

Chapter 5 Identical Particle

5.1 Two particle systems

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$$

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$$

$$\hat{H} = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2, t)$$

$$\int |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = 1$$

for time-independent potential, $\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi(\mathbf{r}_1, \mathbf{r}_2) e^{\frac{-iEt}{\hbar}}$

time-independent Schrödinger equation,

$$-\frac{\hbar^2}{2m_1} \nabla_1^2 \psi - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi + V\psi = E\psi$$

exchange operator P :

$$Pf(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_2, \mathbf{r}_1)$$

$$P[\hat{H}(\mathbf{r}_1, \mathbf{r}_2)\psi(\mathbf{r}_1, \mathbf{r}_2)] = \hat{H}(\mathbf{r}_2, \mathbf{r}_1)\psi(\mathbf{r}_2, \mathbf{r}_1) = \hat{H}(\mathbf{r}_1, \mathbf{r}_2)P\psi(\mathbf{r}_1, \mathbf{r}_2)$$

$$\Rightarrow [P, \hat{H}(\mathbf{r}_1, \mathbf{r}_2)] = 0$$

$$\text{for } Pg(\mathbf{r}_1, \mathbf{r}_2) = \lambda g(\mathbf{r}_1, \mathbf{r}_2)$$

$$P^2 g(\mathbf{r}_1, \mathbf{r}_2) = P[Pg(\mathbf{r}_1, \mathbf{r}_2)] = P[\lambda g(\mathbf{r}_1, \mathbf{r}_2)] = \lambda^2 g(\mathbf{r}_1, \mathbf{r}_2)$$

$$= Pg(\mathbf{r}_2, \mathbf{r}_1) = g(\mathbf{r}_1, \mathbf{r}_2)$$

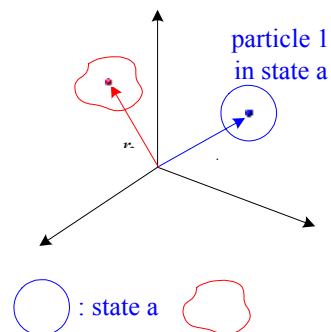
$$\Rightarrow \lambda = 1, -1$$

Two distinguishable particles:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)$$

$$\psi(\mathbf{r}_2, \mathbf{r}_1) = \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)$$

are two states of two distinguishable particles



For two indistinguishable particles :

$$\lambda = 1 \rightarrow \psi_+ = \frac{1}{\sqrt{2}} [\psi(\mathbf{r}_1, \mathbf{r}_2) + \psi(\mathbf{r}_2, \mathbf{r}_1)] = \frac{1}{\sqrt{2}} [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)]$$

$$\lambda = -1 \rightarrow \psi_- = \frac{1}{\sqrt{2}} [\psi(\mathbf{r}_1, \mathbf{r}_2) - \psi(\mathbf{r}_2, \mathbf{r}_1)] = \frac{1}{\sqrt{2}} [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)]$$

ψ_+ , ψ_- are orthonormal and satisfy Schrödinger equation

identical **bosons** : $\psi_+(\mathbf{r}_1, \mathbf{r}_2) = \psi_+(\mathbf{r}_2, \mathbf{r}_1)$ **symmetric**
 identical **fermions** : $\psi_-(\mathbf{r}_1, \mathbf{r}_2) = -\psi_-(\mathbf{r}_2, \mathbf{r}_1)$ **antisymmetric**

Pauli Exclusion Principle :

if any two identical fermion particles have the same state , $a = b$

then $\psi_- = 0$

identical fermion can not occupy the same quantum state(wave function)

➤ **Exchange forces**

for one-dimensional :

particle 1 is in state $\psi_a(x_1)$; particle 2 is in state $\psi_b(x_2)$

$\psi_a(x_1)$, $\psi_b(x_1)$ are orthonormal

distinguishable particles : $\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2)$

identical bosons : $\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) + \psi_a(x_2)\psi_b(x_1)]$

identical fermions : $\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) - \psi_a(x_2)\psi_b(x_1)]$

calculate expectation of distance between two particles

$$\langle (\Delta x)^2 \rangle \equiv \langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle$$

(i) distinguishable particles

$$\begin{aligned}
\langle x_1^2 \rangle &= \iint x_1^2 |\psi(x_1, x_2)|^2 dx_1 dx_2 = \iint x_1^2 |\psi_a(x_1)|^2 |\psi_b(x_2)|^2 dx_1 dx_2 \\
&= \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 \\
&= \int x_1^2 |\psi_a(x_1)|^2 dx_1 \\
&= \langle x^2 \rangle_a
\end{aligned}$$

$$\begin{aligned}
\langle x_2^2 \rangle &= \iint x_2^2 |\psi(x_1, x_2)|^2 dx_1 dx_2 = \iint x_2^2 |\psi_a(x_1)|^2 |\psi_b(x_2)|^2 dx_1 dx_2 \\
&= \int |\psi_a(x_1)|^2 dx_1 \int x_2^2 |\psi_b(x_2)|^2 dx_2 \\
&= \int x_2^2 |\psi_b(x_2)|^2 dx_2 \\
&= \langle x^2 \rangle_b
\end{aligned}$$

$$\begin{aligned}
\langle x_1 x_2 \rangle &= \iint x_1 x_2 |\psi(x_1, x_2)|^2 dx_1 dx_2 = \iint x_1 x_2 |\psi_a(x_1)|^2 |\psi_b(x_2)|^2 dx_1 dx_2 \\
&= \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 \\
&= \langle x \rangle_a \langle x \rangle_b
\end{aligned}$$

$$\langle (\Delta x)^2 \rangle_{dis} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b$$

