

Quantum Ideal gas

(5)

Particles being identical, e.g., the absence of properties that prevent identifying them individually have more consequences in the realm of quantum mechanics than the classical case.

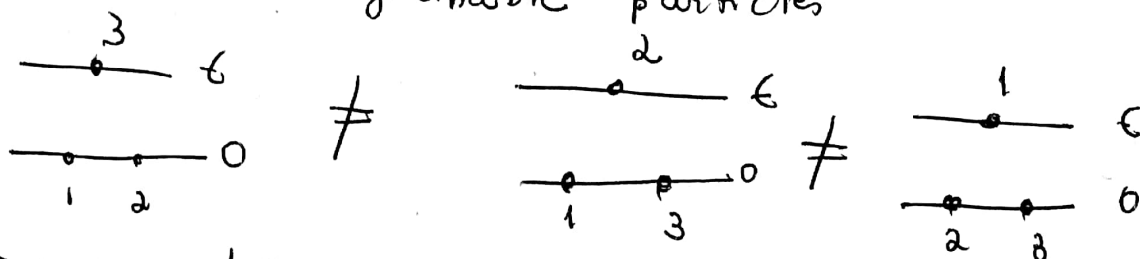
Although particles can be identical, classical mechanics, by following their individual (and well defined) trajectories in the phase space.

it is always possible to distinguish them in

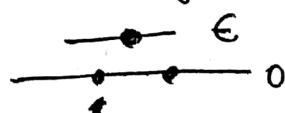
On the other hand, this procedure is not possible in the quantum mechanics anymore, in which the uncertainties relations among variable q, p forbid the achievement of unique/well defined individual trajectories.

In such case, there is no make sense to say "which particles are located in given microscopic state" but "how many particles belong to a given state". Above example describes this:

Localized/distinguishable particles



Identical/Indistinguishable particles



Thereby, permutations among identical particles yield at the same configuration and do not affect the result. This is quite different from the case of localized particles (see e.g. previous example).

More concretely, the wave function ~~has~~ has to take into account that

permutations of a given microscopic configuration will result in the same configuration. Let "P" the

permutation operation.
For example, if a microscopic configuration is specified by the position of particles,

$$P_{ij} \psi(r_1, r_2, \dots, r_i, \dots, r_j, \dots, r_N) \longrightarrow \psi(r_1, r_2, \dots, r_j, \dots, r_i, \dots, r_N)$$

$\swarrow$ positions which were exchanged

Since the operator P_{ij} should satisfy the property

$$P_{ij}^2 \psi(r_1, \dots, r_i, \dots, r_j, \dots, r_N) = \psi(r_1, \dots, r_i, \dots, r_j, \dots, r_N)$$

(its double application over ψ recovers the original result), it has the following set of eigenvalues.

$$P_{ij} \psi = \pm \psi$$

The signal "+" describes $\swarrow$ particles / systems that are symmetric under the exchange between two particles / , whereas

the signal (-) refers to systems whose wave function is anti-symmetric under the permutation between two particles. (9)

In nature, there are two types of particles in which wave functions are "totally" symmetric or "totally" anti-symmetric under the interchange of two particles. The former particles are called bosons and obey the statistics of Bose-Einstein, whereas the latter are named fermions and obey the statistics of Fermi-Dirac. It is worth mentioning that There are no particles of "intermediate"

Symmetry, e.g., their wave functions are neither ^{totally} symmetric nor totally anti-symmetric under the exchange of two particles. This kind of particles are not found in nature.

The symmetric and anti-symmetric wave functions are given by

$$\psi_S(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \text{perm} \begin{pmatrix} \psi_1(\vec{r}_1) & \dots & \psi_1(\vec{r}_N) \\ \langle \vec{r}_1 | \psi_1 \rangle & \dots & \langle \vec{r}_N | \psi_1 \rangle \\ \vdots & & \vdots \\ \psi_N(\vec{r}_1) & \dots & \psi_N(\vec{r}_N) \\ \langle \vec{r}_1 | \psi_N \rangle & \dots & \langle \vec{r}_N | \psi_N \rangle \end{pmatrix}$$

Where $\langle \vec{r}_i | \psi_j \rangle \equiv \psi_j(\vec{r}_i)$ denotes an individual wave function and "perm" attempts for all positive terms in the summation of terms.

