Fundamentals of Solid State Physics

Electronic Properties
- The Free Electron Model

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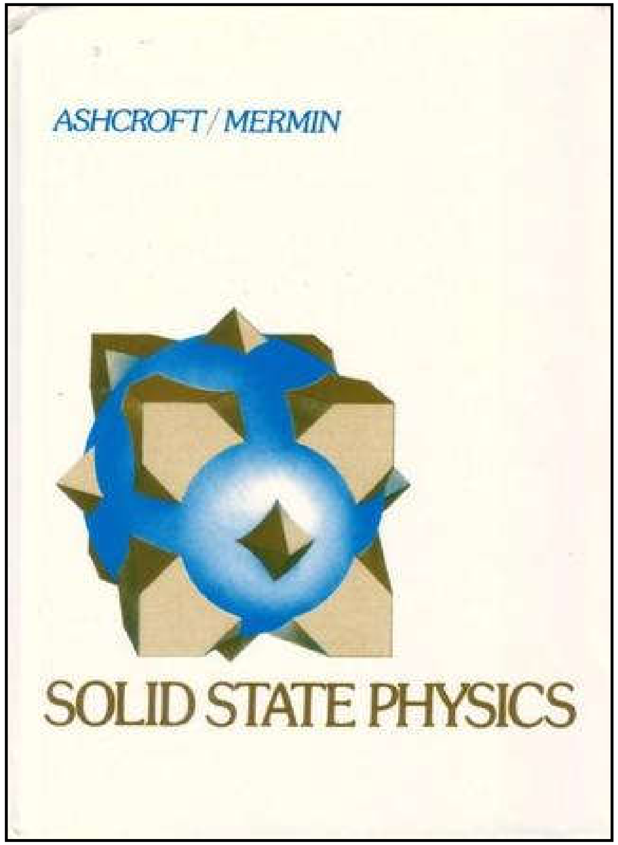
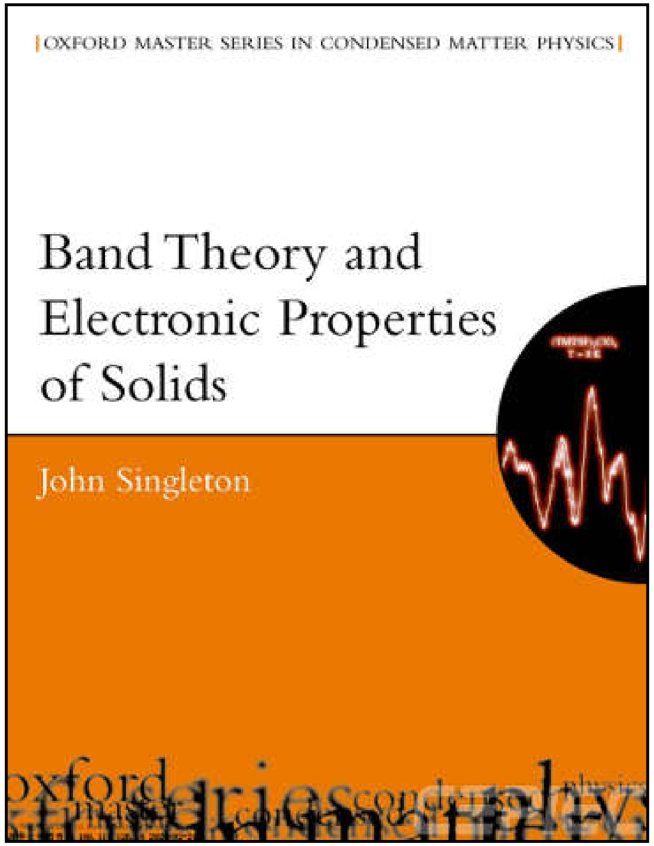
Further Reading

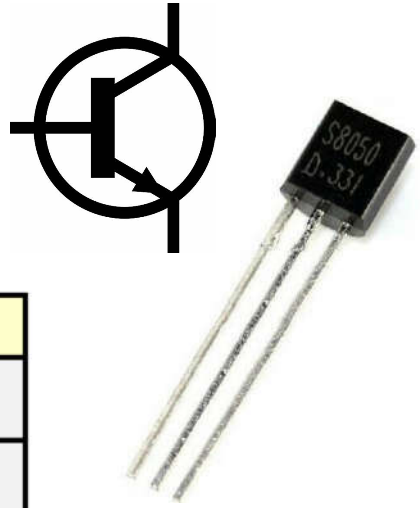
- **Ashcroft & Mermin, Chapter 1, 2, 3**
- **Singleton, Chapter 1**



