Chapter 5

Metals and Semiconductors
(金属与半导体)

Outline

- **Chapter 5.1** Free-Electron Theory of Metals (金属自由电子论)
- **Chapter 5.2** Electron Theory of Semiconductors (半导体电子论)

Outline

- **Chapter 5.1** Free-Electron Theory of Metals (金属自由电子论)
- **Chapter 5.2** Electron Theory of Semiconductors (半导体电子论)

Objectives

- To learn the basic properties of **metals**.
- To learn the **classical free-electron theory**.
- To understand the **quantum free-electron theory**.

Chapter 5.1: Free-Electron Theory of Metals (金属自由电子论)

➢ Metals (金属)

❖ The characteristics of metals:

- **High electrical conductivity (高电导率):** σ

@Room Temperature	Metals	Semiconductors	Insulators
$\sigma\ (\Omega^{-1}m^{-1})$	$10^{6}-10^{8}$	$10^{-4}-10^{5}$	10^{-16}

- **Ohm's law (欧姆定律):** $J=\sigma E$

(J denotes the current density and E the electric field.)

➢ Metals (金属)

❖ The characteristics of metals:

- **High thermal conductivity (高热导率):** $\boldsymbol{\kappa}$

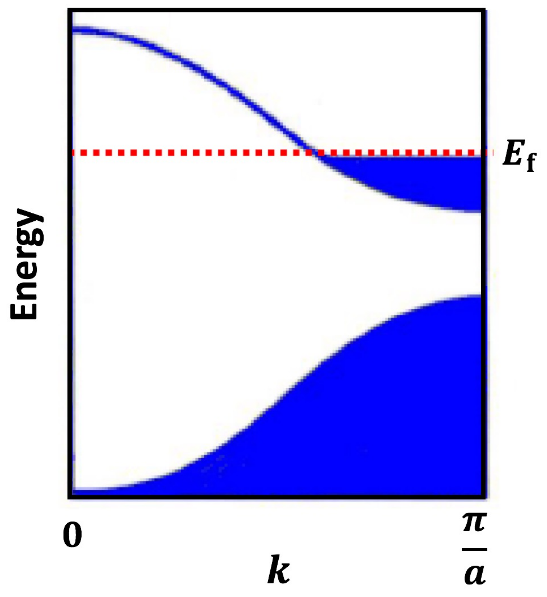
Wiedemann-Franz Law (维德曼-夫兰兹定律):

$$\frac{\boldsymbol{\kappa}}{\boldsymbol{\sigma}} = \boldsymbol{LT} \qquad \left[\boldsymbol{L} = \frac{\pi^2}{3}\left(\frac{k_{\mathrm{B}}}{e}\right)^2 \text{ denotes the Lorenz number and } \boldsymbol{T} \text{ the temperature}\right]$$

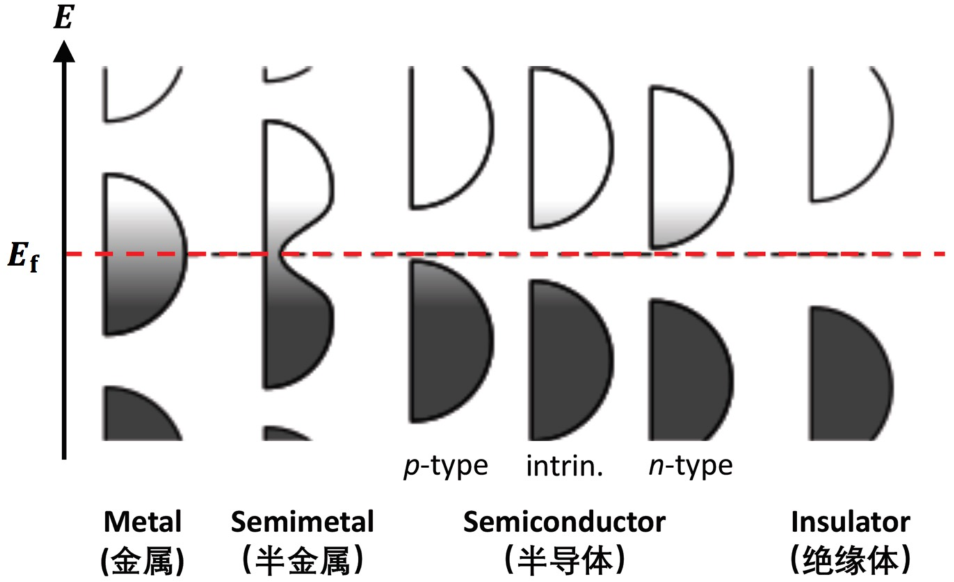
- **Temperature-independent charge-carrier density (载流子密度与温度无关).**

➢ Metals (金属)

❖ From the standpoint of **band theory**, a metal is a conductor of which **the conduction band is partially occupied by electrons**.



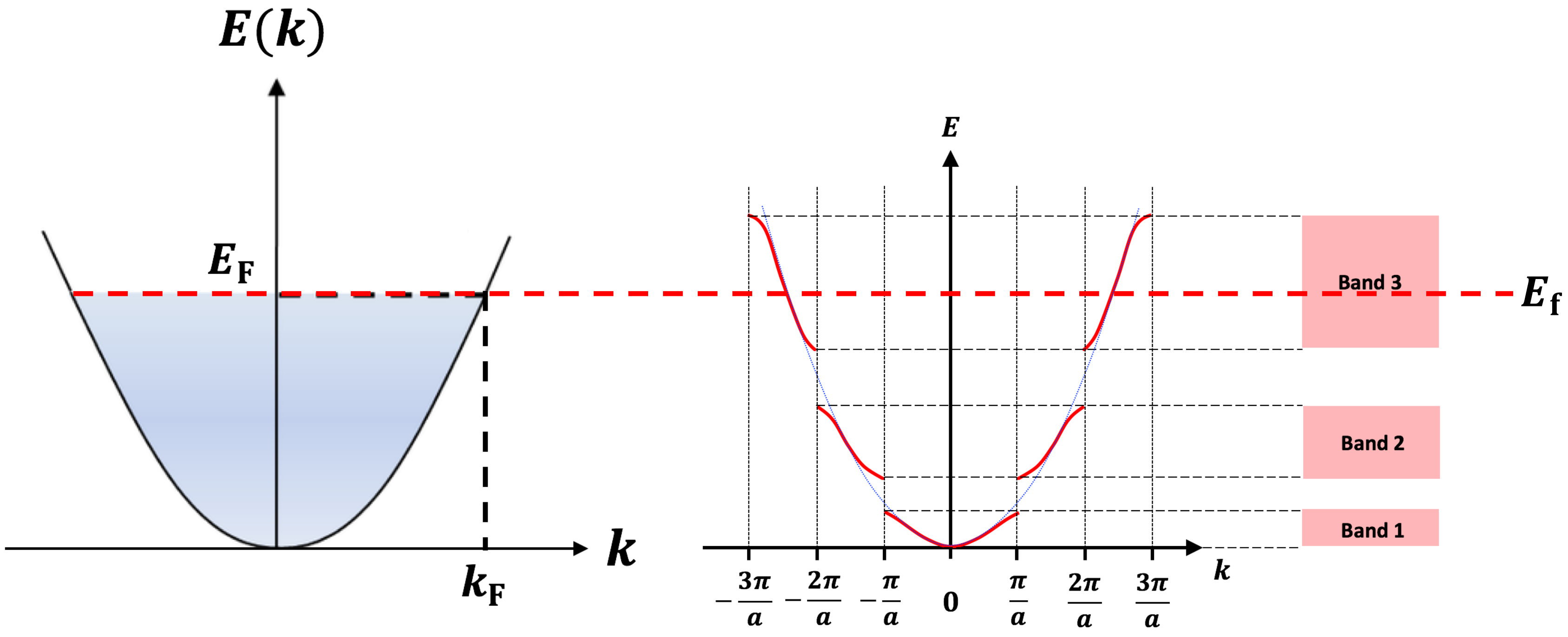
The band dispersion of a metal.