Conversely, the antisymmetric wave function is given by the Slater determinant.

$$\psi_A(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \langle \vec{r}_1 | n_1 \rangle & \dots & \langle \vec{r}_1 | n_N \rangle \\ \vdots & & \vdots \\ \langle \vec{r}_N | n_1 \rangle & \dots & \langle \vec{r}_N | n_N \rangle \end{vmatrix}$$

An fundamental consequence is that the anti-symmetric vanishes when two fermions are in the same state. Such fundamental result is known as Pauli exclusion principle and has profound consequences, not only in the Quantum Mechanics, but also in the scope of statistical Mechanics, as shall be studied further. In such previous case (Slater determinant) states this can be seen as follows: If two are the same, then two of the lines are identical and the determinant is zero.

Statistical Mechanics of (non-interacting) Bosons and Fermions

The quantum state of an ideal gas is characterized by the quantum number $\{n_j\} \equiv \{n_1, n_2, \dots\}$ where n_j denotes the occupation of the j -th orbital [energy level] and other

quantities characterizing the state of the system (e.g. spin)].

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For bosons $n_j = 0, 1, 2, \dots$, in which each j -th orbital can be occupied by 0, 1, 2, ... bosons. On the other hand, for fermions $n_j = 0$ or 1. Note that if the orbital is specified by the energy and spin, it can be occupied by two identical fermions, provided their spins are different.

The energy associated to the quantum state $\{n_j\} = \{n_1, n_2, \dots\}$ is given by

$E\{n_j\} = \sum_j \epsilon_j n_j$, where ϵ_j attempts for the energy of the j -th orbital.

As we have discussed previously, since particles are identical, we are not able to know which particle occupy the j -th orbital, but only how many particles occupy it. Consequently, the canonical partition function can not be evaluated (most of cases), as will be shown as follows:

$$Z = Z(\tau, V, N) = \sum_{\{n_j\}} e^{-\beta \sum_j \epsilon_j n_j}$$

(summation over the orbital occupations
 $\sum_j n_j = N$)
 $\uparrow$ total particle number

Since particles are identical,
 $Z(T, V, N)$ are not evaluated (in general),
 due to the restriction ~~to~~ regarding
 the ^{total} particle number being constant.

In the case of localized ^(non-interacting) particles, we know
 that $Z(T, V, N) = \left(e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2} + e^{-\beta \epsilon_3} + \dots + e^{-\beta \epsilon_N} \right)^N$

Another way to find such expression is
 recalling that in the case of localized
 particles, the total number of ways ^{of}
 distributing n_1 particles in the orbital ϵ_1 ,
 n_2 particles in the orbital with energy ϵ_2
 and so on is given by $\frac{N!}{n_1! n_2! \dots n_N!}$

Since particles are localized (distinguishable),
 each permutation will correspond to a distinct
 configuration and has to be taken into
 account. Hence

$$Z = \sum_{n_1, n_2, \dots, n_N} \frac{N!}{n_1! n_2! \dots n_N!} e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots + n_N \epsilon_N)}$$

$$\begin{aligned} & (n_1 + n_2 + n_3 + \dots = N) \\ & \text{(multinomial theorem)} \\ & = \left(e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2} + \dots + e^{-\beta \epsilon_N} \right)^N, \text{ which} \end{aligned}$$

is the same result we have evaluated, corresponding to the canonical ensemble.

So that, we have to consider the study (ii) of system in the grand-canonical ensemble.

The grand-partition function is then given by

$$\begin{aligned}\Xi(T, V, \mu) &= \sum_{N=0}^{\infty} e^{\beta \mu N} Z(T, V, N) \\ &= \sum_{N=0}^{\infty} e^{\beta \mu (n_1 + n_2 + \dots + n_N)} \sum_{\substack{n_1, n_2, \dots, n_N \\ \sum_j n_j = N}} e^{-\beta \epsilon_1 n_1} \dots e^{-\beta \epsilon_N n_N}\end{aligned}$$

(I) (II)

We have to realize that (I) takes into account in a summation with the restriction $\sum_j n_j = N$ whereas (II) takes into account the summation over the restrictions. Therefore, it results in a non-restrictive summation.

