Intro. to Electro-physics

Sommerfeld's model (1st)

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Drude vs. Sommerfeld models

- Drude model shows…
  - Good agreement with a Wiedemann-Franz law ($\kappa/\sigma = CT$)
  - discrepancy in specific heat $\left(c_V\right)$, mean-square electronic velocity $\left(v^2\right)$, thermopower $\left(Q\right)$ and etc.
- What is wrong about Drude's model?
  - Assumption that electronic velocity distribution follows the Maxwell-Boltzmann distribution **(X)**

    (∵ Electrons are Fermion that must obey Fermi-Dirac Distribution **(O)**!)

	Drude model	**Sommerfeld model**
Electronic velocity distribution	Maxwell-Boltzmann Distribution	Fermi-Dirac Distribution
Formula	$f_{MB}(\boldsymbol{v}) = n\left(\frac{m}{2k_BT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2k_BT}}$	$f_{FD}(\boldsymbol{v}) = \frac{1}{4}\left(\frac{m}{\pi\hbar}\right)^3 \frac{1}{\exp\left(\frac{\frac{1}{2}mv^2 - E_0}{k_BT}\right) + 1}$

The number of electrons per unit volume with velocities in the range of $d\boldsymbol{v}$ about $\boldsymbol{v}$: $f(\boldsymbol{v})\, d\boldsymbol{v}$

- **Sommerfeld model = Drude's free electron model + Fermi-Dirac distribution!**

Quantum theory of the electron gas

- Ground-state characteristics of an electron gas (at $T = 0\ (K)$)

  [Step 1] Find the energy levels available for N electrons in a volume V

  [Step 2] Fill these levels up in a manner consistent with the Pauli Exclusion Principle

- Characteristics of a single electron
  - A wavefunction for a single electron : $\psi(\boldsymbol{r})$
  - $\psi(\boldsymbol{r})$ satisfies time-independent Schrödinger's equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r}) = \mathscr{E}\psi(\boldsymbol{r}),\ \text{where } \mathscr{E} \text{ : an associated energy level with } \psi(\boldsymbol{r})$$

  (Q: Why is there no potential energy term?)

  - $\psi(\boldsymbol{r})$, i.e., the behavior of the electron in V, determined by **Boundary Condition!**

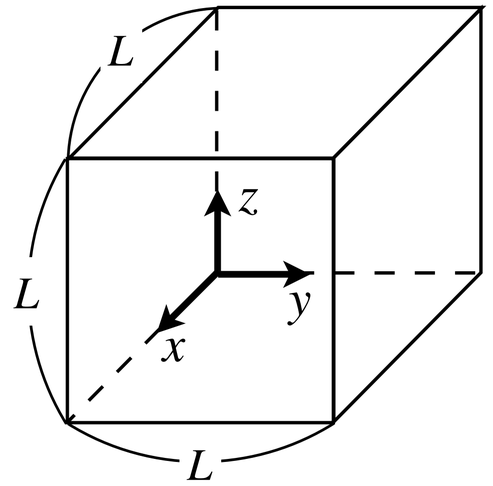
Boundary condition

T.I.S.E.

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r}) = \mathscr{E}\psi(\boldsymbol{r})$$

- Boundary condition for a single electron
  - In a sufficiently large metal, bulk properties **NOT** affected by its interface → Freedom in choosing B.C.!
  - Widely used "periodic B.C.":

$$\begin{cases} \psi(x, y, z+L) = \psi(x, y, z) \\ \psi(x, y+L, z) = \psi(x, y, z) \\ \psi(x+L, y, z) = \psi(x, y, z) \end{cases}$$



$L^3 = V \to \infty$

  - Solution to T.I.S.E. with the given B.C.:

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}},$$ where $\boldsymbol{k}$ is a wavevector associated with $\mathscr{E}(\boldsymbol{k}) = \frac{\hbar^2|\boldsymbol{k}|^2}{2m}$

Here, $1/\sqrt{V}$ obtained by using $\int_V \left|\psi_{\boldsymbol{k}}(\boldsymbol{r})\right|^2 d\boldsymbol{r} = \int_V P(\boldsymbol{r})\, d\boldsymbol{r} = 1$