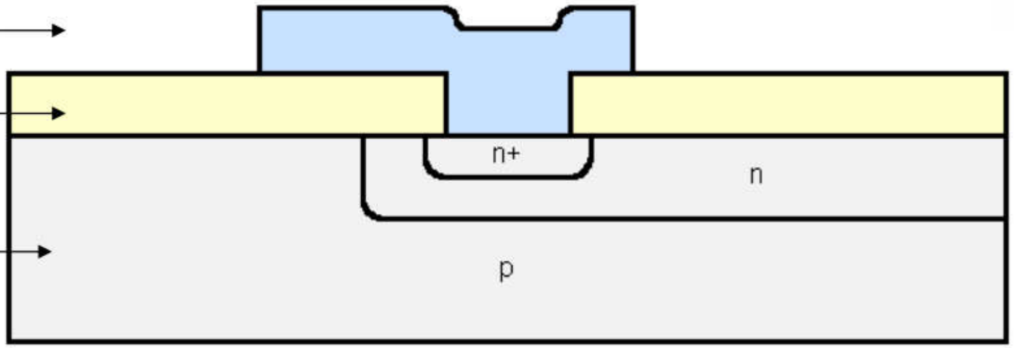


Electronic Properties of Materials

CMOS transistor
- Complementary Metal-Oxide-Semiconductor



conductor Al
insulator SiO_2
semiconductor Si



Metal

SiO_2

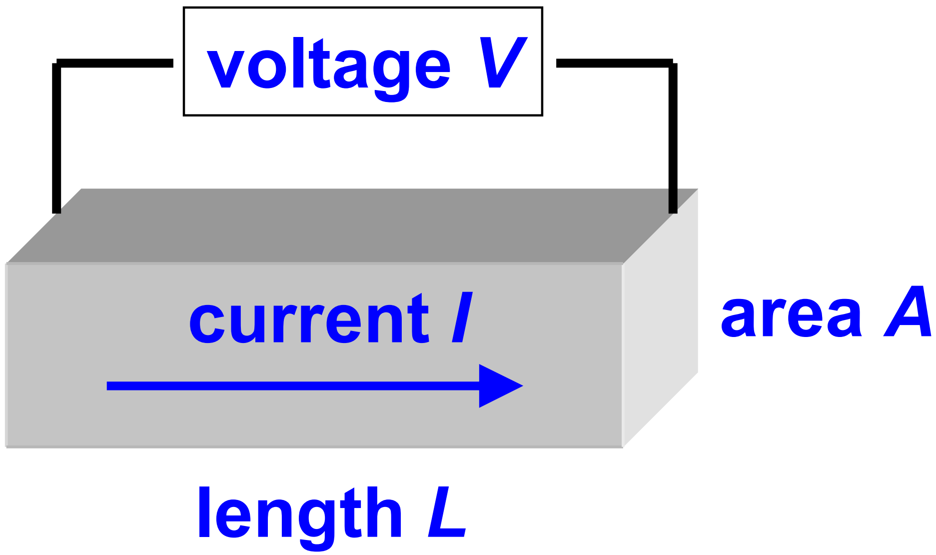
Silicon

Electronic Properties of Metals

- **Ohm's Law (1827)**

$$\boxed{V = IR}$$

macroscopic



$$j = \frac{I}{A} = \frac{V}{AR} = \frac{EL}{A\rho L / A} = \frac{E}{\rho} = \sigma E$$

microscopic

j **- current density (A/m^2)**
E **- electric field (V/m)**
ρ **- resistivity (Ω*m)**
σ **- conductivity (S/m)**