Thereby

$$\Xi(T, V, \mu) = \sum_{n_1, n_2, \dots, n_N} e^{-\beta(\epsilon_1 - \mu)n_1} e^{-\beta(\epsilon_2 - \mu)n_2} \dots e^{-\beta(\epsilon_N - \mu)n_N}$$

↓ since particles are non-interacting

$$= \sum_{n_1} e^{-\beta(\epsilon_1 - \mu)n_1} \sum_{n_2} e^{-\beta(\epsilon_2 - \mu)n_2} \dots$$

For bosons, $n_j = 0, 1, \dots$ and

$$\Xi(T, V, \mu) = \prod_j \left\{ \sum_{n_j} e^{-\beta(\epsilon_j - \mu)n_j} \right\}$$

$$= \prod_j \left\{ 1 + e^{-\beta(\epsilon_j - \mu)} + e^{-2\beta(\epsilon_j - \mu)} + \dots \right\}$$

product over all
 $\tilde{N}$ orbitals

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

On the other hand, for fermions $n_j = 0$, or 1

and

$$\Xi(T, V, \mu) = \prod_j \left\{ 1 + e^{-\beta(\epsilon_j - \mu)} \right\}$$

The grand potential reads

$$\Phi(T, V, \mu) = -k_B T \ln \Xi(T, V, \mu)$$

$$= \mp k_B T \sum_j \ln \left(1 \pm e^{-\beta(\epsilon_j - \mu)} \right)$$

or even $-k_B T \left[\pm \sum_j \ln \left\{ 1 \pm e^{-\beta(\epsilon_j - \mu)} \right\} \right]$

where $(-) \leftrightarrow (+) \longrightarrow$ fermions

$$(+) \leftrightarrow (-) \longrightarrow \text{bosons}$$

Since $\langle n_j \rangle = \frac{\partial \Phi(T, V, \mu)}{\partial \mu}$ (mean particle in the grand-canonical ensemble)

$$= \sum_j \langle n_j \rangle_{FD, BE}, \quad \text{where}$$

$$\langle n_j \rangle_{FD} = \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1} \quad \text{and} \quad \langle n_j \rangle_{BE} = \frac{1}{e^{\beta(\epsilon_j - \mu)} - 1}$$

above $\langle n_i \rangle$'s are called Bose-Einstein and Fermi-Dirac probability distribution and will have a fundamental role for the main features about bosons and fermions.

For example, please note that $\langle n_i \rangle_{FD} = \frac{1}{e^{\beta(E_i - \mu)} + 1}$ is a quantity ranged between 0 and 1 and reflects the fact is forbidden more than one particle in the orbital i .

On the other hand, $\langle n_i \rangle_{BE} = \frac{1}{e^{\beta(E_i - \mu)} - 1}$ can be greater than 1, but since $\langle n_i \rangle_{BE} \geq 0$ it will imply that $e^{\beta(E_i - \mu)} - 1 \geq 0$ or even $e^{\beta\mu} \leq 1$. When $\mu = 0$, we have for a given $T \leq T_C$ the so-called phenomenon of "Bose-Einstein condensation".

Classical Limit

What happens when $\frac{\beta(E_i - \mu)}{e} \gg 1$ for all value of E_i ? Another way of answering / asking this question is by wondering

what happens when $e^{\beta G} \gg e^{\beta \mu}$ or even when $e^{\beta \mu} \ll 1$.

By looking to the $\langle n_f \rangle_{FD, BE}$ we have that

$$\langle n_f \rangle = \frac{1}{e^{\beta(G-\mu)} \pm 1} \xrightarrow[\text{BE}]{\text{FD}} \frac{e^{-\beta(G-\mu)}}{1 \pm e^{-\beta(G-\mu)}} \sim e^{-\beta(G-\mu)} \left(1 \mp e^{-\beta(G-\mu)} + \dots \right) \text{ or}$$

even $\langle n_f \rangle \approx e^{-\beta(G-\mu)}$

Note that above expression for $\langle n_f \rangle$ becomes identical for bosons and fermions and it reflects that the statistics is not important anymore. Therefore, it provides us the first "hint" that we are approaching to the classical limit.