DOS and E_f for conductors and nonconductors.

➢ Metals (金属)

❖ Since the Fermi level is within band of metals (usually far from band gaps), electrons in metals can be described by the **free-electron theories (自由电子论)**.



Metals (金属)

- The free-electron theories in history:

    - **Classical free-electron theory (经典自由电子论)**

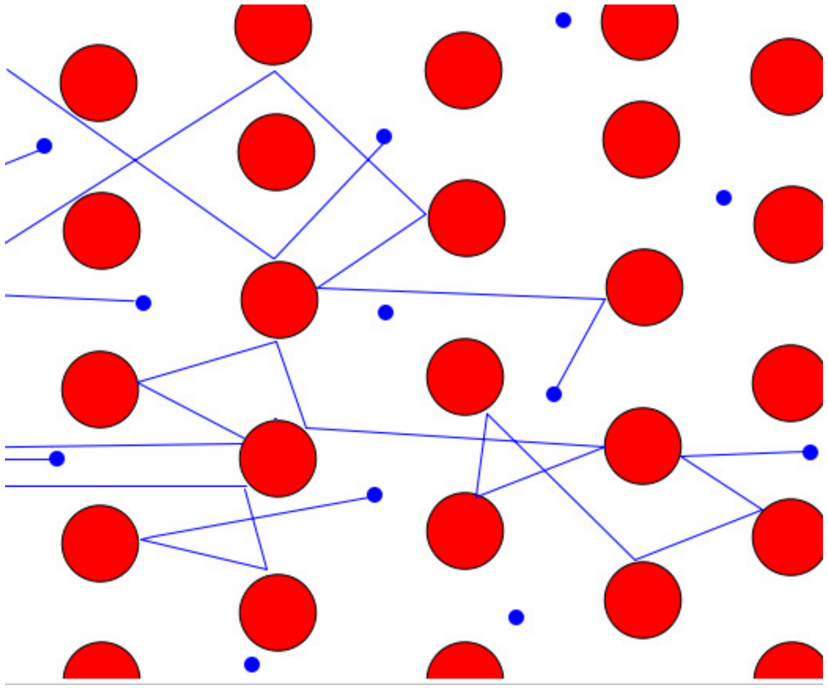
    - **Quantum free-electron theory (量子自由电子论)**

Classical Free-Electron Theory
(经典自由电子论)

Chapter 5.1: Free-Electron Theory of Metals (金属自由电子论)

➢ Classical Free-Electron Theory (经典自由电子论)

❖ The Drude model (德鲁德模型):



Schematic diagram of electron motion in metals of the Drude model.

Pinball machine

P. Drude, **Ann. Phys.** 306, 566 (1900).

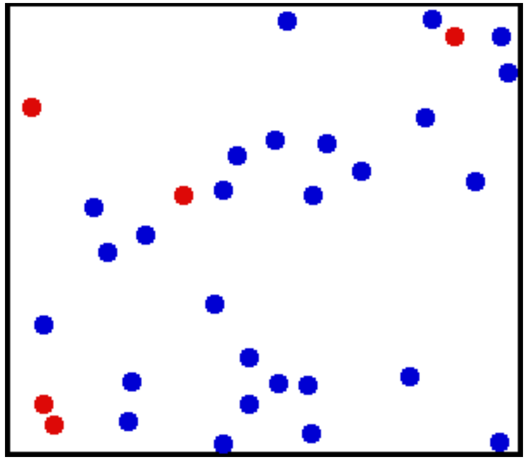
➢ Classical Free-Electron Theory (经典自由电子论)

❖ The Drude model (德鲁德模型):

- The electrons are treated as **classical free-electron gas (经典自由电子气)** scattered by atomic cores in the metals.

- The atomic cores are treated as **immobile positive ions**.

- The classical free-electron gas obeys **Maxwell-Boltzmann statistics**.



Classical free-electron gas

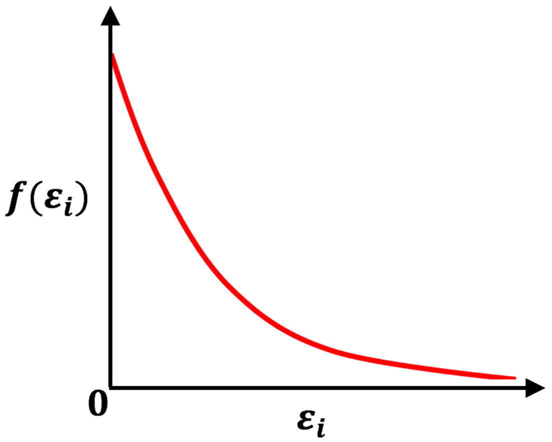
P. Drude, **Ann. Phys.** 306, 566 (1900).

➢ Classical Free-Electron Theory (经典自由电子论)

❖ Maxwell-Boltzmann statistics (麦克斯韦-玻尔兹曼统计):

For a system of **noninteracting classical particles** with thermodynamic equilibrium at temperature $\boldsymbol{T}$, the probability of finding particles with energy $\boldsymbol{\varepsilon_i}$ reads:

$$\boldsymbol{f\,(\varepsilon_i) = \frac{1}{Z}\mathrm{e}^{-\varepsilon_i/k_\mathrm{B}T}}$$



Here, $Z = \sum_j \mathrm{e}^{-\varepsilon_j/k_\mathrm{B}T}$ denotes the **partition function (配分函数)**.

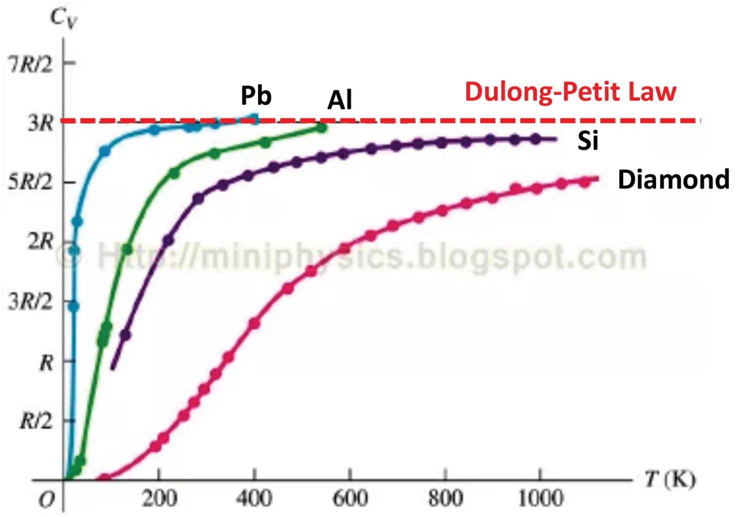
➢ Classical Free-Electron Theory (经典自由电子论)

❖ Problems with the Drude model:

- The contribution of classical free electrons to **heat capacity** of metals is expected to be:

$$C_e = \frac{3}{2} n k_{\mathrm{B}}$$

n denotes the number of electrons.