(ii) identical particles

$$\begin{aligned}
\langle x_1^2 \rangle &= \iint x_1^2 |\psi_{\pm}(x_1, x_2)|^2 dx_1 dx_2 = \frac{1}{2} \iint x_1^2 [\psi_a(x_1)\psi_b(x_2) \pm \psi_a(x_2)\psi_b(x_1)] \\
&\quad [\psi_a(x_1)\psi_b(x_2) \pm \psi_a(x_2)\psi_b(x_1)]^* dx_1 dx_2 \\
&= \frac{1}{2} \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 + \frac{1}{2} \int x_1^2 |\psi_b(x_1)|^2 dx_1 \int |\psi_a(x_2)|^2 dx_2 \\
&\quad \pm \frac{1}{2} \int x_1^2 \psi_a(x_1) \psi_b^*(x_1) dx_1 \int \psi_a^*(x_2) \psi_b(x_2) dx_2 \\
&\quad \pm \frac{1}{2} \int x_1^2 \psi_a^*(x_1) \psi_b(x_1) dx_1 \int \psi_a(x_2) \psi_b^*(x_2) dx_2 \\
&= \frac{1}{2} \langle x^2 \rangle_a + \frac{1}{2} \langle x^2 \rangle_b
\end{aligned}$$

$$\text{similarly } \langle x_2^2 \rangle = \frac{1}{2} \langle x^2 \rangle_b + \frac{1}{2} \langle x^2 \rangle_a$$

$$\langle x_1^2 \rangle = \langle x_2^2 \rangle$$

$$\begin{aligned}
\langle x_1 x_2 \rangle &= \iint x_1 x_2 |\psi_{\pm}(x_1, x_2)|^2 dx_1 dx_2 = \frac{1}{2} \iint x_1 x_2 [\psi_a(x_1)\psi_b(x_2) \pm \psi_a(x_2)\psi_b(x_1)] \\
&\quad [\psi_a(x_1)\psi_b(x_2) \pm \psi_a(x_2)\psi_b(x_1)]^* dx_1 dx_2 \\
&= \frac{1}{2} \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 + \frac{1}{2} \int x_1 |\psi_b(x_1)|^2 dx_1 \int x_2 |\psi_a(x_2)|^2 dx_2 \\
&\quad \pm \frac{1}{2} \int x_1 \psi_a(x_1) \psi_b^*(x_1) dx_1 \int x_2 \psi_a^*(x_2) \psi_b(x_2) dx_2 \\
&\quad \pm \frac{1}{2} \int x_1 \psi_a^*(x_1) \psi_b(x_1) dx_1 \int x_2 \psi_a(x_2) \psi_b^*(x_2) dx_2 \\
&= \frac{1}{2} \langle x \rangle_a \langle x \rangle_b + \frac{1}{2} \langle x \rangle_b \langle x \rangle_a \pm \frac{1}{2} \langle x \rangle_{ba} \langle x \rangle_{ab} \pm \frac{1}{2} \langle x \rangle_{ab} \langle x \rangle_{ba} \\
&= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2
\end{aligned}$$

→ identical bosons :

$$\begin{aligned}
\langle (\Delta x)^2 \rangle_{\pm} &= \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b - 2 |\langle x \rangle_{ab}|^2 \\
&= \langle (\Delta x)^2 \rangle_{dis} - 2 |\langle x \rangle_{ab}|^2 \quad \dots\dots\dots(5.1)
\end{aligned}$$

identical fermions :

$$\langle (\Delta x)^2 \rangle_{dis} + 2 |\langle x \rangle_{ab}|^2 \quad \dots\dots\dots(5.2)$$

exchange force

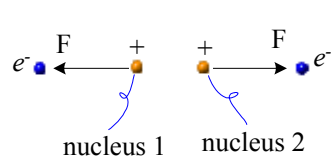
from equation (5.1) , (5.2)

(i) identical bosons tend to be closer together , look like a “*force of attraction*” between bosons to pull them closer .

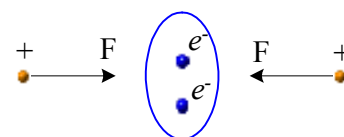
(ii) identical fermions tend to be farther apart , look like a “*force of repulsion*” between fermions to push them apart .

example

a hydrogen molecule H_2



Antisymmetric configuration
produces repulsive force



Symmetric configuration
produces attractive

We call it an exchange force , although it's not really a force at all ;
rather , it is a purely *geometrical* consequence of the symmetrization
requirement .

5.2 Atoms

A neutral atom

$$H = \sum_{j=1}^Z \left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi \epsilon_0} \right) \frac{Ze^2}{r_j} \right\} + \frac{1}{2} \left(\frac{1}{4\pi \epsilon_0} \right) \sum_{j \neq k}^Z \frac{e^2}{|r_j - r_k|} \quad \dots\dots\dots(5.3)$$

$\uparrow$
 kinetic and potential
 energy in electric field
 of nucleu

$\uparrow$
 potential with mutual
 repulsion of electrons

Z : atomic number ; m : mass ; e : charge

$$H\psi = E\psi \quad ; \quad \psi (\mathbf{r}_1 , \mathbf{r}_2 , \dots , \mathbf{r}_Z)$$

complete state (position and spin) :

$$\underbrace{\psi (\mathbf{r}_1 , \mathbf{r}_2 , \dots , \mathbf{r}_Z)}_{\text{spatial wave function}} \underbrace{\chi (\mathbf{s}_1 , \mathbf{s}_2 , \dots , \mathbf{s}_Z)}_{\text{spin state}} \quad \dots\dots\dots(5.4)$$

spatial wave function spin state

equation (5.3) must solve by approximation methods (later chapter)

➤ Helium and electron spin

$$Z = 2 ;$$

$$H = \left[-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{1}{4\pi \epsilon_0} \frac{2e^2}{r_1} \right] + \left[-\frac{\hbar^2}{2m} \nabla_2^2 - \frac{1}{4\pi \epsilon_0} \frac{2e^2}{r_2} \right] + \frac{1}{4\pi \epsilon_0} \frac{e^2}{|r_1 - r_2|}$$

helium have two electrons , for chapter 4
there are three symmetric spin states :

$$\begin{aligned} &\alpha(1)\alpha(2) \\ &\beta(1)\beta(2) \\ &\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \end{aligned}$$

and one antisymmetric spin state : $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

from equation (5.4) ,when spatial wave function and spin states combined

(i) $s = 0$, there is a antisymmetric singlet state

$$\begin{aligned}\psi_{+}\chi &= \frac{1}{2} [\psi(\mathbf{r}_1, \mathbf{r}_2) + \psi(\mathbf{r}_2, \mathbf{r}_1)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ &= \frac{1}{2} [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]\end{aligned}$$

(ii) $s = 1$, antisymmetric triplet state

$$\psi_{-}\chi = \frac{1}{\sqrt{2}} [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)] \times \begin{cases} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \end{cases}$$

the triplet states are called **orthohelium**
the singlet states are called **parahelium**

➤ The periodic table

Electrons configuration :

(i) According to Pauli exclusion principle , electrons cannot all settle down to ($n = 1$) ground state . Each spatial state only contains two electrons .