Analogously, the logarithm of grand canonical partition function reads

$$\ln \Xi_{FD, BE} = \pm \sum_j \ln(1 \pm e^{-\beta(G-\mu)}) \approx \sum_j e^{-\beta(G-\mu)}$$

and also do not depend on the signals $\pm \rightarrow$ FD (fermions)

In the case of free-particles, whose spectrum of energy is given by (13)

$$\epsilon_j = \frac{\hbar^2 k_j^2}{2M} \quad \left(\text{where } \vec{k} = \frac{2\pi}{L} (n_x \hat{i} + n_y \hat{j} + n_z \hat{k}) \right)$$

and $n_x, n_y, n_z = 0, \pm 1, \pm 2, \dots$

and for $L \rightarrow \infty$ we have that

$$\ln \Omega_{FD, BE} \rightarrow \frac{V}{(2\pi)^3} \int d^3 \vec{k} e^{-\beta \left(\frac{\hbar^2 k^2}{2M} - \mu \right)}$$

By considering the spherical coordinates $\downarrow$ we have that ∞

$$= \frac{V}{(2\pi)^3} 4\pi e^{\beta\mu} \int_0^\infty k^2 e^{-\beta \frac{\hbar^2 k^2}{2M}}$$

$$\ln \Omega_{FD, BE} = \frac{V}{(2\pi)^3} e^{\beta\mu} \left(\frac{2\pi M}{\beta \hbar^2} \right)^{3/2} \quad \text{and}$$

$$\text{hence } \phi(T, V, \mu) = -(k_B T)^{5/2} V \left(\frac{2\pi M}{\hbar^2} \right)^{3/2} e^{\mu/k_B T}$$

which corresponds to the grand canonical potential of a classical ideal gas, revealing us (once again) that the limit $e^{\beta(\epsilon - \mu)} \gg 1$ corresponds, actually, to the classical limit.

This justifies the "ad-hoc" inclusion of the $N!$ in the partition function in our previous lectures (classical ideal gas)

In order to understand the validity of classical result, we resort to the

expression $\frac{\Sigma \langle n_i \rangle}{2} = - \left(\frac{\partial \phi}{\partial \mu} \right)_T =$

$$= (K_B T)^{3/2} V \left(\frac{2 \pi M}{h^2} \right)^{3/2} e^{\mu / K_B T}$$

since for $V \rightarrow \infty$ $\frac{\Sigma \langle n_i \rangle}{2} \longrightarrow N$ (average total particle number)

above expression can be rewritten as

$$\frac{N}{V} = (K_B T)^{3/2} \left(\frac{2 \pi M}{h^2} \right)^{3/2} e^{\mu / K_B T}.$$

or even under the following form

$$e^{\mu / K_B T} = \frac{h^3}{(2 \pi M K_B T)^{3/2}} \frac{N}{V}.$$

Since such limit is valid when $e^{\mu / K_B T} \ll 1$, it implies that $\rho \ll 1$ (low densities) or

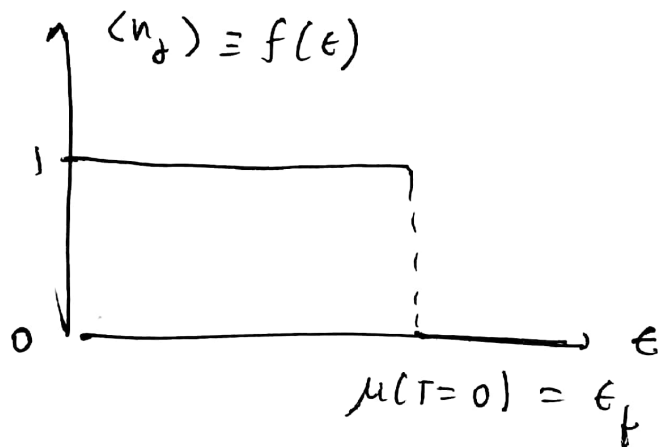
$T \gg 1$ (large temperatures), reinforcing

previous discussions about the validity of (classical) ideal gas regime.