Electronic Properties of Metals

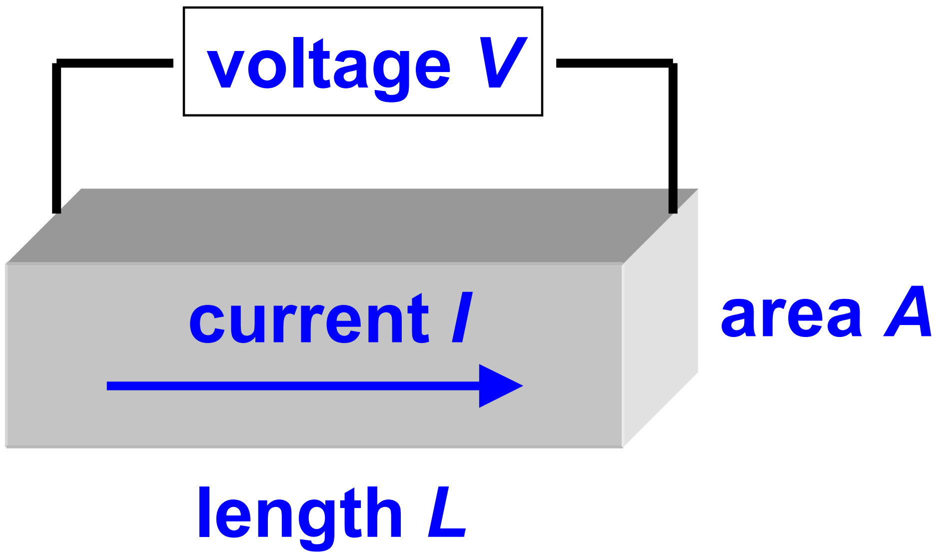
- **conductivity and mobility**

$$I = \frac{\partial Q}{\partial t} = ne\frac{\partial V}{\partial t} = neA\frac{\partial L}{\partial t} = neAv$$

$$j = \frac{I}{A} = nev$$

$$\sigma = \frac{j}{E} = ne\frac{v}{E} = ne\mu$$

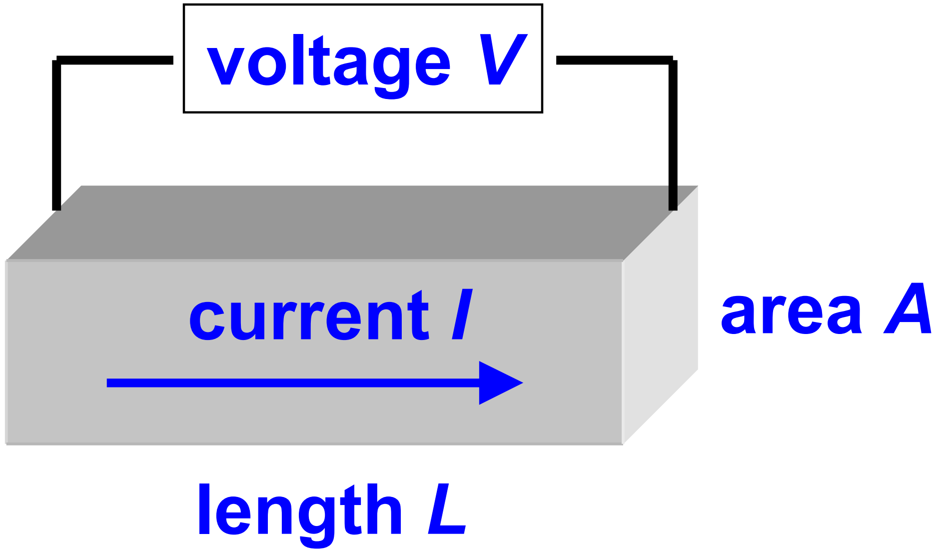
$$\mu = \frac{v}{E}$$



n **- density of electrons (#/m^3)**
v **- velocity of electrons (m/s)**
μ **- electron mobility (m^2/V/s)**

How to get Ohm's Law?

- assume free electrons in vacuum



$$\boxed{F = ma = eE}$$

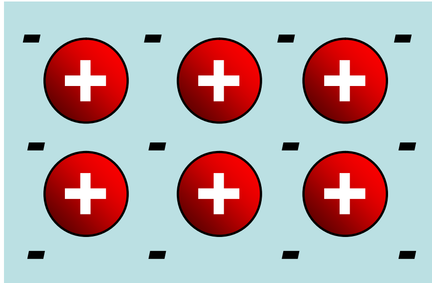
$$\boxed{a = \frac{dv}{dt} = \frac{F}{m} = \frac{eE}{m}}$$

$$\boxed{v = \frac{eE}{m} t \rightarrow \infty}$$

and $$\boxed{\sigma = ne\frac{v}{E} \rightarrow \infty}$$

what is wrong?