(ii) $m = -l, \dots, l$; has $(2l+1)$ values

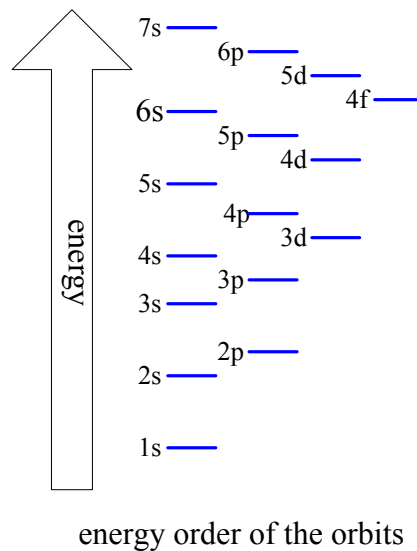
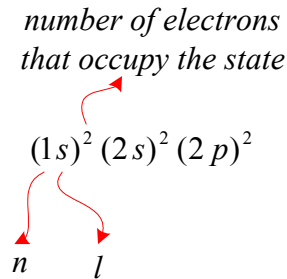
$$2 \sum_{l=0}^{n-1} (2l+1) = 2n^2$$

So the n th shell can accommodate $2n^2$ electrons .

(iii) The horizontal row on the Periodic Table corresponding to filling out each shell .

(iv) For single-electron atom , the energy related only to n .
[Bohr energies (section 4.2)]

- (v) For multi-electrons atom , effect of the repulsion force between electrons must be considered . The energy depends on n and l now .
- (vi) For the same n , the state of lower l have lower energy , energy increasing with increasing l . In general electrons would fill the lower energy state first .
- (vii) configuration :



5.3 Solids

➤ Free electron gas of Sommerfeld

$$V(x, y, z) = \begin{cases} 0, & 0 < x < l_x, 0 < y < l_y, 0 < z < l_z \\ \infty, & \text{otherwise} \end{cases}$$

ignore all interactive forces

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E \psi = (E_x + E_y + E_z) \psi \quad ; \quad \psi(x, y, z) = X(x)Y(y)Z(z)$$

$$-\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} = E_x X, \quad -\frac{\hbar^2}{2m} \frac{d^2 Y}{dy^2} = E_y Y, \quad -\frac{\hbar^2}{2m} \frac{d^2 Z}{dz^2} = E_z Z$$

$$\text{set } k_x = \frac{\sqrt{2mE_x}}{\hbar}, \quad k_y = \frac{\sqrt{2mE_y}}{\hbar}, \quad k_z = \frac{\sqrt{2mE_z}}{\hbar}$$

$$X(x) = A_x \sin(k_x x) + B_x \cos(k_x x)$$

$$\rightarrow Y(y) = A_y \sin(k_y y) + B_y \cos(k_y y)$$

$$Z(z) = A_z \sin(k_z z) + B_z \cos(k_z z)$$

$$\text{boundary conditions : } X(0) = Y(0) = Z(0) = 0 ; X(l_x) = Y(l_y) = Z(l_z) = 0$$

$$\rightarrow B_x = B_y = B_z = 0 ; k_x l_x = n_x \pi, k_y l_y = n_y \pi, k_z l_z = n_z \pi$$

$$k_x = \frac{n_x \pi}{l_x}, k_y = \frac{n_y \pi}{l_y}, k_z = \frac{n_z \pi}{l_z}, \quad n_x, n_y, n_z = 1, 2, 3, \dots$$

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right) \dots \text{the normalized wave function}$$

$$E = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) = \frac{\hbar^2 k^2}{2m} \dots \text{the allowed energies}$$

$$\text{where wave vector } \mathbf{k} = (k_x, k_y, k_z) \quad ; \quad k^2 = k_x^2 + k_y^2 + k_z^2$$

If electrons were bosons, they would all settle down to the ground state.

But electrons are in fact identical fermions subject to the *Pauli Exclusion Principle*, so only two of them can occupy any given spatial state.

Each given states can regard as each block in k – space [Fig (5.1)],
three-dimensional k -space : k_x, k_y, k_z

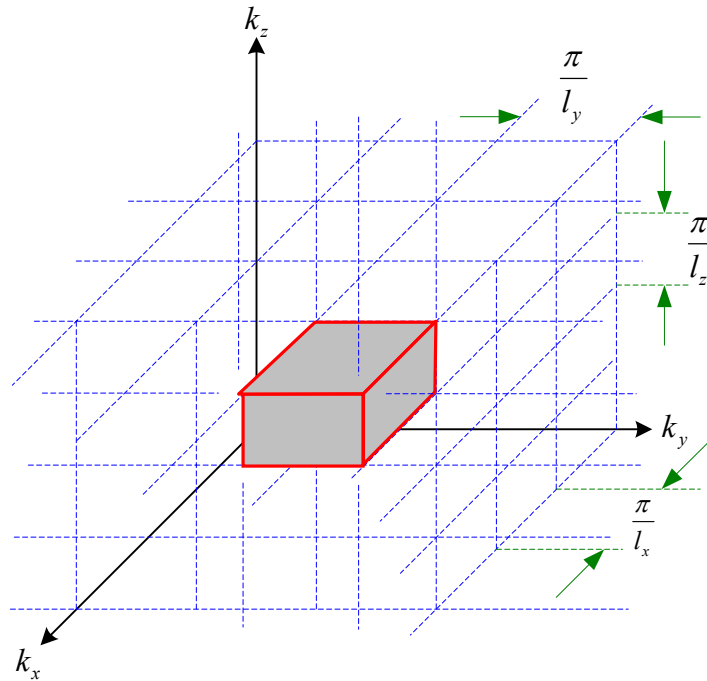
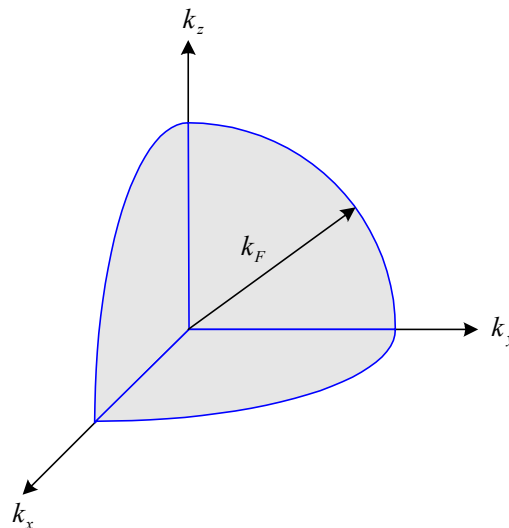