Wavevector $\boldsymbol{k}$

Periodic B.C.

$$\begin{cases} \psi(x, y, z+L) = \psi(x, y, z) \\ \psi(x, y+L, z) = \psi(x, y, z) \\ \psi(x+L, y, z) = \psi(x, y, z) \end{cases}$$

- Meaning of $\boldsymbol{k}$
  - As a particle
    - Momentum of the electron : $\boldsymbol{p} = \hbar \boldsymbol{k}$
    - a velocity of the electron : $\boldsymbol{v} = \dfrac{\boldsymbol{p}}{m} = \dfrac{\hbar \boldsymbol{k}}{m}$
    - Kinetic energy : $\mathscr{E} = \dfrac{1}{2} m |\boldsymbol{v}|^2 = \dfrac{\hbar^2 |\boldsymbol{k}|^2}{2m}$
  - As a wave
    - $\boldsymbol{k}$: a wave-vector for the plane wave $e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ that propagates in a direction parallel to $\boldsymbol{k}$
    - $e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ = constant in any plane perpendicular to $\boldsymbol{k}$
    - $e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ = periodic along the line parallel to $\boldsymbol{k}$

      with a wavelength $\lambda = \dfrac{2\pi}{|\boldsymbol{k}|}$ — de Broglie wavelength
- How to obtain $\boldsymbol{k}$?
  - $\psi_{\boldsymbol{k}}(\boldsymbol{r}) \sim e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ satisfies the given B.C., only if

$$e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1 \longrightarrow \boxed{k_x = \frac{2\pi n_x}{L},\ k_y = \frac{2\pi n_y}{L},\ k_z = \frac{2\pi n_z}{L}}$$, where n_x, n_y, n_z: integers

The k-space

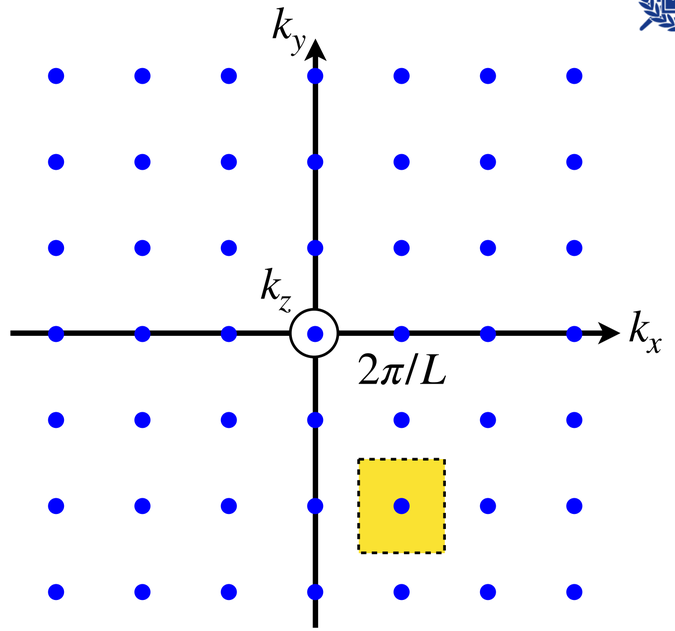
- The $\boldsymbol{k}$-space = momentum space = reciprocal space*
  - Allowed $\boldsymbol{k}$-vectors are given by integer multiples of $2\pi/L$ along three axes, i.e., $\boldsymbol{k} = \left(k_x, k_y, k_z\right) = \left(\frac{2\pi}{L}n_x, \frac{2\pi}{L}n_y, \frac{2\pi}{L}n_z\right)$
  - Number of allowed $\boldsymbol{k}$-points in the unit volume in $\boldsymbol{k}$-space:

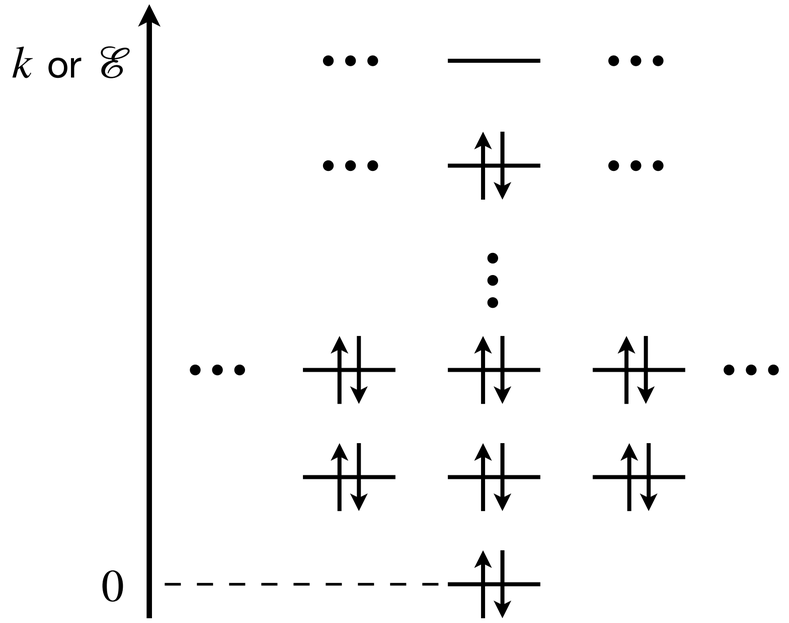
$$\frac{1}{(2\pi/L)^3} = \frac{L^3}{8\pi^3} = \frac{V}{8\pi^3}$$

  - At each $\boldsymbol{k}$ with the associated $\mathscr{E} = \frac{\hbar^2|\boldsymbol{k}|^2}{2m}$,

    only two electrons are allowed with two spin projection directions

    (∵ Pauli Exclusion Principle)





The Fermi sphere

- The Fermi wavevector $\boldsymbol{k}_F$
  - Within a sphere of a radius $\left|\boldsymbol{k}_F\right| = k_F$,

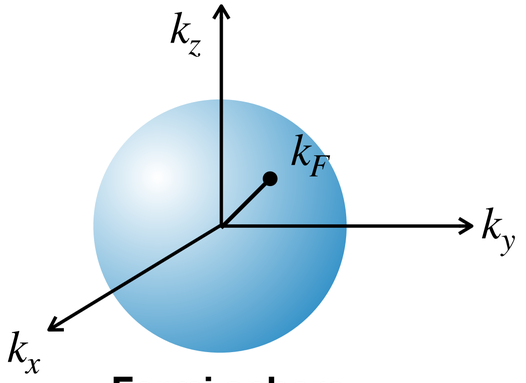
    the energy levels (or $\boldsymbol{k}$ values) are **occupied by N electrons;**

    Outside the sphere, the energy levels are **NOT occupied!**
  - Number of allowed $\boldsymbol{k}$ points within the Fermi sphere:

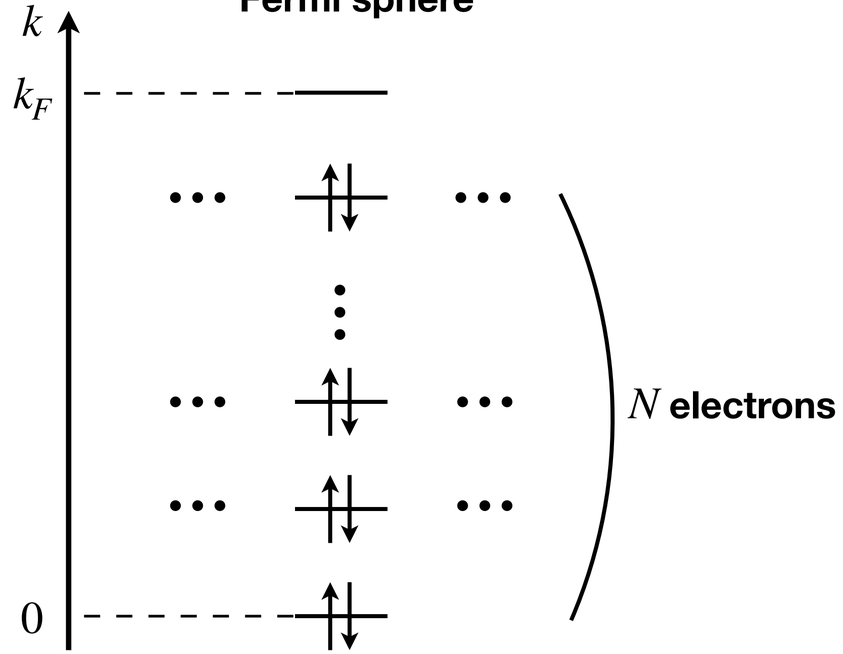
$$n_F \triangleq \left(\frac{4}{3}\pi k_F^3\right) \times \left(\frac{V}{8\pi^3}\right) \text{ (volume x density)}$$

