsilon_i - \mu)$ for the three cases is shown in figure.

Curve 1 — Fermions

Curve 2 — Bosons

Curve 3 — M-B particles.

For large values of $\beta(\epsilon_i - \mu)$ the quantum curves ① and ③ merge into the classical curve. At high T classical statistics is valid. At high T, $\beta(\epsilon_i - \mu)$ must be large which is possible only when μ is negative and large in magnitude. It means that fugacity of the system must be smaller than unity.

For fermions, i.e electrons fermi energy is equivalent to chemical potential at absolute zero.

$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

So the condition for classical statistics to hold will also be

$$\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\frac{V}{N} >> 1$$

or,
$$\left(\frac{2\pi mKT}{h^2}\right)^{3/2} \cdot 3\pi^2\left(\frac{\hbar^2}{2mE}\right)^{3/2} >> 1$$

or,
$$3\pi^2\left(\frac{KT}{4\pi E_F}\right)^{3/2} >> 1$$

It means $KT >> E_F$ which is equivalent to $T >> T_F$.

The classical limit of the Fermi and Bose distributions automatically treats the particles as indistinguishable.

We know that

$$\frac{z}{N} = e^{-\beta\mu}\quad , \text{ z is single particle canonical partition function}$$

and
$$\left(\frac{\partial}{\partial N}\ln Z_N\right)_{T,V} = -\beta\mu$$
$$= \ln\frac{z}{N} = \ln z - \ln N$$

$$\therefore \quad \ln Z_N = N\ln z - N\ln N + N = \ln z^N - \ln \underline{|N}$$

$$\Rightarrow \quad Z_N = \frac{z^N}{\underline{|N}}$$, presence of $\underline{|N}$ is accountable for the indistinguishability of particles.

References:

- Statistical Mechanics by R. K. Pathria
- Statistical Mechanics by B. K. Agarwal and M. Eisner
- An Introductory Course of Statistical Mechanics by P. B. Pal
- Elementary Statistical Physics by C. Kittel
- Fundamentals of Statistical and Thermal Physics by F. Reif
- Statistical and Thermal Physics by R. S. Gambhir and S. Lokanathan

Thank You

For any questions/doubts/suggestions and submission of assignments

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