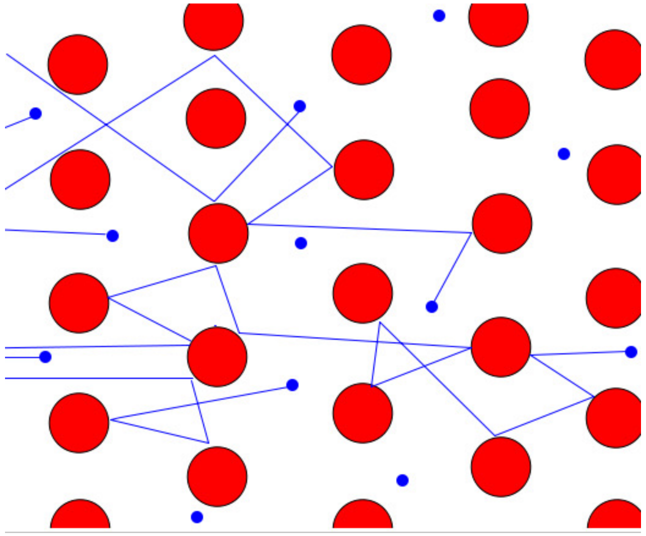
No such extra heat capacity was observed in metals!

➢ Classical Free-Electron Theory (经典自由电子论)

❖ Problems with the Drude model:

- The **mean-free path (平均自由程)** of classical electrons in metals is expected to be not very large.

$$l \sim 10^2 a$$



The actual mean-free path observed in metals is much larger (about $10^8 a$)!

Quantum Free-Electron Theory
(量子自由电子论)

➢ Quantum Free-Electron Theory (量子自由电子论)

❖ The Drude-Sommerfeld model (德鲁德-索莫菲模型)

Classical free-electron gas → **Quantum free-electron gas**

(Free-electron Fermi gas)

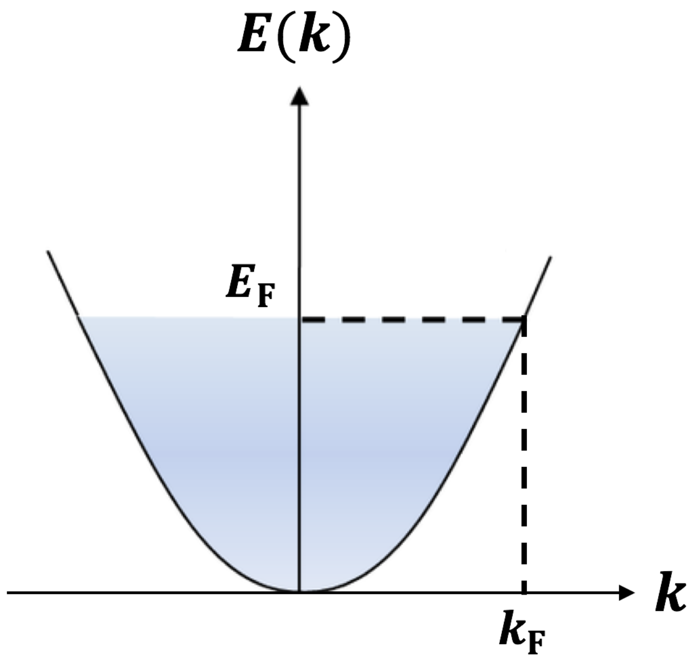
This model is also called the **free-electron model (自由电子模型).**

A. Sommerfeld, **Z. Phys.** 47, 1 (1928).

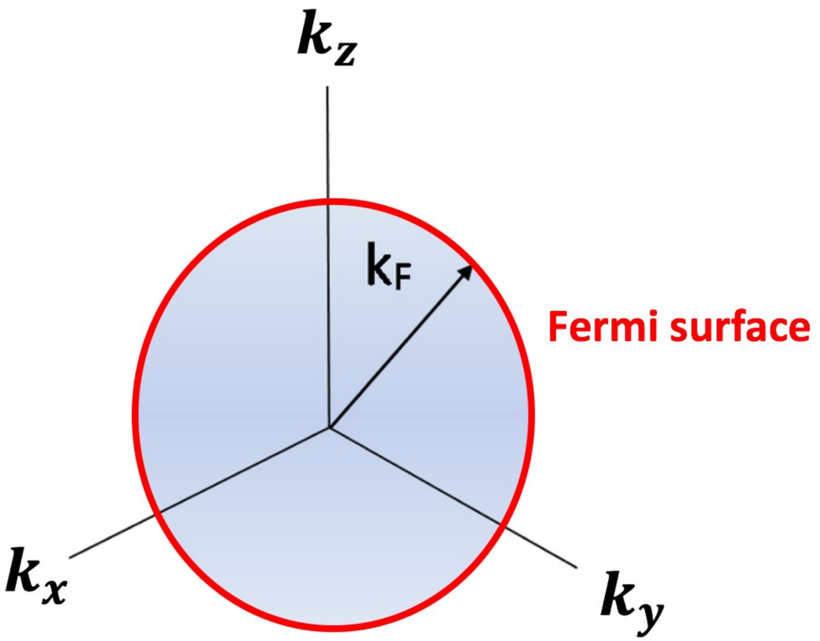
Chapter 5.1: Free-Electron Theory of Metals (金属自由电子论)

➢ Quantum Free-Electron Theory (量子自由电子论)

❖ The Drude-Sommerfeld model (德鲁德-索莫菲模型)



Free-electron Fermi gas



A. Sommerfeld, **Z. Phys.** 47, 1 (1928).

Chapter 5.1: Free-Electron Theory of Metals (金属自由电子论)

➢ Quantum Free-Electron Theory (量子自由电子论)

❖ The Drude-Sommerfeld model (德鲁德-索莫菲模型)

Arnold Sommerfeld
索莫菲 (1868-1951)
German Physicist

Some notable students of Sommerfeld:

Peter Debye
德拜 (1884-1966)
Dutch Physicist
Nobel Prize in Chemistry (1936)

Werner Heisenberg
海森堡 (1901-1976)
German Physicist
Nobel Prize in Physics (1932)

Wolfgang Pauli
泡利 (1900-1958)
Austrian Physicist
Nobel Prize in Physics (1945)

Hans Bethe
贝特 (1906-2005)
German Physicist
Nobel Prize in Physics (1967)