Fig (5.2) k-space shading , indicates one block,
one spatial state for every block

the volume of one block :

$$\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V}$$

These electrons will contains a pair of electrons fill up one octant of a sphere in k – space [Fig(5.2)], whose radius k_F is determined by



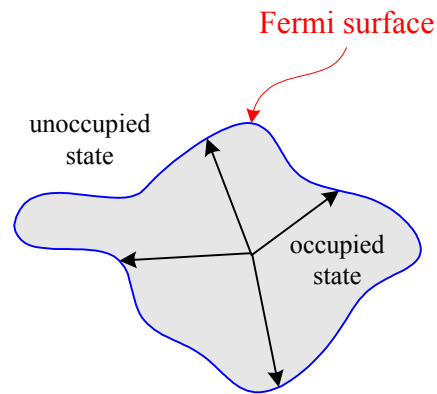
Fig(5.2) one octant of spherical
in k -space

$$\text{so } \frac{1}{8} \left(\frac{4}{3} \pi k_F^3 \right) = \frac{Nq}{2} \frac{\pi^3}{V} \quad ; \quad q : \text{each atom have } q \text{ free electrons}$$

N : total number of atoms ; N is enormous

→ $k_F = (3\rho\pi^2)^{1/3}$ with $\rho = \frac{Nq}{V}$: free electron density

Fermi surface : the boundary separating occupied and unoccupied states

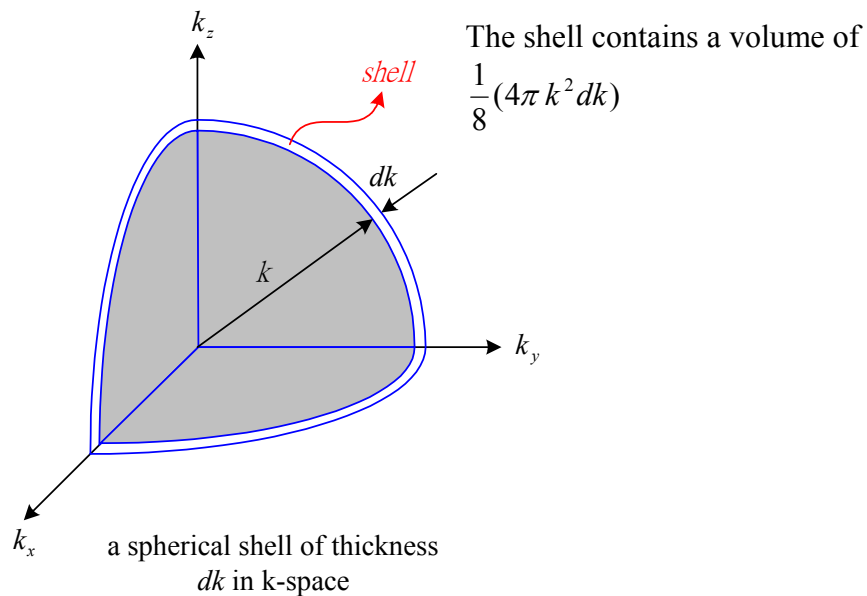


inside Fermi surface , quantum states been occupied by electrons(such as the shade)

Fermi Energy (E_F) : the maximum occupied energy

$$E_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} (3\rho\pi^2)^{2/3}$$

Total Energy



number of electron state of the shell

$$\frac{2(\frac{1}{2}\pi k^2 dk)}{\pi^3 / V} = \frac{V}{\pi^2} k^2 dk \dots\dots\dots(5.5)$$

each of states carries energy $\frac{\hbar^2 k^2}{2m}$, so the energy of the shell :

$$dE = \frac{\hbar^2 k^2}{2m} \frac{V}{\pi^2} k^2 dk$$

$$E_{total} = \frac{\hbar^2 V}{2\pi^2 m} \int_0^{k_F} k^4 dk = \frac{\hbar^2 (3\pi^2 Nq)^{5/3}}{10\pi^2 m} V^{-2/3}$$

This quantum mechanical energy , E_{total} , plays a role rather analogous to the internal thermal energy (U) of an ordinary gas .

If the box expands by an amount dV , E_{total} decreases and this show up as work done on the outside

from **thermodynamics first law**

$$dE = dQ + dW = dQ - PdV$$

adiabatic process $dQ = 0$

$$\rightarrow dE = -PdV$$

$$\rightarrow dE_{total} = -\frac{2}{3} \frac{\hbar^2 (3\pi^2 Nq)^{5/3}}{10\pi^2 m} V^{-5/3} dV = -\frac{2}{3} E_{total} \frac{dV}{V} \equiv (dW = -PdV)$$

$$P = \frac{2}{3} \frac{E_{total}}{V} = \frac{(3\pi^2)^{2/3} \hbar^2}{5m} \rho^{5/3} ;$$

P : **degeneracy pressure** (quantum exclusion pressure)

The reason why cold solid doesn't collapse

➤ **Band structure**

Bloch's theorem :

$$\text{to } -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x)\psi = E\psi$$