  - In order for these points to accommodate N electrons,

$$N = 2 \times n_F = 2 \times \left(\frac{4}{3}\pi k_F^3 \times \frac{V}{8\pi^3}\right) \longrightarrow \boxed{\frac{N}{V} = \frac{k_F^3}{3\pi^2}} \longrightarrow$$



Fermi sphere



The ground state of N electrons within a volume V is formed by occupying all electron levels with $k < k_F$ and leaving all those with $k > k_F$ unoccupied

The Fermi parameters (1/2)

N vs. k_F

$$\frac{N}{V} = \frac{k_F^3}{3\pi^2}$$

- Electronic property vs. k_F
  - Recall the volume per conduction electron in real space, i.e.,

$$\frac{V}{N} = \frac{1}{n} = \frac{4\pi r_s^3}{3} \longrightarrow r_s = \left(\frac{3}{4\pi n}\right)^{\frac{1}{3}}$$

  - From the Fermi sphere,

$$n = \frac{N}{V} = \frac{k_F^3}{3\pi^2} = \frac{3}{4\pi r_s^3} \longrightarrow \boxed{k_F = \frac{3.63}{r_s/a_0}\ \left(\text{Å}^{-1}\right)}, \text{ where } a_0 = \frac{\hbar^2}{me} = 0.529\ \left(\text{Å}\right)$$

  - For most metallic elements, $r_s/a_0 = 2 \sim 6 \longrightarrow k_F \sim \text{Å}^{-1} \longrightarrow \boxed{\lambda_F = \frac{2\pi}{k_F} \sim \text{Å}}$

Metallic electron's wavelength by de Broglie wavelength

The Fermi parameters (2/2)

- Electronic property vs. k_F (contd.)
  - **Fermi velocity** (i.e., the velocity of the electron in the highest occupied state at the Fermi surface)

$$v_F = \frac{\hbar k_F}{m} = \frac{4.20}{r_s/a_0} \times 10^6 \text{ (m/s)}$$

c.f.) Thermal velocity of a classical particle, $v_{th} \approx \sqrt{\frac{3k_BT}{m}} \sim \begin{cases} 10^{2\sim3} \text{ (m/s) at } T = 298\,K \\ 0 \text{ (m/s) at } T = 0\,K \end{cases}$

Even at $T = 0\,K$, $v_F \approx 0.01c \gg v_{th} = 0$, where c : the speed of light

  - **Fermi Energy** (i.e., the kinetic energy of the electron in the highest occupied state)

$$\mathscr{E}_F = \frac{\hbar^2 k_F^2}{2m} = \left(\frac{e^2}{2a_0}\right)\left(k_F a_0\right)^2 = \frac{50.1}{\left(r_s/a_0\right)^2} \text{ (eV).} \quad \mathscr{E}_F = 1.5 \sim 15 \text{ (eV) for metals}$$

Ground state energy of an electron gas (1/2)

- **Ground state energy** of N electrons in a volume V

$$E = 2 \sum_{|\boldsymbol{k}|<|\boldsymbol{k}_F|} \frac{\hbar^2 |\boldsymbol{k}|^2}{2m} \quad \text{(within the Fermi sphere)}$$