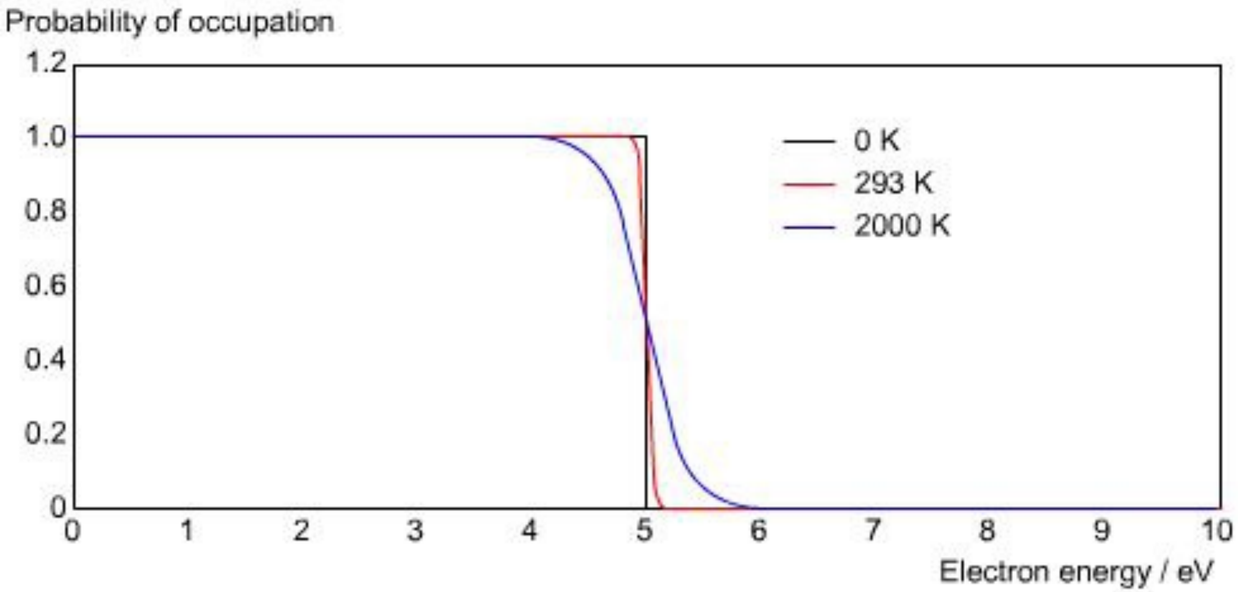
Linus Pauling
鲍林 (1901-1994)
American Chemist
Nobel Prizes in Chemistry (1954) and Peace (1962)


➢ Quantum Free-Electron Theory (量子自由电子论)

❖ Fermi-Dirac statistics (费米-狄拉克统计):

For a system of identical **noninteracting fermions** with thermodynamic equilibrium at temperature $\boldsymbol{T}$, the probability of occupying a single-particle state with energy $\boldsymbol{E}$ reads:

$$\boldsymbol{f(E) = \frac{1}{e^{(E-E_f)/k_B T}+1}}$$



Fermi-Dirac distribution for several temperatures

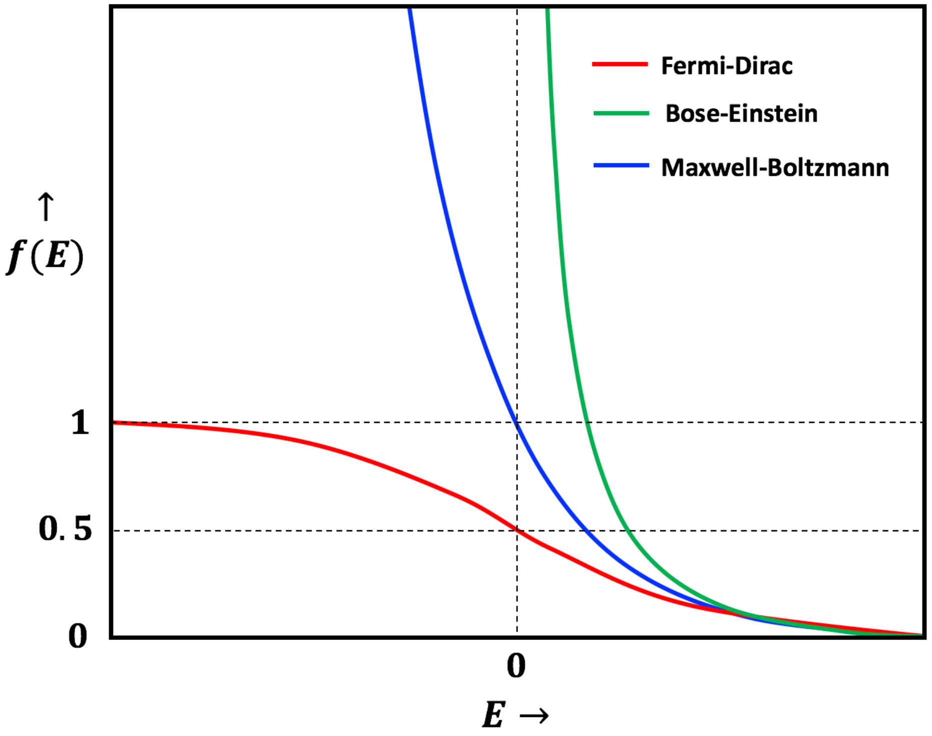
➢ Quantum Free-Electron Theory (量子自由电子论)

❖ Fermi-Dirac statistics (费米-狄拉克统计):

Fermi-Dirac distribution: $$f(E) = \frac{1}{e^{E/k_B T} + 1}$$

Bose-Einstein distribution: $$f(E) = \frac{1}{e^{E/k_B T} - 1}$$

Maxwell-Boltzmann distribution: $$f(E) = \frac{1}{e^{E/k_B T}}$$



Comparison between the three distribution functions

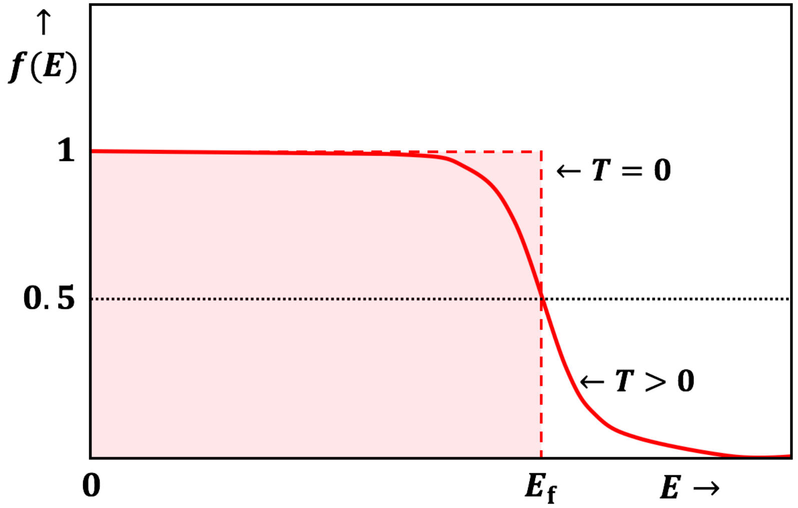
*The chemical potential is set to be zero.

➢ Quantum Free-Electron Theory (量子自由电子论)

❖ Heat capacity of metals (金属热容):

- Only electrons near the Fermi level E_f have contributions to heat capacity of metals:

$$C_\mathrm{e} = \frac{\pi^2}{2} N_\mathrm{A} k_\mathrm{B} \left(\frac{T}{T_\mathrm{F}}\right)$$



Here, $T_\mathrm{F} = E_\mathrm{f}/k_\mathrm{B}$ denotes the **Fermi temperature**.