Ground state for the free electron gas

(14)

In the case of electrons at zero temperatures (fermions with spin $1/2$), the occupation distribution is a step function in which all energy levels at $\epsilon < \epsilon_f$ are occupied and empty for $\epsilon > \epsilon_f$. The chemical potential at zero temperature is named Fermi energy. Schematically, $f(\epsilon) \equiv \langle n_j \rangle$ is given by



A direct (and remarkable) consequence of its fermionic nature is that due to the Pauli exclusion principle, electrons have to occupy energy levels higher than the ^(ground) fundamental level. Consequently, there will exist a pressure, even at $T=0$. This is another way of viewing above graph. If we have a gas of photons, ^(bosons) all particles will occupy the ground state at $T=0$ and the pressure will be zero.

Next we shall evaluate the main thermodynamic properties at $T=0$

$$N = \sum_j \langle n_j \rangle = \sum_j \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1} \quad (*)$$

Let $\epsilon_j = \frac{\hbar^2 k_j^2}{2M}$ the spectrum of energy
(as considered before) and $\vec{k}_j = \frac{2\pi}{L} (n_x \hat{i} + n_y \hat{j} + n_z \hat{k})$

[where j has been used for distinguishing from j]
(*) see a more detailed discussion in page 15-B

(we should note we are dealing with free particles in which $\vec{p}_i | \vec{k}_i \rangle = \hbar \vec{k}_i | \vec{k}_i \rangle$ and

$$\hat{H} = \frac{\vec{p}_i^2}{2M} \text{ in which } \hat{H} | \vec{k}_i \rangle = \frac{\hbar^2 k_i^2}{2M} | \vec{k}_i \rangle$$

from (*) N is then given by

$$N = \sum_{k_j} \frac{1}{e^{\beta(\frac{\hbar^2 k_j^2}{2M} - \mu)} + 1} \xrightarrow{L \rightarrow \infty} \left(\frac{L}{2\pi} \right)^3 \int \frac{d^3 k}{e^{\beta(\frac{\hbar^2 k^2}{2M} - \mu)} + 1}$$

By considering the spherical coordinate system
(as before) and using the fact that
there are two spin states for each value

of momentum, above integral becomes

$$N \rightarrow 2 \left(\frac{L}{2\pi} \right)^3 \int_0^{k_F} \frac{k^2}{e^{\beta(\frac{\hbar^2 k^2}{2M} - \mu)} + 1} dk$$

(15)

From 14th page, we see that all electrons will occupy energy levels until $E < E_F$. One can consider such assumption in terms of the vector $\vec{k}$ in which $\frac{\hbar^2 k^2}{2M} \leq \frac{\hbar^2 k_F^2}{2M}$ and

then
$$N \rightarrow 2 \left(\frac{L}{2\pi} \right)^3 \int_0^{k_F} k^2 dk, \quad \text{where}$$

$f(k)$ is a step function reading 1 for $k \leq k_F$ and 0 for $k > k_F$.

Hence
$$N = \frac{8\pi V}{(2\pi)^3} \frac{k_F^3}{3}$$

By performing similar calculations for the mean energy, we have that

$$\begin{aligned} U &= \sum_j \epsilon_j \langle n_j \rangle = \sum_j \epsilon_j \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1} = \\ &= 2 \sum_k \frac{\left(\hbar^2 k^2 / 2M \right)}{e^{\beta(\hbar^2 k^2 / 2M - \mu)} + 1} \xrightarrow{L \rightarrow \infty} \frac{2 \hbar^2}{2M} \left(\frac{L}{2\pi} \right)^3 \int d^3 \vec{k} \frac{k^2}{e^{\beta(\frac{\hbar^2 k^2}{2M} - \mu)} + 1} \\ &= \frac{\hbar^2 V}{2\pi^2 M} \frac{k_F^5}{5} \end{aligned}$$

Hence
$$U = \frac{3}{5} N E_F.$$

The mean energy is $\frac{3}{5} \times N \times \text{Fermi energy}$

Quantum states of a single particle.