  - Conversion of summation to integral

$$\sum_{\boldsymbol{k}} F(\boldsymbol{k}) = \frac{V}{8\pi^3} \sum_{\boldsymbol{k}} F(\boldsymbol{k}) \Delta\boldsymbol{k} = \frac{V}{8\pi^3} \int d\boldsymbol{k} F(\boldsymbol{k}) \longrightarrow \lim_{V\to\infty} \frac{1}{V} \sum_{\boldsymbol{k}} F(\boldsymbol{k}) = \frac{1}{8\pi^3} \int d\boldsymbol{k} F(\boldsymbol{k})$$

$$\Delta\boldsymbol{k} = \frac{8\pi^3}{V}$$

: The volume in a $\boldsymbol{k}$-space per allowed $\boldsymbol{k}$ value

$$\lim_{V\to\infty} (\Delta\boldsymbol{k} \to 0)$$

In a macroscopically large volume ($V \to \infty$),

$F(\boldsymbol{k})$ does not significantly vary over distances of order $\frac{2\pi}{k}$ in $\boldsymbol{k}$-space.

Ground state energy of an electron gas (2/2)

$$\lim_{V\to\infty}\frac{1}{V}\sum_{\boldsymbol{k}}F(\boldsymbol{k})=\frac{1}{8\pi^3}\int d\boldsymbol{k}F(\boldsymbol{k})$$

- Ground state energy of N electrons in a volume V (contd.)

$$E=2\sum_{k<k_F}\frac{\hbar^2k^2}{2m}\longrightarrow\frac{E}{V}=\frac{2}{8\pi^3}\int_{k<k_F}d\boldsymbol{k}\frac{\hbar^2k^2}{2m}=\frac{1}{4\pi^3}\int_{k<k_F}\left(4\pi k^2dk\right)\frac{\hbar^2k^2}{2m}$$

- Energy per unit volume and per electron:

$\frac{E}{V}=\frac{1}{\pi^2}\frac{\hbar^2k_F^5}{10m}$. And since $n=\frac{N}{V}=\frac{k_F^3}{3\pi^2}$,

$$\frac{E/V}{N/V}=\frac{E}{N}=\frac{3}{10}\frac{\hbar^2k_F^2}{m}=\frac{3}{5}\mathscr{E}_F$$

Energy per electron

- Overall energy at $T=0\ (K)$,

$$\begin{cases}\text{Electron gas: } \mathscr{E}_F=\frac{\hbar^2k_F^2}{2m}=1.5\sim15\ (eV)\\ \text{Classical gas: } \mathscr{E}_{th}=\frac{3}{2}k_BT=0\ (eV)\end{cases}$$

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Sommerfeld's model (2nd)

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Excited state of an electron gas

- Excited state of N-electronic system at $T > 0\ (K)$
  - The property of the system calculated by averaging such a property over all possible states
  - The probability of the system being in a state i

$$p_N(E_i) \propto e^{-\frac{E_i}{k_B T}} = \frac{1}{Q} e^{-\frac{E_i}{k_B T}}, \text{ where } Q \triangleq \sum_i e^{-\frac{E_i}{k_B T}}$$

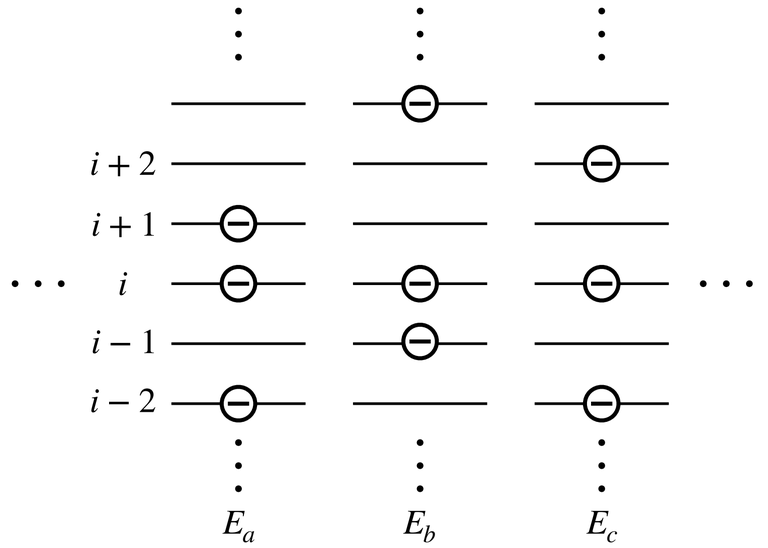
  - Partition function

$$Q = \sum_{i=1} e^{-\frac{E_i}{k_B T}} \triangleq e^{-\frac{F_N}{k_B T}}, \text{ where } F_N = U - TS$$