➢ Quantum Free-Electron Theory (量子自由电子论)

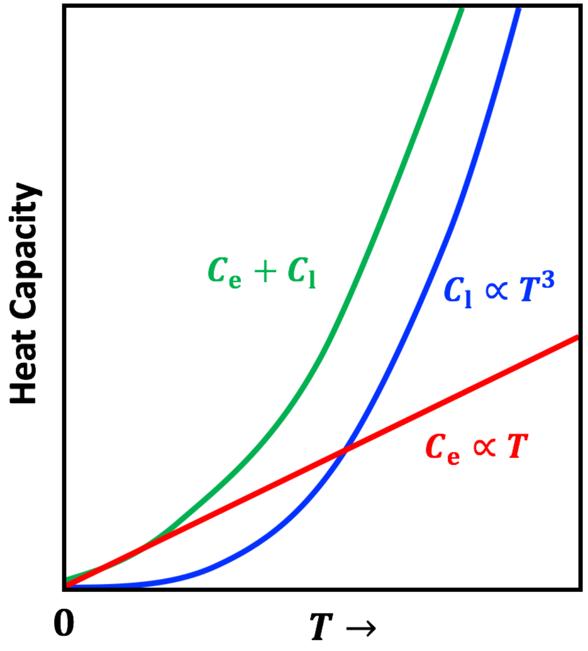
❖ Heat capacity of metals (金属热容):

- The contributions to heat capacity of metals from electrons and lattice vibrations are comparable only **at very low temperature**:

$$C_\mathrm{e} = \frac{\pi^2}{2} N_\mathrm{A} k_\mathrm{B} \left(\frac{T}{T_\mathrm{F}}\right) \propto T$$

$$C_\mathrm{l} = \frac{12\pi^4}{5} N_\mathrm{A} k_\mathrm{B} \left(\frac{T}{T_\mathrm{D}}\right)^3 \propto T^3$$

Note that $C_\mathrm{e}/C_\mathrm{l} \approx 0.01$ near room temperature in metals.



Electrical and Thermal Conduction
(导电性与导热性)

➢ Electrical Conduction (导电性)

❖ Electrical conductivity (电导率)

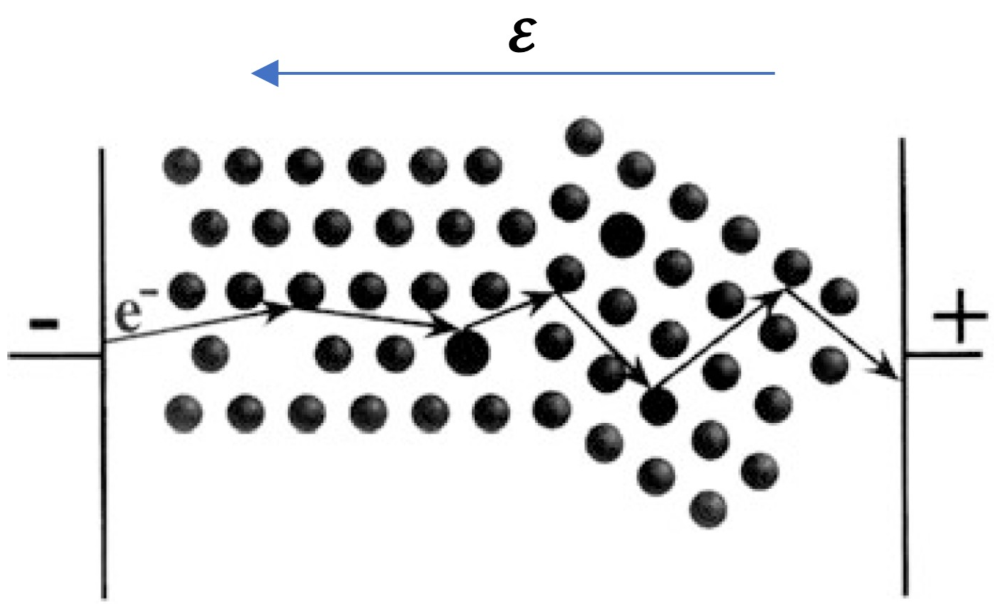
▪ **Classical free-electron theory (经典自由电子论):**

$$\boxed{m\frac{\mathrm{d}v}{\mathrm{d}t}+\gamma v=e\mathcal{E}}$$

Drift (漂移): $m\frac{\mathrm{d}v}{\mathrm{d}t}$

Collision (碰撞): γv

Electric field: $\mathcal{E}$



Schematic diagram of an electron path through a metal under an electric field.

➢ Electrical Conduction (导电性)

❖ Electrical conductivity (电导率)

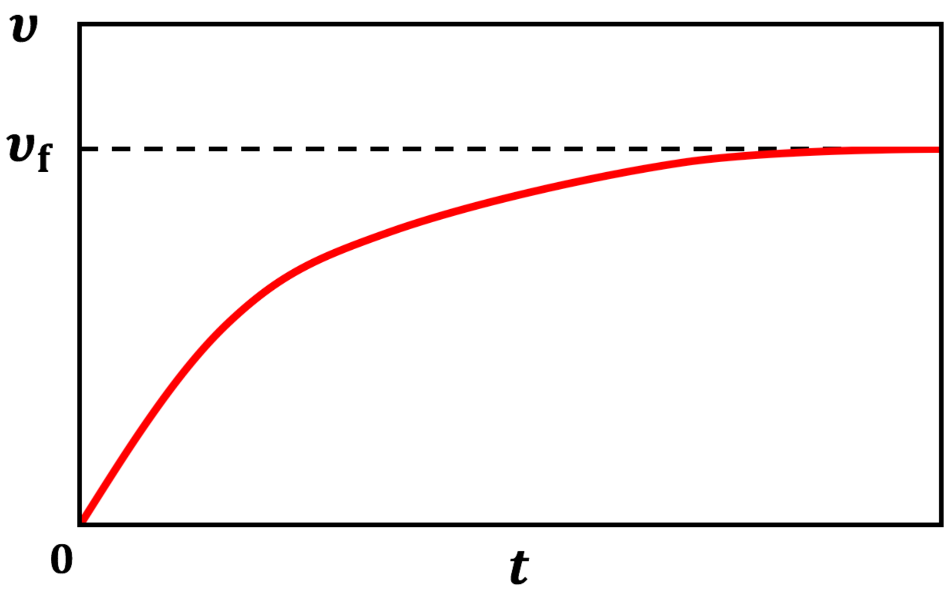
- **Classical free-electron theory (经典自由电子论):**

For the final **steady state (稳态)**:

$$v = v_{\mathrm{f}}$$

$$\longrightarrow \quad \frac{\mathrm{d}v}{\mathrm{d}t} = 0$$

$$\longrightarrow \quad \gamma = \frac{e\mathcal{E}}{v_{\mathrm{f}}}$$



Schematic diagram of the velocity of the drifting electron as a function of time.