The Drude Model 德鲁德模型



positive ions
+
electron cloud

Free electron 'gas'

- Independent
  - electrons do not interact with each other
- Free
  - electrons do not interact with ions, except collision
- Collision (Origin of the resistance)
  - electrons are scattered by the ions instantaneously
- Relaxation time τ
  - average time between two collisions
  - electron mean free path $l = v^*\tau$
- Maxwell–Boltzmann distribution
  - average kinetic energy

$$\boxed{\frac{1}{2}mv^2 = \frac{3}{2}k_BT}$$

P. Drude
1863–1906

The Drude Model 德鲁德模型

Drude-Lorentz Model

$$F = m\frac{dv}{dt} + m\frac{v}{\tau} = eE(t)$$

τ - relaxation time (s)

when *E* is constant, *v* is constant

$$v = eE\frac{\tau}{m}$$

$$\mu = \frac{v}{E} = e\frac{\tau}{m}$$

mobility

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

conductivity

$$j = nev = \sigma E$$

Ohm's law

Successes of The Drude Model

- **Ohm's Law**

$$\boxed{j = \sigma E}$$

- **Electronic conductivity σ**

$$\boxed{\frac{1}{2}mv^2 = \frac{3}{2}k_B T} \qquad \boxed{\tau = \frac{l}{v}} \qquad \boxed{\sigma = ne^2 \frac{\tau}{m}}$$

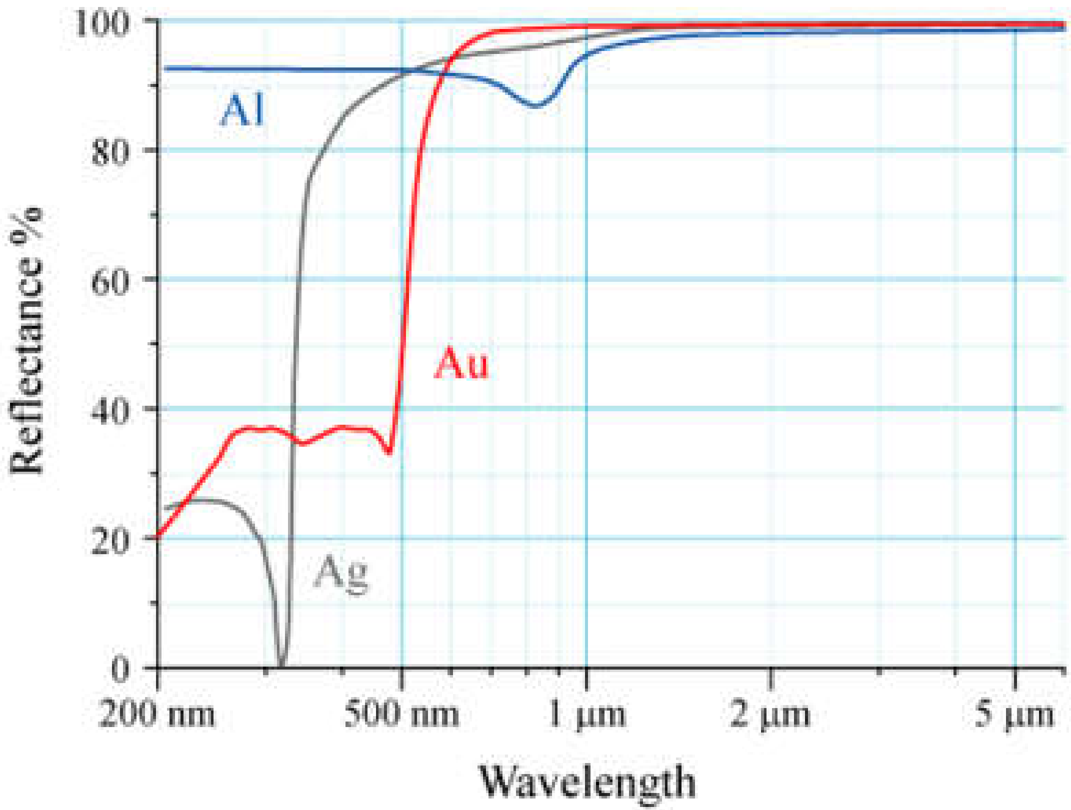
$v \sim 10^5$ m/s $\qquad \tau \sim 10^{-14}$ s $\qquad \sigma \sim 10^7$ S/m

m = electron mass 9.11×10^{-31} kg
k = 1.38×10^{-23} J/K
e = 1.6×10^{-19} C
T = 300 K, room temperature
l = mean free path 0.1~1 nm
n = atomic density ~ 10^{29} #/m^3