$$\therefore p_N(E_i) = e^{-\frac{E_i - F_N}{k_B T}}$$

- F_N: The Helmholtz free energy, the thermodynamic potential that measures the useful work obtainable from a closed thermodynamic system at a given temperature T
- U : Internal energy
- S : Entropy

Derivation of Fermi-Dirac distribution (1/4)



- **Electronic state** for the N-electronic system
  - In each electronic state, N single-electron levels are filled in a way consistent with the Pauli Exclusion principle
  - A useful quantity to define : f_i

- **The probability that an electron occupies the i-th level of N-electronic system:**

$$(1)\ f_{i,N} \triangleq \sum_{\alpha} p_N\left(E_{\alpha,N}\right), \quad (\alpha = 1,2,\cdots)$$

$E_{\alpha,N}$: The energy of α-th N-electronic state whose i-th level is occupied

$\sum_{\alpha}$: Sum of probabilities for the system being in any of such states $(\alpha = 1,2,\cdots)$

$$(2)\ f_{i,N} \triangleq 1 - \sum_{\beta} p_N\left(E_{\beta,N}\right), \quad (\gamma = 1,2,\cdots)$$

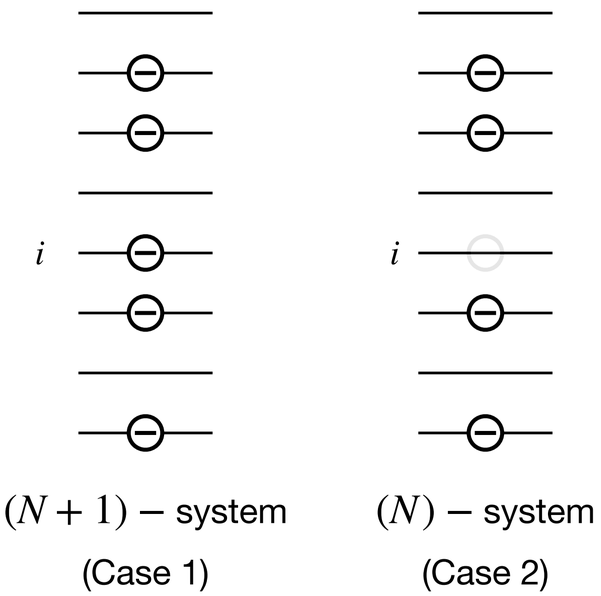
$E_{\beta,N}$: The energy of β-th N-electronic state whose i-th level is **NOT** occupied

$\sum_{\beta}$: Sum of probabilities for a system being in any of such states $(\beta = 1,2,\cdots)$

Derivation of Fermi-Dirac distribution (2/4)

- **Electronic state** for the $(N+1)$-electronic system
  - $(N+1)$-electronic states **having** an electron in their i-th level ···*(case 1)*

    = N-electronic states **without** an electron in their i-th level, while leaving all the other levels **unaltered** ···*(case 2)*
  - Energy of the states for case (1) $\triangleq E_{\alpha,N+1}$
  - Energy of the i-th level $\triangleq \mathscr{E}_i$
  - Energy of the states for case (2) $= E_{\alpha,N+1} - \mathscr{E}_i$



- **The probability that an electron occupies the i-th level of N-electronic system:**

$$(3)\ f_{i,N} = 1 - \boxed{\sum_{\alpha} p_N \left(E_{\alpha,N+1} - \mathscr{E}_i\right)}$$

$E_{\alpha,N+1}$: The energy of α-th $(N+1)$**-electronic state** whose i-th level is occupied