Electrical Conduction (导电性)

Electrical conductivity (电导率)

- **Classical free-electron theory (经典自由电子论):**

$$\longrightarrow \quad m\frac{\mathrm{d}v}{\mathrm{d}t}+\frac{e\mathcal{E}}{v_{\mathrm{f}}}v=e\mathcal{E} \quad \longrightarrow \quad v=v_{\mathrm{f}}\left(1-e^{-t/\tau}\right)$$

Here, τ denotes the **relaxation time (弛豫时间，即两次连续碰撞之间的平均时间):**

$$\tau=\frac{mv_{\mathrm{f}}}{e\mathcal{E}} \quad \longrightarrow \quad l=\tau v$$

(mean-free path 平均自由程)

➢ Electrical Conduction (导电性)

❖ Electrical conductivity (电导率)

- **Classical free-electron theory (经典自由电子论):**

The current density: $\boldsymbol{J = env_{\mathrm{f}}}$

The Ohm's law: $\boldsymbol{J = \sigma \mathcal{E}}$

The relaxation time: $\boldsymbol{\tau = \frac{mv_{\mathrm{f}}}{e\mathcal{E}}}$

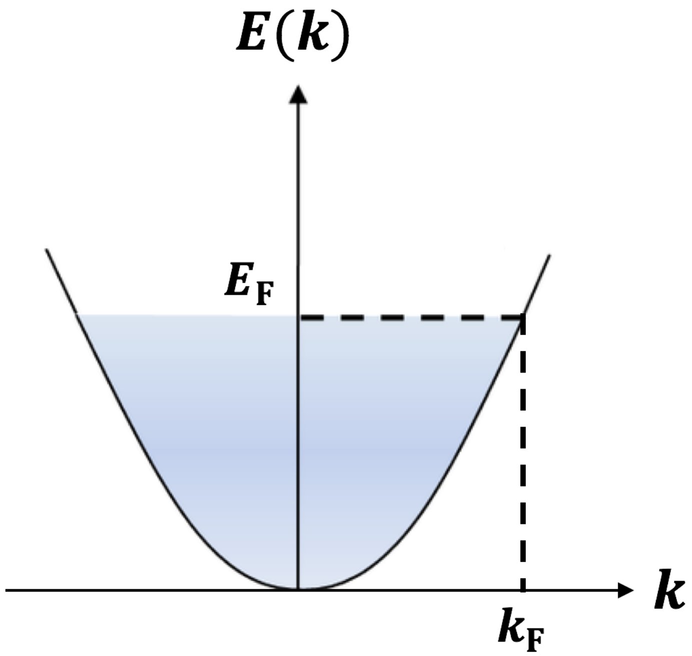
$$\boxed{\boldsymbol{\sigma = \frac{ne^2\tau}{m}}}$$

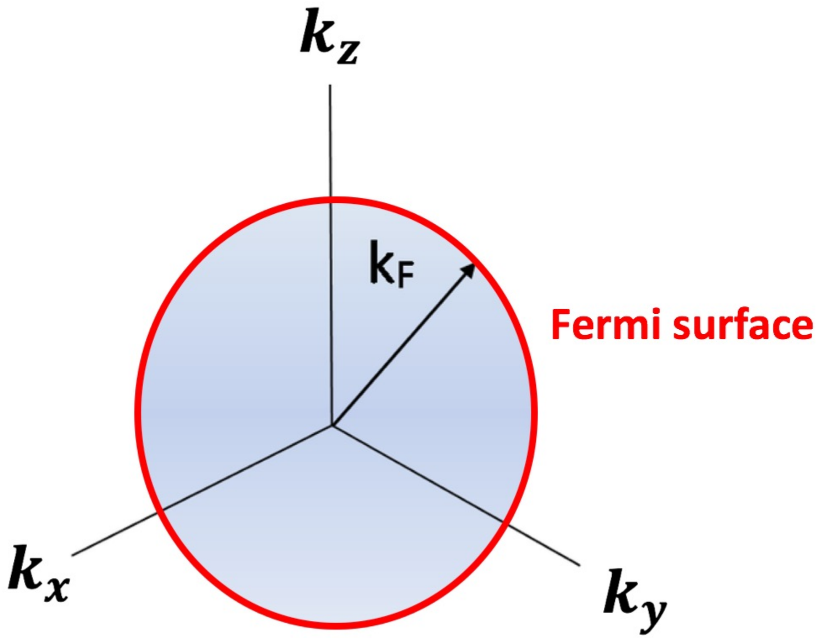
Here, $\boldsymbol{n}$ denotes the electron density.

➢ Electrical Conduction (导电性)

❖ Electrical conductivity (电导率)

- **Quantum free-electron theory (量子自由电子论):**





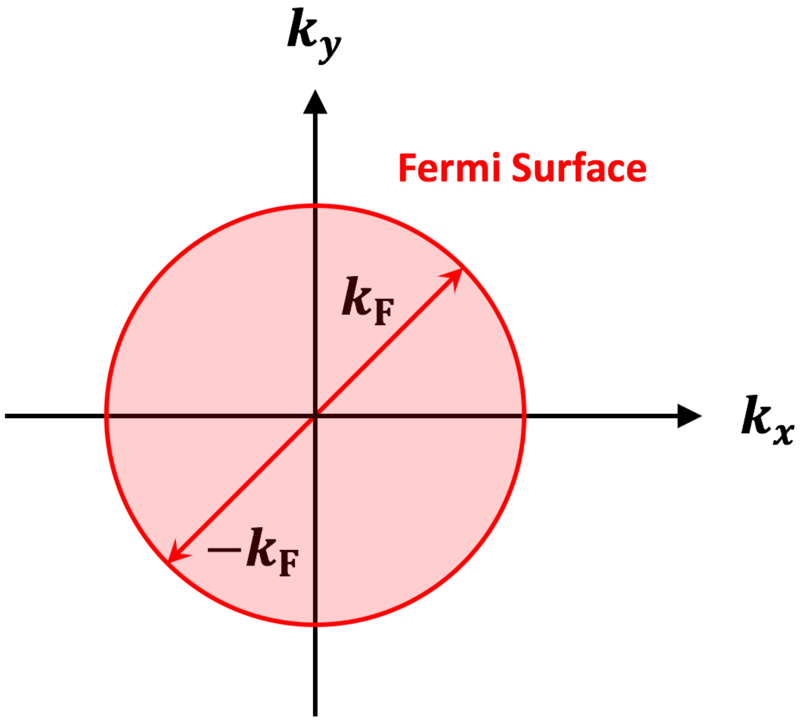
➢ Electrical Conduction (导电性)

❖ Electrical conductivity (电导率)

▪ **Quantum free-electron theory (量子自由电子论):**

In the absence of electric field, there is no **net electric current** in metals as a result of the symmetry of electron distribution in k space.

$$\boldsymbol{v}(\boldsymbol{k}) = -\boldsymbol{v}(-\boldsymbol{k})$$



Electron distribution in k space in the absence of electric field.

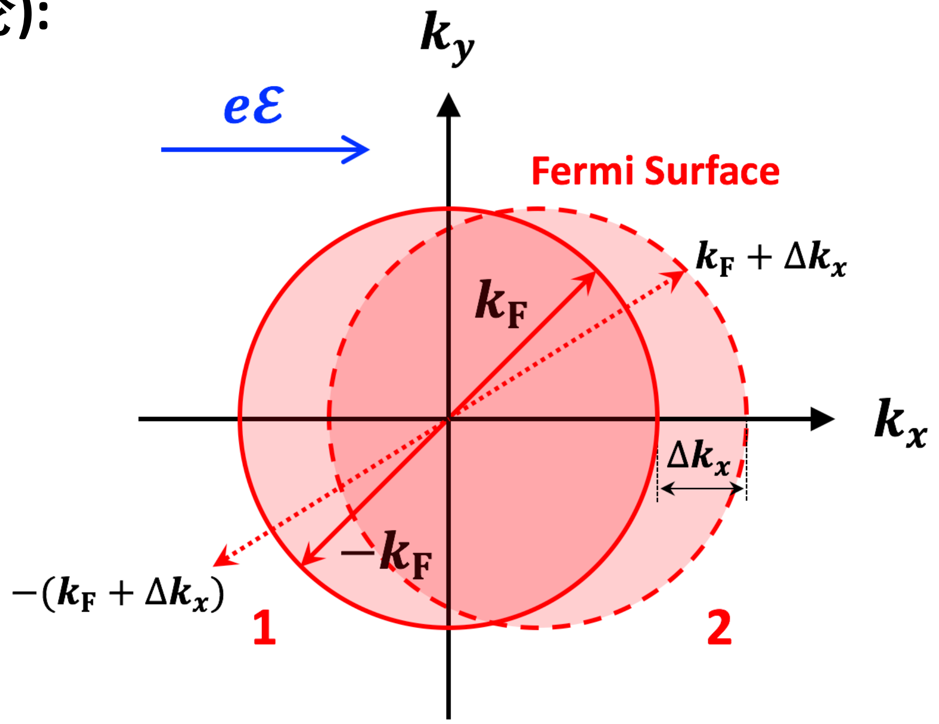
➢ Electrical Conduction (导电性)