metals	conductivity (S/m) at 300 K
Ag	6.3×10^7
Cu	6.0×10^7
Al	3.5×10^7

Successes of The Drude Model

- **Optical Reflectivity of Metals**



mirror reflection

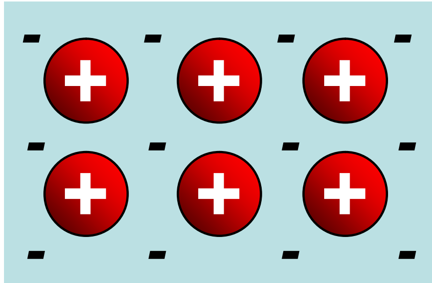
Failures of the Drude Model

It *cannot* explain

- **Electronic heat capacity**
- **Thermal conductivity**
- **Hall effect / Hall coefficient**
- **Insulators / Semiconductors**
- **...**

What was wrong?

The Drude Model 德鲁德模型



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Free electron 'gas'

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$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T$$

P. Drude
1863–1906

The Sommerfeld Model 索末菲模型

Free electron 'Fermi' gas

- Introduce quantum mechanics
  - "semi-classical" model

- ~~Maxwell–Boltzmann distribution~~

→ Fermi–Dirac distribution

A. Sommerfeld
1868–1951

The Electron Wave Function

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\cdot\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

free electron

$$V(\mathbf{r}) = 0$$

→ $$\nabla^2\psi(\mathbf{r}) = -k^2\psi(\mathbf{r})$$

$$k^2 = \frac{2mE}{\hbar^2}$$

→ $$\psi(\mathbf{r}) = \sum_{\mathbf{k}} A_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r})$$

$$\int_V \psi^* \cdot \psi d\mathbf{r} = 1$$

→ **one solution is**

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}}\exp(i\mathbf{k}\cdot\mathbf{r})$$

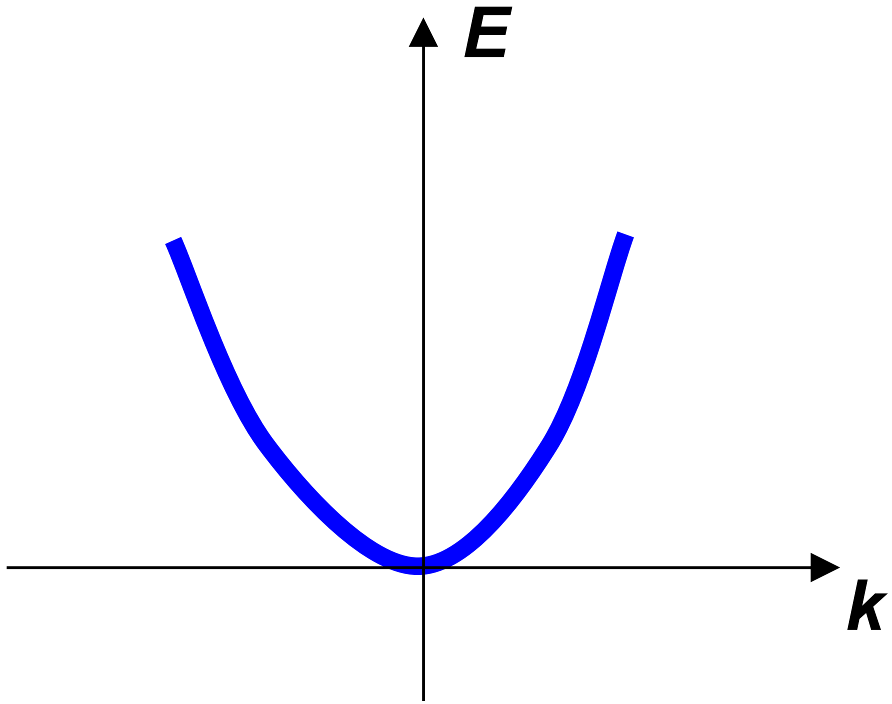
The Electron Wave Function

energy
$$E(k) = \frac{\hbar^2 k^2}{2m}$$

velocity
$$v = \frac{\hbar k}{m} = \frac{1}{\hbar}\frac{dE(k)}{dk}$$

momentum
$$p = \hbar k$$

electron mass
$$\frac{1}{m} = \frac{1}{\hbar^2}\frac{d^2E(k)}{dk^2}$$



***E*-*k* diagram**
(energy dispersion curve)

Classical vs. Quantum

	Classical	Quantum	
velocity	$\boxed{v}$	wavenumber 波数 wavevector 波矢	$\boxed{k = \frac{2\pi}{\lambda}}$
momentum 动量	$\boxed{p = mv}$		$\boxed{p = \hbar k}$
energy 能量	$\boxed{E = \frac{p^2}{2m}}$		$\boxed{E = \frac{\hbar^2 k^2}{2m}}$