15-B

Let us consider a particle (nonrelativistic) and

let $\underline{m}$ its mass. The Schrödinger equation describing the time evolution of the wave function,

$\psi(\vec{r}, t)$ is given by

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi, \text{ where } \psi(\vec{r}, t) = \tilde{\psi}(\vec{r}) e^{-i\omega t}$$

Where $\tilde{\psi}(\vec{r}) = A e^{i\vec{k} \cdot \vec{r}}$, where

$$\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

The wave function $\tilde{\psi}(\vec{r}) = A e^{i(k_x x + k_y y + k_z z)}$

$$= \psi_x(x) \psi_y(y) \psi_z(z)$$

$$\text{and } E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

Boundary Conditions

The above wave boundary condition $\tilde{\psi}$ must satisfy certain boundary conditions.

Accordingly, not all possible values of $\vec{k}$ are allowed, but only certain discrete

values. Hence, the corresponding energies of the particle are then also quantized.

One of boundary condition is the periodic one

$$\psi(x + L_x, y, z) = \psi(x, y, z)$$

$$\psi(x, y + L_y, z) = \psi(x, y, z)$$

$$\psi(x, y, z + L_z) = \psi(x, y, z)$$

For satisfying above conditions one has

$$k_x = \frac{2\pi}{L_x} n_x$$

$$k_y = \frac{2\pi}{L_y} n_y$$

$$k_z = \frac{2\pi}{L_z} n_z$$

Where n_x, n_y, n_z are positive, negative or zero and

$$E_{\vec{k}} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

$$= \frac{2\pi^2 \hbar^2}{m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

For $k_x, k_y, L_z \rightarrow \infty$ (large)

$$\sum_{\vec{k}} \rightarrow \frac{V}{(2\pi)^3} \int d^3 \vec{k}$$

Another boundary condition is obtained by considering a rectangular parallelepiped with walls located at $(x=0 \text{ and } x=L_x)$, $(y=0 \text{ and } y=L_y)$ and $(z=0 \text{ and } L_z)$.

One assumes that walls are perfectly reflecting, i.e., the potential energy is $U=0$ inside the box and $U=\infty$ outside the box.

Hence $\tilde{\psi} = 0$ } whenever $x=0 \text{ or } x=L_x$
 $y=0 \text{ or } y=L_y$
 $z=0 \text{ or } z=L_z$.

As previously, $\tilde{\psi}(\vec{r}) = \psi_x(x) \psi_y(y) \psi_z(z)$ and in order to attempt previous boundary conditions we have, for each component, something like that

$$\psi_x(x) = A e^{i k_x x} + B e^{-i k_x x} \quad \text{or}$$

equivalently $\psi_x(x) = \tilde{A} \cos k_x x + \tilde{B} \sin k_x x$ (also it is necessary to consider the reflecting component)

By imposing $\psi_x(0) = \psi_x(L_x) = 0 \Rightarrow$ one obtains that

$$k_x L_x = n_x \pi \quad (n_x = 1, 2, 3, \dots)$$

and hence $k_x = \frac{n_x \pi}{L_x}$, $k_y = \frac{n_y \pi}{L_y}$, $k_z = \frac{n_z \pi}{L_z}$

and also $\sum_{\vec{k}} \rightarrow \frac{V}{(2\pi)^3} \int d^3 k$

Completely degenerate and degenerate Ideal Fermi gas

A metallic solid is constituted by positive ions (located at the sites ^{belonging to} a given spatial structure) and electrons. Although positive ions are not resting, they vibrate around their equilibrium.

The quantization of normal modes gives rise to the phonons. Thereby, we can deal a metallic solid as composed of phonons and conducting electrons,

in which one can neglect interactions among electrons and phonons. Also, we shall consider the gas of free (non interacting) electrons. Although

collisions among electrons are possible, they are strongly hardly. This is due to the Pauli exclusion principle. Since electrons can occupy only empty orbitals, such a restriction, together the conservation of energy ^{drastically} reduces the ~~pos~~ occurrence of free orbitals in which the collision is possible.

In this lecture we shall investigate the properties of Fermi ideal gas beyond the ground state. The reliability of such analysis, by means of a linear treatment, is presented as follows.