Consider a periodic potential in one dimension $V(x+a) = V(x) \dots\dots\dots(5.6)$

$$\text{then } \psi(x+a) = e^{iKa} \psi(x)$$

proof

let D be the displacement operator

$$Df(x) = f(x+a)$$

from equation (5.6), D commutes with Hamiltonian

$[D, H] = 0$, D and H have the same eigenfunctions

$$\Rightarrow D\psi = \lambda\psi \quad \Rightarrow \quad \psi(x+a) = \lambda\psi(x)$$

like any nonzero complex number, it can be expressed as an exponential

$$\lambda = e^{iKa}$$

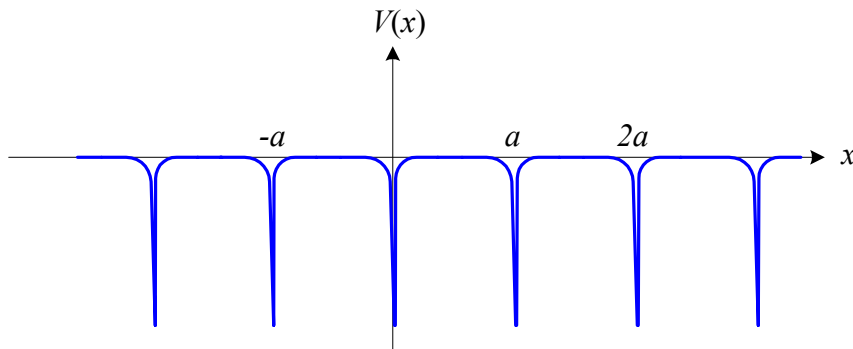
$$\text{so } \psi(x+a) = e^{iKa}\psi(x)$$

$$|\psi(x+a)|^2 = |\psi(x)|^2$$

$$\psi(x+Na) = \psi(x) \quad ; \quad N : \text{large number atoms}$$

$$\Rightarrow e^{iNKa}\psi(x) = \psi(x) \quad \Rightarrow \quad K = \frac{2\pi n}{Na}, \quad n = 0, 1, -1, 2, -2, \dots$$

$$\text{Dirac comb : } V(x) = -\alpha \sum_{j=0}^{N-1} \delta(x - ja)$$



one-dimension Dirac comb

solve wave function within a single cell $0 < x < a$, and $V = 0$

see former section 2.4

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad \Rightarrow \quad \frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2} E\psi = -k^2\psi$$

$$\psi(x) = A \sin(kx) + B \cos(kx) \quad , \quad k = \frac{\sqrt{2mE}}{\hbar}$$

from $\psi(x) = e^{-iKa} \psi(x+a)$

→ $\psi(x) = e^{-iKa} [A \sin k(x+a) + B \cos k(x+a)]$, $-a < x < 0$

from boundary conditions :

$$\begin{cases} \psi(0) = B = e^{-iKa} [A \sin(ka) + B \cos(ka)] \dots\dots\dots(5.7) \end{cases}$$

$$\begin{cases} \Delta\left(\frac{d\psi}{dx}\right)\Big|_{x=0} = kA - e^{-iKa} k[A \cos(ka) - B \sin(ka)] = -\frac{2m\alpha}{\hbar^2} B \dots\dots\dots(5.8) \end{cases} \star$$



review

from $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x)$

→ $-\frac{\hbar^2}{2m} \int_{-\epsilon}^{\epsilon} \frac{d^2\psi}{dx^2} dx + \int_{-\epsilon}^{\epsilon} V(x)\psi(x) dx = E \int_{-\epsilon}^{\epsilon} \psi(x) dx$

→ $\Delta\left(\frac{d\psi}{dx}\right)\Big|_{x=0} = \frac{2m}{\hbar^2} \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{\epsilon} V(x)\psi(x) dx$

$$= -\frac{2m}{\hbar^2} \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{\epsilon} \alpha \delta(x) \psi(x) dx = -\frac{2m\alpha}{\hbar^2} \psi(0) = -\frac{2m\alpha}{\hbar^2} B$$

pull equation (5.7) into (5.8)

so $[e^{iKa} - \cos(ka)][1 - e^{-iKa} \cos(ka)] + e^{-iKa} \sin^2(ka) = -\frac{2m\alpha}{\hbar^2 k} \sin(ka)$

→ $e^{iKa} - \cos(ka) - \cos(ka) + e^{-iKa} \cos^2(ka) + e^{-iKa} \sin^2(ka)$

$$= e^{iKa} - 2\cos(ka) + e^{-iKa}$$

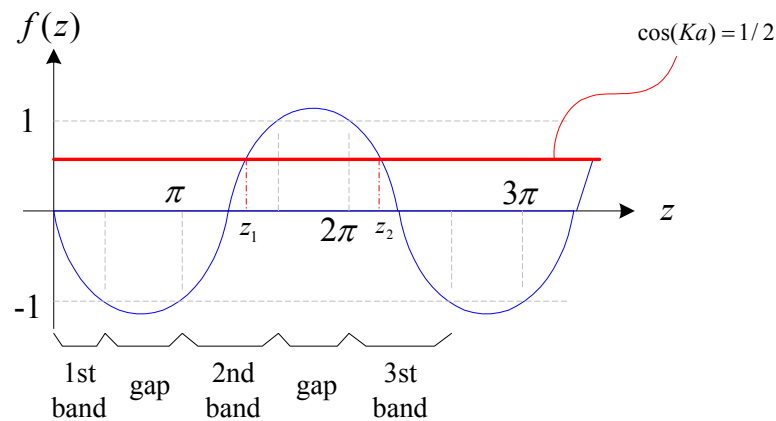
$$= 2\cos(Ka) - 2\cos(ka) = -\frac{2m\alpha}{\hbar^2 k} \sin(ka)$$

→ $\cos(Ka) = \cos(ka) - \frac{m\alpha}{\hbar^2 k} \sin(ka)$

let $z = ka$, $\beta = \frac{m\alpha a}{\hbar^2}$ → $\cos(Ka) = \cos(z) - \frac{\beta}{z} \sin(z)$

and let $f(z) = \cos(z) - \beta \frac{\sin(z)}{z}$ (5.9)

for $\beta = 1$, equation (5.9) plotted in Fig (5.3)



Fig(5.3) for $\beta = 1$, the graph of $f(z)$

→ $\cos(Ka) = \cos(z) - \frac{\sin(z)}{z}$

Because of $|\cos(Ka)| \leq 1$, see Fig(5.3) within the region of $f(z) \in (-1, +1)$ we can find various solutions “ k ” .