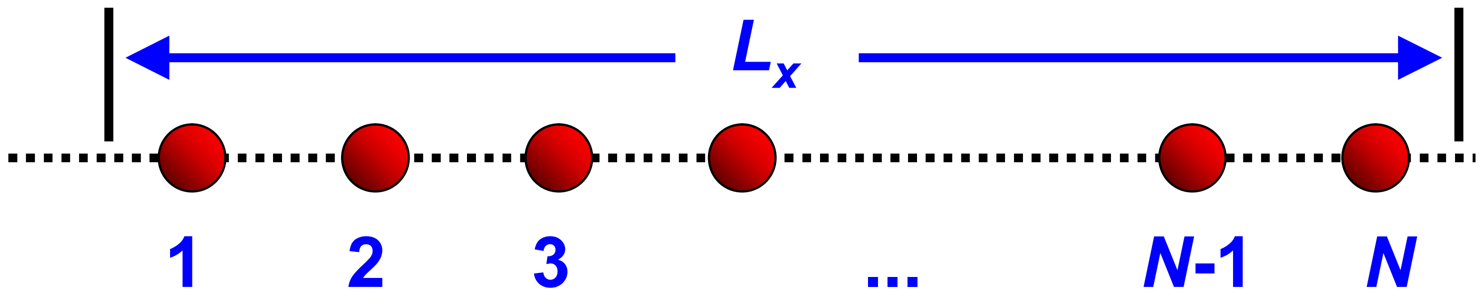
1D atomic chain

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} \exp(i\mathbf{k}\cdot\mathbf{r})$$