❖ Electrical conductivity (电导率)

- **Quantum free-electron theory (量子自由电子论):**

In the presence of an electric field $\mathcal{E}$, the electron distribution in k space is shifted along the direction of the electric force:

$$\hbar \frac{\mathrm{d}\boldsymbol{k}}{\mathrm{d}t} = \boldsymbol{F} = e\boldsymbol{\mathcal{E}}$$



Electron distribution in k space in the presence of an electric field along x.

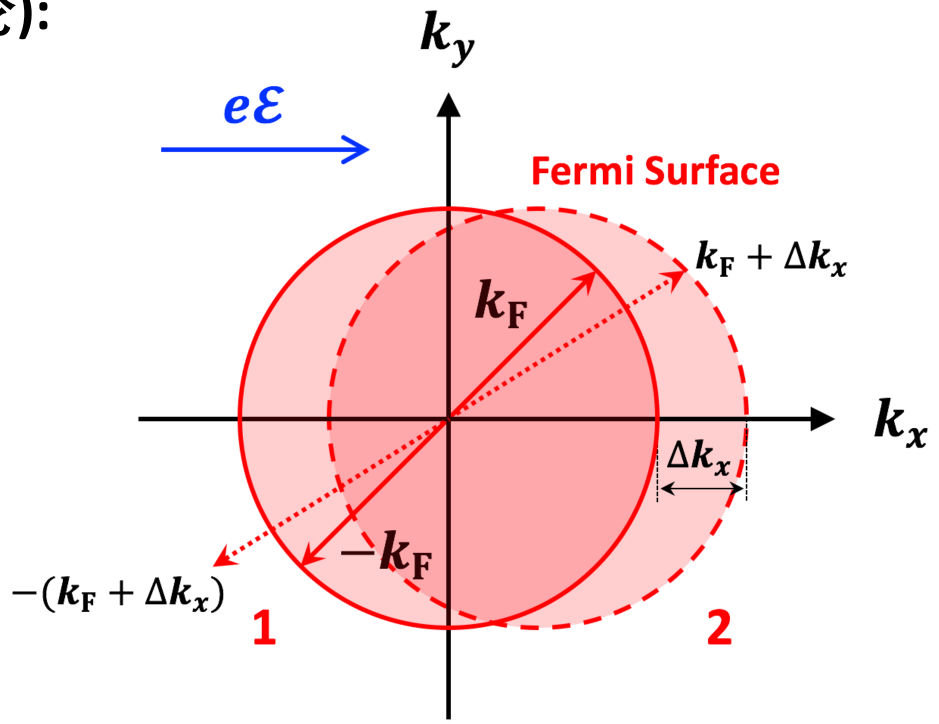
➢ Electrical Conduction (导电性)

❖ Electrical conductivity (电导率)

- **Quantum free-electron theory (量子自由电子论):**

The great majority of electrons still cancel each other in motion as a result of the symmetric distribution in k space, **except for those around the Fermi surface that will induce net electric current**.

*For instance (see the figure), in the presence of an electron field along x, the state with $k_{\mathrm{F}} + \Delta k_x$ is occupied but that with $-(k_{\mathrm{F}} + \Delta k_x)$ is unoccupied.



Electron distribution in k space in the presence of an electric field along x.

➢ Electrical Conduction (导电性)

❖ Electrical conductivity (电导率)

- **Band theory (能带理论):**

For electrons moving in the periodic potential of metals, the electron mass $\boldsymbol{m}$ can be replaced by its effective mass $\boldsymbol{m}^*$, and similar results can be obtained:

$$\boldsymbol{\sigma} = \frac{\boldsymbol{n}\boldsymbol{e}^2\boldsymbol{\tau}}{\boldsymbol{m}} \longrightarrow \boxed{\boldsymbol{\sigma} = \frac{\boldsymbol{n}\boldsymbol{e}^2\boldsymbol{\tau}_{\mathbf{F}}}{\boldsymbol{m}^*}}$$

➢ Electrical Conduction (导电性)

❖ Electrical conductivity (电导率)

- **Boltzmann theory (玻尔兹曼理论):**

The Boltzmann equation (玻尔兹曼方程):

$$\boxed{\frac{\mathrm{d}f}{\mathrm{d}t} = \left(\frac{\partial f}{\partial t}\right)_{\mathrm{force}} + \left(\frac{\partial f}{\partial t}\right)_{\mathrm{diff}} + \left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}}}$$

Here, f denotes the **distribution function (分布函数),** which can either obey the classical (Maxwell-Boltzmann) or quantum (Fermi-Dirac or Bose-Einstein) statistics.

➢ Electrical Conduction (导电性)

❖ Electrical conductivity (电导率)

- **Boltzmann theory (玻尔兹曼理论):**

The Boltzmann equation (玻尔兹曼方程):

$$\boxed{\frac{\mathrm{d}f}{\mathrm{d}t} = \left(\frac{\partial f}{\partial t}\right)_{\mathrm{force}} + \left(\frac{\partial f}{\partial t}\right)_{\mathrm{diff}} + \left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}}}$$

The “force” term denotes the force of electric field, “diff” the diffusion of particles, and “coll” the collision between particles.

➢ Electrical Conduction (导电性)

❖ Electrical conductivity (电导率)

- **Boltzmann theory (玻尔兹曼理论):**

The general form of Ohm's law (欧姆定律的一般形式):

$$J_\alpha = \sum_\beta \sigma_{\alpha\beta} \mathcal{E}_\beta$$

The **electrical conductivity $\sigma_{\alpha\beta}$ tensor (电导率张量)** reads:

$$\boxed{\sigma_{\alpha\beta} = -\frac{2q^2}{(2\pi)^3} \int \tau(\boldsymbol{k}) v_\alpha(\boldsymbol{k}) v_\beta(\boldsymbol{k}) \left(\frac{\partial f_0}{\partial E}\right) \mathrm{d}\boldsymbol{k}}$$

➢ Thermal Conduction (导热性)

❖ Thermal conductivity (热导率)

- **The Fourier's law (傅里叶定律) for thermal conduction:**

$$\boldsymbol{j} = -\boldsymbol{\kappa}\frac{\boldsymbol{dT}}{\boldsymbol{dx}}$$

Here, j denotes the flux of thermal energy (热流密度), κ the thermal conductivity (热导率), and T the temperature.

➢ Thermal Conduction (导热性)

❖ Thermal conductivity (热导率)

- **Thermal conductivity:**

$$\boldsymbol{\kappa = \frac{1}{3} c_{\mathrm{e}} v_{\mathrm{F}} l}$$

Here, c_{e} denotes the volume-specific heat capacity (体积比热容) of electrons, v_{F} the Fermi velocity, and l the electron mean-free path.