The energy and pressure of an ideal Fermi gas at $T=0$ is given by

$$u = \frac{\hbar^2 v}{2\pi^2 M} \frac{k_F^5}{5}$$

Since $\frac{N}{V} = \frac{1}{3\pi^2} k_F^3$, we then have that

$$u = \frac{\hbar^2 v}{2\pi^2 M} \frac{1}{5} \left(3\pi^2 \frac{N}{V} \right)^{5/3}$$

Since $u = \frac{3}{2} N \epsilon_F$, the Fermi energy then reads

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

By defining the Fermi temperature as $T_F = \epsilon_F / k_B$,

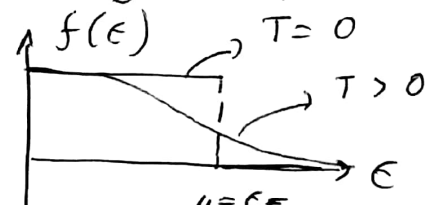
we have that

$$T_F = \frac{\hbar^2}{2M k_B} \left(3\pi^2 \frac{N}{V} \right)^{2/3}$$

The Fermi temperature T_F is high for several metals. For example for the lithium or sodium, $T_F \approx 10^4 \text{ K}$ (much higher than the ambient temperature). For the Cu, $T_F \approx 8 \cdot 10^4 \text{ K}$. Such values justify

the analysis of fermions (Fermi-Dirac) in the limit of low temperatures (beyond the $T=0$) in which $\frac{T}{T_F} \ll 1$. In such case, the

Fermi-Dirac distribution is slightly different to the $T=0$ case, consistent to the occupations of some energy levels beyond ϵ_F .



Mathematically, analysis consists of obtaining the following thermodynamic quantities: (2)

$$N = g \frac{V}{(2\pi)^3} \int d^3 k \frac{1}{\left[e^{\beta \left(\frac{\hbar^2 k^2}{2M} - \mu \right)} + 1 \right]}$$

$$U = g \frac{V}{(2\pi)^3} \int d^3 k \frac{\hbar^2 k^2}{2M} \frac{1}{\left[e^{\beta \left(\frac{\hbar^2 k^2}{2M} - \mu \right)} + 1 \right]}$$

where $g = 2$ (electrons of spin $\frac{1}{2}$ have degeneracy $= 2$)

Also $\vec{k} = k_x \hat{x} + k_y \hat{y} + k_z \hat{z}$ and

$$\begin{cases} k_x = \frac{2\pi}{L_x} n_x \\ k_y = \frac{2\pi}{L_y} n_y \\ k_z = \frac{2\pi}{L_z} n_z \end{cases}$$

$$n_x, n_y, n_z = 0, \pm 1, \pm 2, \pm 3, \dots$$

Due to the spherical symmetry of the spectrum of energy, it is more convenient to rewrite such above expressions in terms of energy (instead of the "wave number" vector). We then have that

$$\ln \Xi = g V \int_{-\infty}^{\infty} \mathcal{D}(\epsilon) \ln \left\{ 1 + e^{-\beta(\epsilon - \mu)} \right\} d\epsilon$$

$$N = g V \int_{-\infty}^{\infty} \mathcal{D}(\epsilon) f(\epsilon) d\epsilon, \quad (*)1$$

$$U = g V \int_0^{\infty} \epsilon \mathcal{D}(\epsilon) f(\epsilon) d\epsilon, \quad (*)2$$

where $f(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1}$

$$D(\epsilon) = \frac{1}{4\pi^2} \left(\frac{2M}{\hbar^2} \right)^{3/2} \epsilon^{1/2}$$

From Eqs. (*1) and (*2), we see that all of them have the form $I(T) = \int_0^\infty \frac{g(\epsilon)}{e^{\beta(\epsilon-\mu)} + 1} d\epsilon$,

where $g(\epsilon)$ does not depend on T nor μ .

For low temperatures, we are going to

show that

$$I(T) = \int_0^\mu g(\epsilon) d\epsilon + \frac{\pi^2}{6} g'(\mu) (k_B T)^2$$

By subtracting $I(T)$ from $I(0) = \int_0^\mu g(\epsilon) d\epsilon$,

We have that

$$I(T) - I(0) = \int_0^\mu \frac{g(\epsilon)}{e^{\beta(\epsilon-\mu)} + 1} d\epsilon + \int_\mu^\infty \frac{g(\epsilon)}{e^{\beta(\epsilon-\mu)} + 1} d\epsilon - \int_0^\mu g(\epsilon) d\epsilon$$