$\rightarrow$

1D atomic chain

$$\psi(x) = \frac{1}{\sqrt{L_x}} \exp(ik_x x)$$

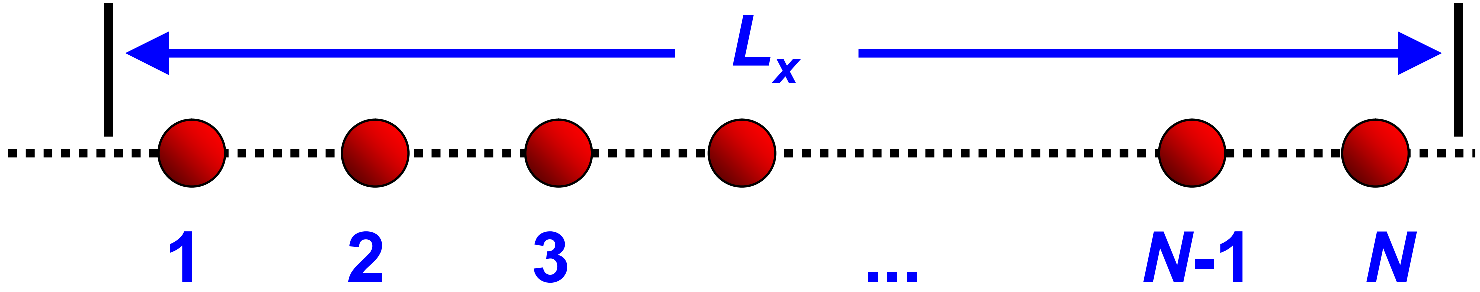


***N* is large ~ 10^{23}**

Born-von Karman *periodic* boundary condition

$$\psi(x) = \psi(x + L_x) \quad \rightarrow \quad \exp(ik_x L_x) = 1$$

1D atomic chain



N is large ~ 10^{23}

Born-von Karman *periodic* boundary condition

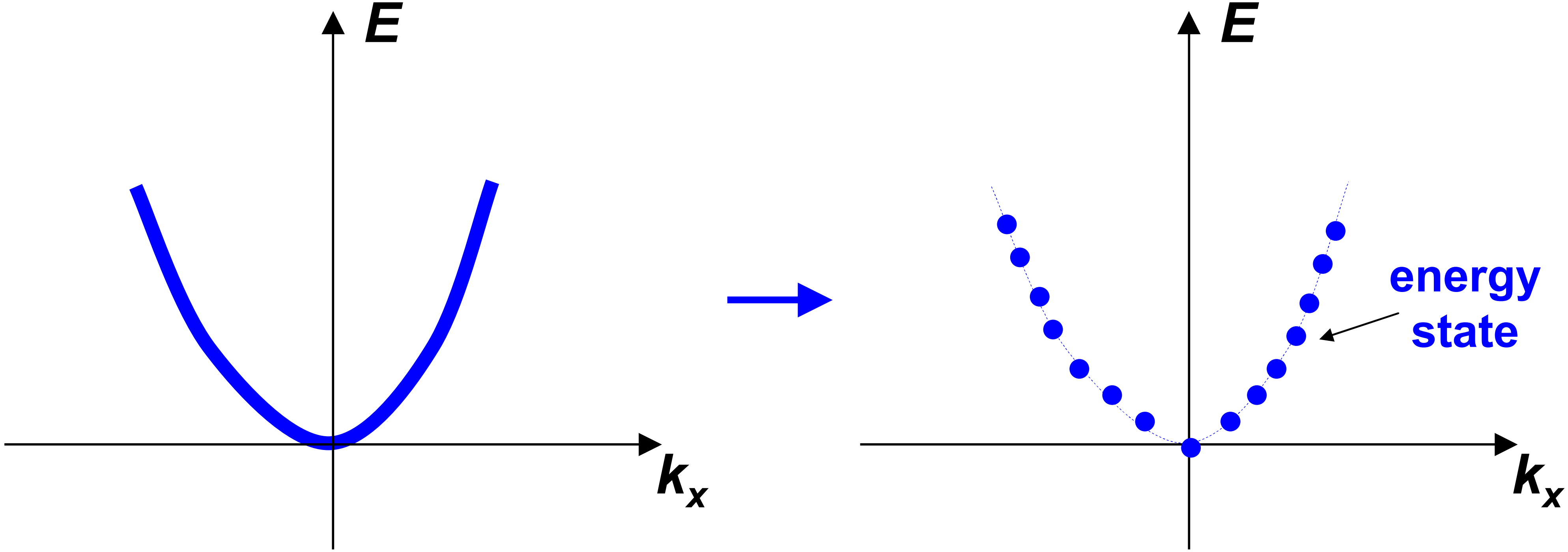
$$\psi(x)=\psi(x+L_x) \rightarrow \exp(ik_xL_x)=1$$

$$\rightarrow k_x=\frac{2\pi n_x}{L_x} \qquad n_x=0,\pm1,\pm2,\ldots$$

***k* is a *quantized* value**

1D atomic chain

$$\boxed{k_x = \frac{2\pi n_x}{L_x}} \qquad n_x = 0, \pm 1, \pm 2, \ldots$$



E-k **diagram**
(energy dispersion curve)

quantized energy state / level

1D atomic chain

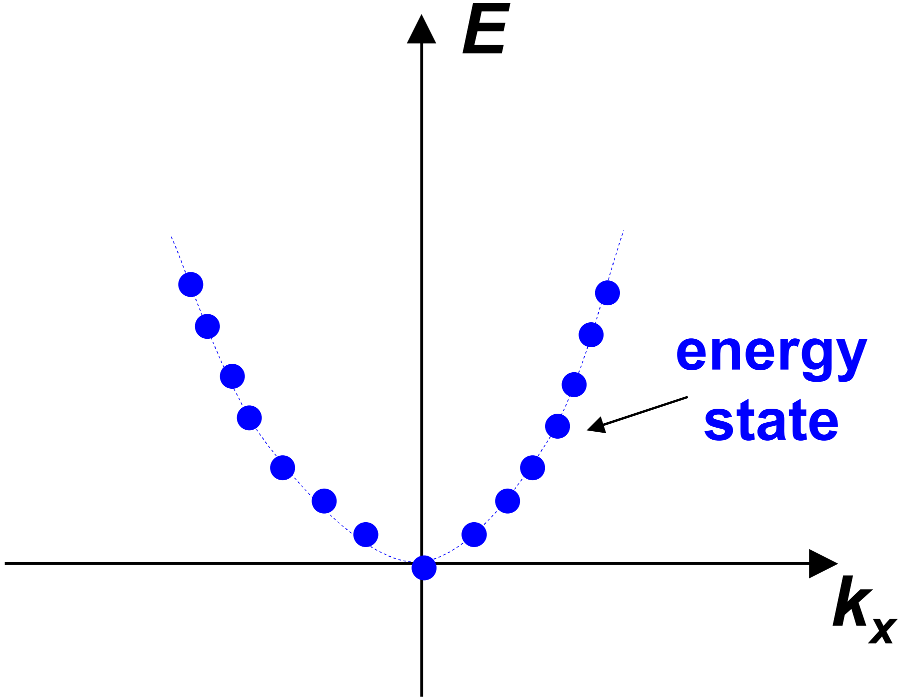
energy $$E(k) = \frac{\hbar^2 k^2}{2m}$$