Then we can find various allowed energy .

example

$\cos(Ka) = \frac{1}{2}$, can find $z_1 = k_1 a$, $z_2 = k_2 a$, ...

and find $E_1 = \frac{\hbar^2 k_1^2}{2m}$ for the first energy band

$E_2 = \frac{\hbar^2 k_2^2}{2m}$ for the second energy band
 $\vdots$

now

(i) $\cos(Ka) = \cos \frac{2n\pi}{N}$ from $1(n=0)$ to $-1(n=N/2)$

there are $N/2$ solutions

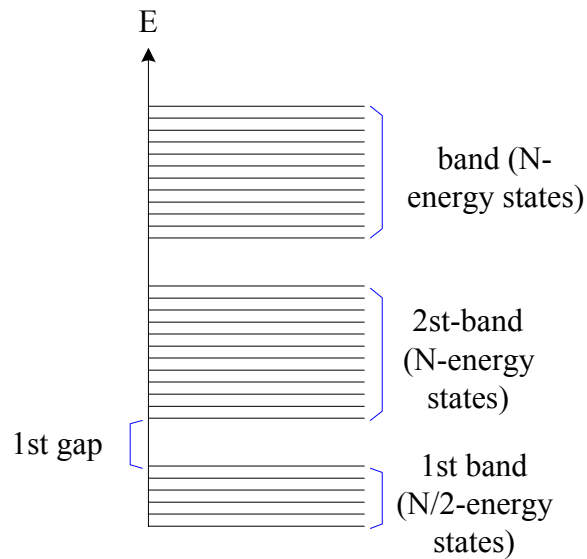
(ii) $\cos \frac{2n\pi}{N}$ from $-1(n=N/2)$ to $1(n=N-1)$ have $N/2$ solutions

there are $N/2$ solutions

so within the region of $f(z) \in (-1, +1)$;there are $(N/2 + N/2) = N$ solutions

(a) in first band , there are $N/2$ positive-energy states ,
 → and joined by negative-energy states

From Fig(5.3) (b) in higher band , there are N energy states
 (spatial states) and $2N$ completely states



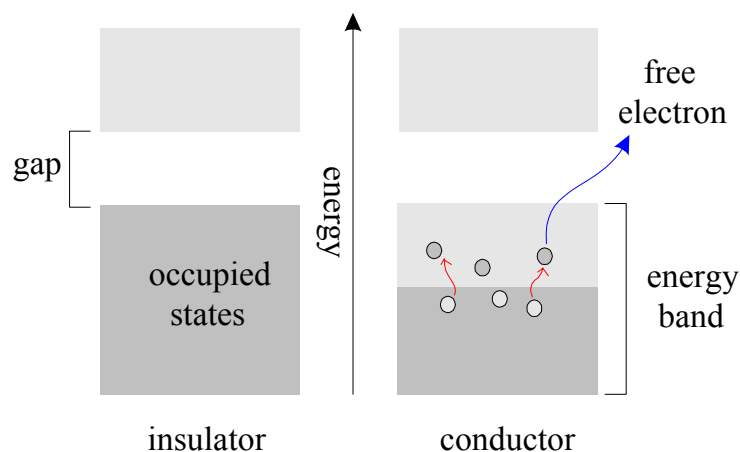
(iii) Assume there are N atoms with q “free” electrons for each atom .

then if $q = 1$, the electron in each atom fill the negative-energy of the first band

if $q = 2$, the two electrons in each atom fill up the first band
(namely all energy states be filled completely)

if $q = 3$, the first band be filled up and the second band be filled half
(namely there are $N/2$ energy states be filled in the second band)

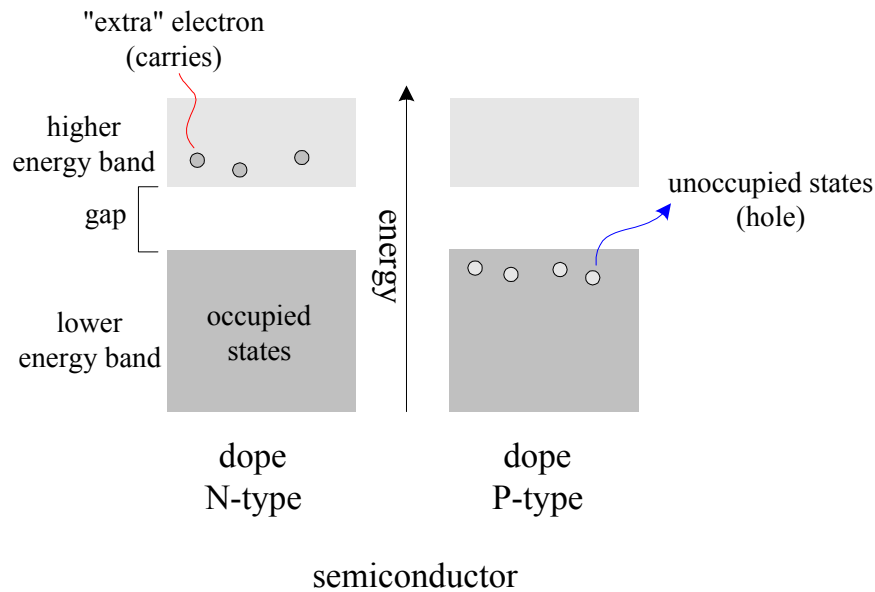
(iv) illustration of energy band in three materials



exert very small energy to insulator and conductor

insulator : no electrons still can leap to the higher band energy

conductor : partial electrons leap to the unoccupied state where are in the same energy band .



If we dope atoms (example phosphorous or aluminum) into an insulator (example silicon) , this puts some “ extra “ electrons into the next higher energy band , or create **holes** in the previously filled energy band .

5.4 Quantum statistical mechanics

For large number particles we could not keep track each one separately.

The **fundamental assumption** is that **in thermal equilibrium** every distinct state with the same total energy is equally probable.

The total energy is fixed by conservation of energy in **thermal equilibrium**.