$E_{\alpha,N+1} - \mathscr{E}_i$: The energy of α-th N**-electronic state** whose i-th level is **NOT** occupied

Derivation of Fermi-Dirac distribution (3/4)

$$p_N(E) = \exp\left(-\frac{E - F_N}{k_B T}\right)$$

- **The probability that an electron occupies the i-th electron level of the system:**

$$f_{i,N} = 1 - \sum_{\alpha} p_N\left(E_{\alpha,N+1} - \mathscr{E}_i\right)$$

$E_{\alpha,N+1}$: The energy of α-th $(N+1)$-**electronic state** whose i-th level is occupied

$E_{\alpha,N+1} - \mathscr{E}_i$: The energy of α-th N-**electronic state** whose i-th level is **NOT** occupied

Here, $P_N\left(E_{\alpha,N+1} - \mathscr{E}_i\right) = \exp\left(-\frac{\left(E_{\alpha,N+1} - \mathscr{E}_i\right) - F_N}{k_B T}\right)$

$$= \exp\left(-\frac{E_{\alpha,N+1} - F_{N+1}}{k_B T}\right) \cdot \exp\left(\frac{\mathscr{E}_i - \left(F_{N+1} - F_N\right)}{k_B T}\right)$$

$$= p_{N+1}\left(E_{\alpha,N+1}\right) \cdot \exp\left(\frac{\mathscr{E}_i - \mu}{k_B T}\right), \text{ where } \boxed{F_{N+1} - F_N \triangleq \mu}$$

Chemical potential

: The change of free energy due to a change of the particle number

$$\therefore f_{i,N} = 1 - \exp\left(\frac{\mathscr{E}_i - \mu}{k_B T}\right) \sum_{\alpha} p_{N+1}\left(E_{\alpha,N+1}\right) = 1 - \exp\left(\frac{\mathscr{E}_i - \mu}{k_B T}\right) f_{i,N+1}$$

Derivation of Fermi-Dirac distribution (4/4)

- **The probability that an electron occupies the i-th electron level of the system:**

If $N \gg 10^{22}\,\mathrm{cm}^{-3}$, the change in a probability by the adding an extra electron is **negligible**!

$$f_{i,N} = 1 - \exp\left(\frac{\mathscr{E}_i - \mu}{k_B T}\right) f_{i,N+1} \xrightarrow[\lim N\to\infty]{} f_{i,N} \approx 1 - \exp\left(\frac{\mathscr{E}_i - \mu}{k_B T}\right) f_{i,N}$$

$$\therefore f_i = \frac{1}{\exp\left(\frac{\mathscr{E}_i - \mu}{k_B T}\right) + 1}$$

* The term N is dropped since N-dependence is considered in μ

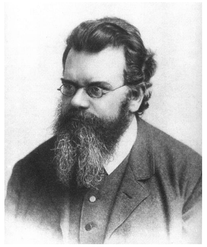
Fermi-Dirac distribution

- The probability of the electron occupying the i-th level of an N-electronic system
- The mean number of electrons that are in i-th level:

$$\bar{n}_i \triangleq 0 \times (1 - f_i) + 1 \times f_i = f_i \longrightarrow \sum_i \bar{n}_i = \sum_i \frac{1}{\exp\left(\frac{\mathscr{E}_i - \mu}{k_B T}\right)} = N$$

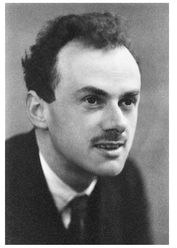
Basics of quantum statistics

- Quantum statistics
  - determines **how particles occupy a system** that consists of several energy levels
  - Three major types:
    - **Maxwell-Boltzmann** stats for **distinguishable** particles
    - **Fermi-Dirac** stats for **indistinguishable** particles that obey exclusion principle
    - **Bose-Einstein** stats for **indistinguishable** particles that DON'T obey exclusion principle