➢ Thermal Conduction (导热性)

❖ Thermal conductivity (热导率)

- **Thermal conductivity:**

$$c_e = \frac{\pi^2}{2} n k_B \left(\frac{k_B T}{E_F}\right)$$

$$E_F = \frac{1}{2} m v_F^2$$

$$l = v_F \tau_F$$

$$\longrightarrow \quad \boxed{\kappa = \frac{n\pi^2 k_B^2 T \tau_F}{3m}}$$

➢ Thermal Conduction (导热性)

❖ Wiedemann-Franz Law (维德曼-夫兰兹定律):

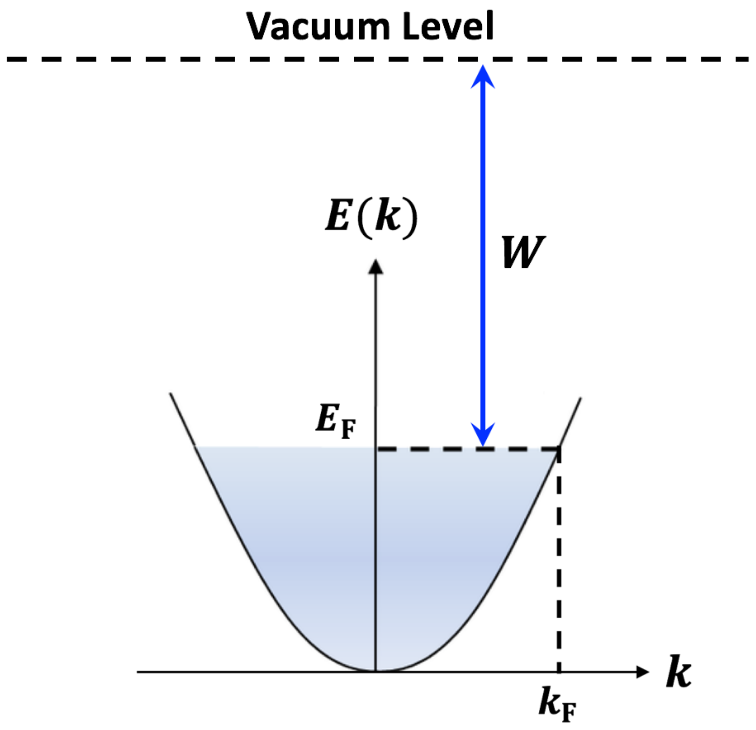
- This **empirical law (经验定律)** states that, when the temperature is not too low, the ratio of thermal conductivity to electrical conductivity of a metal is proportional to temperature, and the coefficient L (Lorenz number 洛伦兹常数) is independent of the metal:

$$\left.\begin{aligned} \kappa &= \frac{n\pi^2 k_B^2 T \tau_F}{3m} \\ \sigma &= \frac{ne^2\tau_F}{m} \end{aligned}\right\} \longrightarrow \boxed{\frac{\kappa}{\sigma} = LT} \qquad L = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2$$

Work Function and Contact Potential
(功函数与接触势)

➢ Work Function (功函数)

❖ The **work function** of a metal is defined as the **energy difference between the vacuum level (真空能级) and the Fermi level**:



➢ Work Function (功函数)

❖ The work function of some real metals:

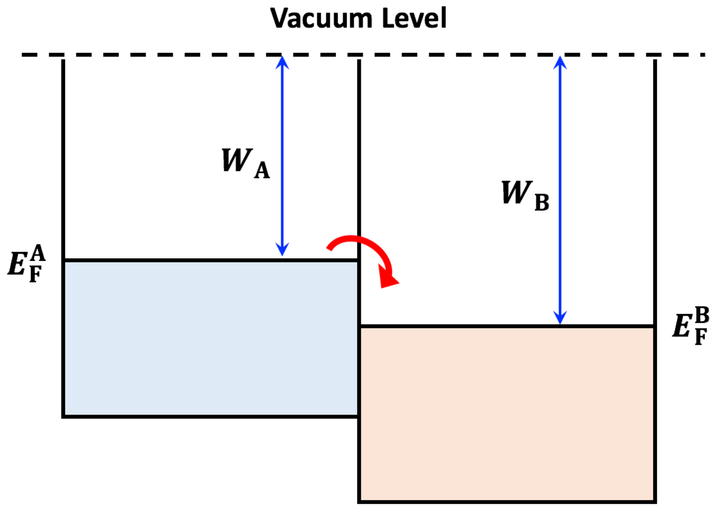
Metals	**Li**	**Na**	**Mg**	**Al**	**Cu**	**Ag**	**Au**	**Pt**
W **(eV)**	2.48	2.28	3.67	4.2	4.45	4.46	4.89	5.36

*Note that, since Fermi level is dependent on temperature, **work function is also dependent on temperature in real materials**.

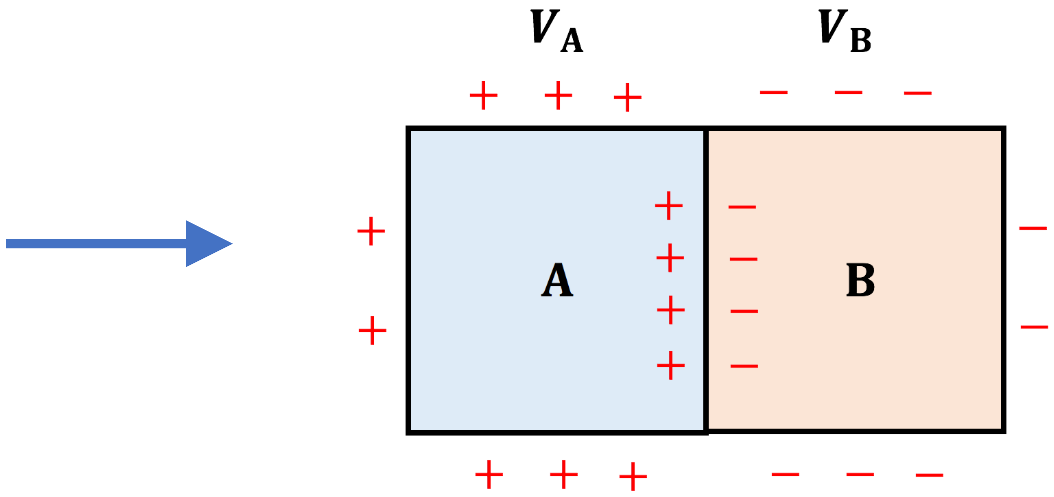
Chapter 5.1: Free-Electron Theory of Metals (金属自由电子论)

➢ Contact Potential (接触势)

❖ When two metals with different work functions are contacted to each other, electrons will transfer from the metal with smaller work function to that with larger work function, leading to a **contact potential** at the interface.



$W_A < W_B$



Summary (总结)

Summary

Classical free-electron theory:

- Electrons obey the **Maxwell-Boltzmann statistics.**
- **All electrons** have contributions to the thermal and electrical properties of metals (**which is essentially incorrect**).

Quantum free-electron theory:

- Electrons obey the **Fermi-Dirac statistics.**
- **Only electrons around the Fermi surface (or Fermi level)** have contributions to the thermal and electrical properties of metals.

More accurate descriptions should resort to band theory, which is beyond both classical and quantum free-electron theories!