The temperature T is a measure of the total energy

➤ General case

- (a) there are d_n distinct one-particle states with the same energy E_n
- (b) In thermal equilibrium , there are N total particles which
 there are N_1 particles with energy E_1 , N_2 particles with energy E_2 , ...
 N_n particles with energy E_n
 or say configuration $(N_1, N_2, \dots)$

example : (1 , 0 , 3, ...)

for energy 1 has one particle
 for energy 3 has three particles

the number of different ways to the configuration $(N_1, N_2, \dots)$ is

$$Q(N_1, N_2, \dots)$$

annotation

pick out M quantities from N quantities, the number of selection is

$$N(N-1)(N-2)\dots(N-M+1) = \frac{N!}{(N-M)!}$$

and we don't care the different permutations among these M quantities, so divide by $M!$

→ **Binomial coefficient** $\binom{N}{M} = \frac{N!}{M!(N-M)!}$

(i) particles are distinguishable

for first "bin" (N choose N_1)

pick out N_1 particles from N particles, → $\binom{N}{N_1} = \frac{N!}{N_1!(N-N_1)!}$

then the number of ways to put these N_1 particles into d_1 distinct states is

$$\frac{N! d_1^{N_1}}{N_1!(N-N_1)!}$$

for second "bin" ($N-N_1$ choose N_2)

similarly the number of ways is $\frac{(N-N_1)! d_2^{N_2}}{N_2!(N-N_1-N_2)!}$

so $Q(N_1, N_2, \dots) = \frac{N! d_1^{N_1}}{N_1!(N-N_1)!} \frac{(N-N_1)! d_2^{N_2}}{N_2!(N-N_1-N_2)!} \dots$

$$= N! \frac{d_1^{N_1}}{N_1!} \frac{d_2^{N_2}}{N_2!} \dots = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!}$$

(ii) particles are identical fermions

There is only one ways to pick out N_1 particles from N particles.

Only one particle can occupy any given state, there are d_1 states for first "bin"

then the number of ways is $\binom{d_1}{N_1} = \frac{d_1!}{N_1!(d_1 - N_1)!}$

so $Q(N_1, N_2, \dots) = \frac{d_1!}{N_1!(d_1 - N_1)!} \frac{d_2!}{N_2!(d_2 - N_2)!} \dots$

$$= \prod_{n=1}^{\infty} \binom{d_n}{N_n} = \prod_{n=1}^{\infty} \frac{d_n!}{N_n!(d_n - N_n)!}$$

(iii) particles are identical bosons

there is no restriction on the number of particles that can share the same one-particle state
for example the n th bin

$d_n = 3$ (three states) , $N_n = 4$ (four particles $\bullet$) ,
 $\times$ represent partitions (separated from states)

	state 1	partition	state 2	partition	state 3
Configuration 1	$\bullet \quad \bullet$	$\times$	$\bullet$	$\times$	$\bullet$
Configuration 2	$\bullet \quad \bullet \quad \bullet$	$\times$	$\bullet$	$\times$	

Then the configuration may be configuration1 or configuration 2 or others

We image “ $\bullet$ ” and “ $\times$ ” as positions ;

$\bullet$: the position been occupied by particle (N_n)
 $\times$: no particle occupy ($d_n - 1$)

total positions are $(N_n + d_n - 1) = 6$

Also there is only one ways to pick out N_n particles from N particles .

thus the number of permutations, which select N_n positions among $N_n + d_n - 1$ positions is

$$\binom{N_n + d_n - 1}{N_n} = \frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!}$$

so $Q(N_1, N_2, \dots) = \prod_{n=1}^{\infty} \binom{N_n + d_n - 1}{N_n} = \prod_{n=1}^{\infty} \frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!}$

- **The most probable configuration**
(find maximum Q with respect to change N_n)

$$\sum_{n=1}^{\infty} N_n = N \quad , \quad \sum_{n=1}^{\infty} N_n E_n = E$$

Lagrange multipliers :

the method to find the problem of maximizing a function F of several variables , subject to $f_1 = 0, f_2 = 0, \dots, f_n = 0$,

$$G(x_1, x_2, \dots, \lambda_1, \lambda_2, \dots) = F + \lambda_1 f_1 + \lambda_2 f_2 + \dots$$

$$\text{and } \frac{\partial G}{\partial x_n} = 0 \quad ; \quad \frac{\partial G}{\partial \lambda_n} = 0 \quad ;$$

It is noted that the maxima of Q and $\ln Q$ occur at the same point

$$\text{So we can let } G \equiv \ln(Q) + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]$$

(i) particles are distinguishable

$$G = \ln(N!) + \sum_{n=1}^{\infty} [N_n \ln(d_n) - \ln(N_n!)] + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]$$

Stirling's approximation :

$$\ln(z!) \approx z \ln(z) - z \quad \text{for } z \gg 1$$

$$G \approx \sum [N_n \ln(d_n) - N_n \ln(N_n) + N_n - \alpha N_n - \beta E_n N_n] + \ln(N!) + \alpha N + \beta E$$

$$\frac{\partial G}{\partial N_n} = \ln(d_n) - \ln(N_n) - \alpha - \beta E_n = 0$$

$$\rightarrow N_n = d_n e^{-(\alpha + \beta E_n)} \quad \dots\dots\dots(5.10)$$

(ii) particles are identical fermions

$$G = \sum_{n=1}^{\infty} \{ \ln(d_n!) - \ln(N_n!) - \ln[(d_n - N_n)!] \} + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]$$

$$G \approx \sum_{n=1}^{\infty} [\ln(d_n!) - N_n \ln(N_n) + N_n - (d_n - N_n) \ln(d_n - N_n) + (d_n - N_n) - \alpha N_n - \beta E_n N_n] + \alpha N + \beta E$$

$$\frac{\partial G}{\partial N_n} = -\ln(N_n) + \ln(d_n - N_n) - \alpha - \beta E_n = 0$$

$$\Rightarrow N_n = \frac{d_n}{e^{(\alpha + \beta E_n)} + 1} \dots\dots\dots(5.11)$$

(iii) particles are identical bosons

$$G = \sum_{n=1}^{\infty} \{ \ln[(N_n + d_n - 1)!] - \ln(N_n!) - \ln[(d_n - 1)!] \} + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]$$

$$G \approx \sum_{n=1}^{\infty} \{ (N_n + d_n - 1) \ln(N_n + d_n - 1) - (N_n + d_n - 1) - N_n \ln(N_n) + N_n - \ln[(d_n - 1)!] - \alpha N_n - \beta E_n N_n \} + \alpha N + \beta E$$

$$\frac{\partial G}{\partial N_n} = \ln(N_n + d_n - 1) - \ln(N_n) - \alpha - \beta E_n = 0$$

$$\Rightarrow N_n = \frac{d_n - 1}{e^{(\alpha + \beta E_n)} - 1} \approx \frac{d_n}{e^{(\alpha + \beta E_n)} - 1} \dots\dots\dots(5.12)$$