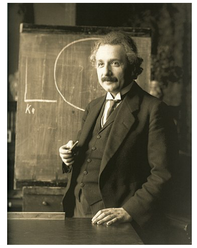

Ludwig Boltzmann
(Austria)
1844-1906


James C. Maxwell
(United Kingdom)
1831-1879


Enrico Fermi
(Italy)
1901-1954


Paul Dirac
(England)
1902-1984

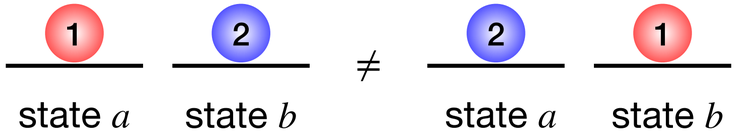

Satyendra N. Bose
(India)
1894-1974


Albert Einstein
(Germany)
1879-1955

- Wavefunction for two particles
  - Distinguishable

$$\psi\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)=\phi_a\left(\boldsymbol{r}_1\right)\phi_b\left(\boldsymbol{r}_2\right)\neq\phi_a\left(\boldsymbol{r}_2\right)\phi_b\left(\boldsymbol{r}_1\right)\quad\begin{cases}\text{particle } 1 \text{ in state } a\\ \text{particle } 2 \text{ in state } b\end{cases}$$

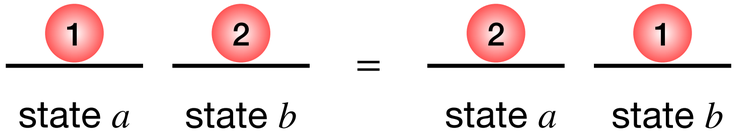
Classical particles



  - Indistinguishable

$$\psi\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)=\begin{cases}\dfrac{1}{\sqrt{2}}\left(\phi_a\left(\boldsymbol{r}_1\right)\phi_b\left(\boldsymbol{r}_2\right)+\phi_b\left(\boldsymbol{r}_1\right)\phi_a\left(\boldsymbol{r}_2\right)\right)\triangleq\psi_B\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right) & \cdots \text{ Boson}\\ \dfrac{1}{\sqrt{2}}\left(\phi_a\left(\boldsymbol{r}_1\right)\phi_b\left(\boldsymbol{r}_2\right)-\phi_b\left(\boldsymbol{r}_1\right)\phi_a\left(\boldsymbol{r}_2\right)\right)\triangleq\psi_F\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right) & \cdots \text{ Fermion}\end{cases}$$

Quantum mechanical particles



Implications of Pauli Exclusion principle?

$$\begin{cases} \psi_B(\boldsymbol{r}_1,\boldsymbol{r}_2) \triangleq \frac{1}{\sqrt{2}}\left(\phi_a(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2)+\phi_b(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2)\right) \\ \psi_F(\boldsymbol{r}_1,\boldsymbol{r}_2) \triangleq \frac{1}{\sqrt{2}}\left(\phi_a(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2)-\phi_b(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2)\right) \end{cases}$$

- Pauli exclusion principle
  - **Fermions** cannot occupy the same quantum state!
  - If states a and b are the same,

$$\begin{cases} \psi_B(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{\sqrt{2}}\left(\phi_a(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2)+\phi_a(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2)\right) = \sqrt{2}\phi_a(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2) \neq 0 \\ \psi_F(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{\sqrt{2}}\left(\phi_a(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2)-\phi_a(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2)\right) = 0 \end{cases} \longrightarrow \text{No wavefunction exists for such a case!}$$

- General expression for the wavefunctions of Boson and Fermion

$$\begin{cases} \psi(\boldsymbol{r}_1,\boldsymbol{r}_2) = \psi(\boldsymbol{r}_2,\boldsymbol{r}_1) & \cdots \text{ Symmetric under particle exchange (Bosons)} \\ \psi(\boldsymbol{r}_1,\boldsymbol{r}_2) = -\psi(\boldsymbol{r}_2,\boldsymbol{r}_1) & \cdots \text{ Anti-symmetric under particle exchange (Fermions)} \end{cases}$$

- **Number of allowed particles per state** vs. type of particles

Type of particles		Particles per state	Statistics
Distinguishable		Unlimited	Maxwell-Boltzmann
Indistinguishable	Boson	Unlimited	Bose-Einstein
	Fermion	**Only one**	Fermi-Dirac