Above expression can be rewritten as

$$I(T) - I(0) = \int_\mu^\infty \frac{g(\epsilon)}{e^{\beta(\epsilon-\mu)} + 1} d\epsilon - \int_0^\mu \frac{g(\epsilon)}{1 - e^{-\beta(\epsilon-\mu)}} d\epsilon$$

By performing a change in the variables in the first and second integrals, we have that

$$I(T) - I(0) = k_B T \left[\int_0^\infty \frac{g(\mu + k_B T \xi)}{e^\xi + 1} d\xi + \int_{\beta\mu}^0 \frac{g(\mu - k_B T \xi)}{e^\xi + 1} d\xi \right]$$

(3)

In the limit of low temperatures ($\beta \ll 1$), one can approximate the upper limit in the second integral for infinity. Thus,

$$I(T) - I(0) = K_B T \left[\int_0^{\infty} \frac{g(\mu + K_B T \xi) - g(\mu - K_B T \xi)}{e^{\xi} + 1} d\xi \right]$$

By considering a linear contribution

$$g(\mu + K_B T \xi) \approx g(\mu) + g'(\mu) (K_B T \xi)$$

$$g(\mu - K_B T \xi) \approx g(\mu) - g'(\mu) (K_B T \xi)$$

and hence

$$I(T) - I(0) = 2 g'(\mu) (K_B T)^2 \int_0^{\infty} \frac{\xi}{e^{\xi} + 1} d\xi \quad \frac{\pi^2}{12}$$

Finally, $I(T) = I(0) + \frac{\pi^2}{6} g'(\mu) (K_B T)^2$ (linear)

By using above simplified expression, the expressions for N and u reads.

$$N = \frac{2}{4\pi^2} \left(\frac{2M}{h^2} \right)^{3/2} \cdot \frac{2}{3} \mu^{3/2} \left[1 + \frac{\pi^2}{6} \left(\frac{K_B T}{\mu} \right)^2 \right] \quad (*)3$$

$$u = \frac{2}{4\pi^2} \left(\frac{2M}{h^2} \right)^{3/2} \cdot \frac{2}{5} \mu^{5/2} \left[1 + \frac{15\pi^2}{24} \left(\frac{K_B T}{\mu} \right)^2 \right] \quad (*)4$$

hold valid for $K_B T \ll \mu$.

Experimentally, thermodynamic properties are measured for fixed N . This justifies to replace $(*)4$ and the specific heat C_V in terms of T, V, N .

Since $\epsilon_F = \mu = \frac{\hbar^2}{2M} \left(3\pi^2 \frac{N}{V} \right)^{2/3}$ and
from Eq. (3) we have that

$$\epsilon_F = \mu \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 \right]^{2/3}$$

or even

$$\mu = \epsilon_F \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 \right]^{-2/3}$$

For low temperatures, ^{in which we are also interested in the linear contribution,} one can replace

$\frac{k_B T}{\mu}$ for $\frac{k_B T}{\epsilon_F} = \frac{T}{T_F}$ and then we have that

$$\mu = \epsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right]$$

Above expression means that $\mu = \mu(T, V, N)$
since ϵ_F and T_F depend on V and N .

Eqs. (3) and (4) then becomes

$$\frac{U}{N} = \frac{3}{5} \mu \left[1 + \frac{15}{24} \pi^2 \left(\frac{k_B T}{\mu} \right)^2 \right] \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 \right]^{-1}$$

$$\frac{U}{N} = \frac{3}{5} \epsilon_F \left(1 + \frac{5\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right)$$

Note that for $T=0$, one recovers the
ground state result $U = \frac{3}{5} N \epsilon_F$.

Finally, the specific heat at constant
volume is given by:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} = \frac{3}{5} N E_F \cdot \frac{10}{12} \pi^2 \frac{T}{T_F^2}$$

(4)

or even $C_V = \frac{3}{2} N K_B \left(\frac{\pi^2}{3} \frac{T}{T_F} \right)$

Typically, $\frac{K_B T}{K_B T_F} \approx 10^{-2}$ and therefore

$C_V \ll$ classical result $\frac{3}{2} N K_B$. The lower electronic heat capacity is understood as follows:
 Since most of ^{electrons} occupy orbitals of lower energies, and are fully occupied, they do not participate in electron conduction.