➤ Physical significance of α and β

As the case of a three-dimensional infinite square well (section 5.3)

$$E_k = \frac{\hbar^2}{2m} k^2$$

$$d_n \equiv d_k = \frac{\pi k^2 dk}{\pi^3 / V} = \frac{V}{2\pi^2} k^2 dk$$

$$N_k = d_k e^{-(\alpha + \beta E_k)}$$

for particles are distinguishable

$$N = \int_0^{\infty} N_k dk = \frac{V}{2\pi^2} e^{-\alpha} \int_0^{\infty} e^{-\frac{\beta \hbar^2 k^2}{2m}} k^2 dk$$

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

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

$$E = \frac{V}{2\pi^2} e^{-\alpha} \frac{\hbar^2}{2m} \int_0^\infty e^{-\frac{\beta\hbar^2 k^2}{2m}} k^4 dk = \frac{3V}{2\beta} e^{-\alpha} \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2}$$

$$\text{so } E = \frac{3N}{2\beta}$$

for the classical formula

$$\text{average kinetic energy of an atom at } T: \frac{E}{N} = \frac{3}{2} k_B T, \quad ,$$

k_B is Boltzmann constant

$$\beta = \frac{1}{k_B T}, \quad \beta \text{ is related to temperature}$$

with replacing α by the so-called **chemical potential**

$$\mu(T) = -\alpha k_B T$$

rewrite equation (5.10), (5.11), (5.12) for the most probable number of particles in a particular state with energy ϵ

$$n(\epsilon) = \begin{cases} e^{\frac{\epsilon - \mu}{k_B T}}, & \text{Maxwell - Boltzmann distribution} \\ \frac{1}{e^{\frac{\epsilon - \mu}{k_B T}} + 1}, & \text{Fermi - Dirac distribution} \\ \frac{1}{e^{\frac{\epsilon - \mu}{k_B T}} - 1}, & \text{Bose - Einstein distribution} \end{cases}$$

➤ The blackbody spectrum

Photons are identical bosons with spin 1 and massless particles .

(i) energy of a photon is $E = h\nu = \hbar\omega$

(ii) wave number $k = \frac{2\pi}{\lambda} = \frac{\omega}{c}$

(iii) only two spin states occur ($m = -1, 1$)

(iv) when temperature rises, the number of photons of per unit volume increases

from equation (5.12) the most probable occupation number for photons is

$$N_{\omega} = \frac{d_k}{e^{\hbar\omega/k_B T} - 1}$$

example for photons in a box of volume V ,

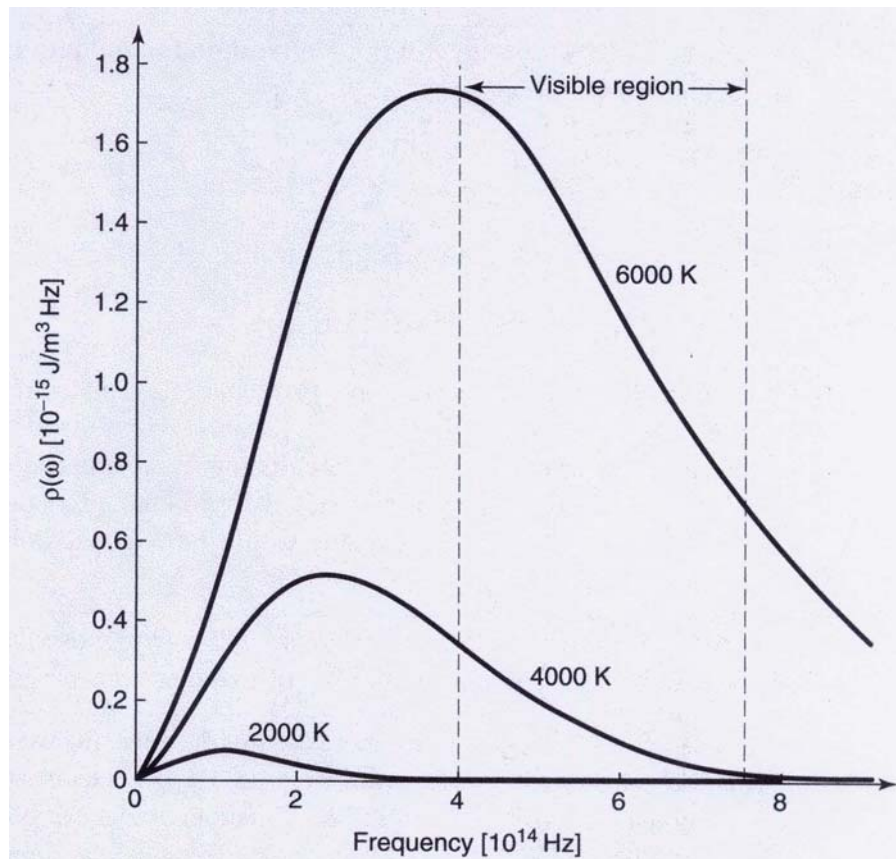
from equation (5.5)

$$d_k = \frac{V}{\pi^2} k^2 dk = \frac{V}{\pi^2} \left(\frac{\omega}{c} \right)^2 \frac{d\omega}{c} = \frac{V}{\pi^2 c^3} \omega^2 d\omega$$

$$\text{energy density } \frac{N_{\omega} \hbar \omega}{V} = \rho(\omega) d\omega$$

Planck's **blackbody spectrum** :

$$\rho(\omega) = \frac{N_{\omega} \hbar \omega}{V d\omega} = \frac{V \omega^2 d\omega / \pi^2 c^3}{e^{\hbar\omega/k_B T} - 1} \frac{\hbar \omega}{V d\omega} = \frac{\hbar \omega^3}{\pi^2 c^3 (e^{\hbar\omega/k_B T} - 1)}$$



Planck's formula for the blackbody spectrum for three different temperatures