velocity $$v = \frac{\hbar k}{m} = \frac{1}{\hbar}\frac{dE(k)}{dk}$$

momentum $$p = \hbar k$$

electron mass $$\frac{1}{m} = \frac{1}{\hbar^2}\frac{d^2E(k)}{dk^2}$$

$$k_x = \frac{2\pi n_x}{L_x} \quad n_x = 0, \pm1, \pm2, \ldots$$



When *L* is large,
k and *E(k)* are *quasi-continuous*
(准连续)

quantized energy state / level

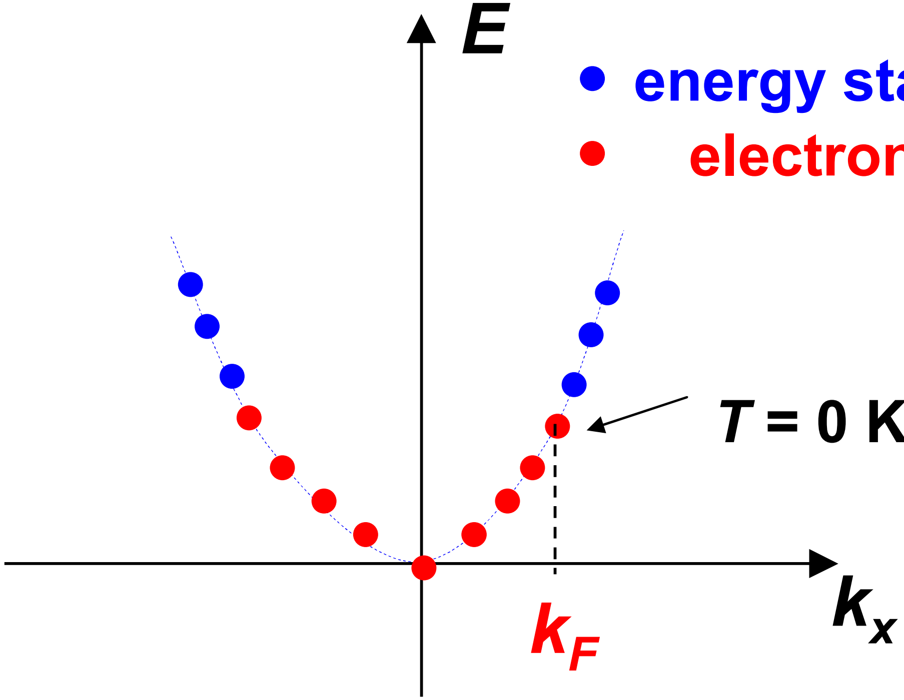
State vs. Electron

energy state / level / orbital
能态 / 能级 / 轨道

determined by space, lattice, environments, ...

electron / phonon / ...
电子 / 声子 / ...

1D atomic chain



$$k_x = \frac{2\pi n_x}{L_x} \qquad n_x = 0, \pm 1, \pm 2, \ldots$$

k_F - Fermi wavevector
highest *occupied* state at $T = 0$ K

Fermi-Dirac distribution:
spin up and down

$$-k_F < k_x < +k_F$$

$$N = 2 \cdot \frac{2k_F}{2\pi / L_x} \rightarrow k_F = \frac{\pi}{2} \frac{N}{L_x}$$

N **- total number of free electrons**

N/L **- free electron density**

1D atomic chain

$$N = 2 \cdot \frac{2k_F}{2\pi / L_x}$$

1D atomic chain

$$k_F = \frac{\pi}{2} \frac{N}{L_x}$$

$$v_F = \frac{\hbar k_F}{m_e}$$

***k*$_F$ - Fermi wavevector**
***E*$_F$ - Fermi energy**
***v*$_F$ - Fermi velocity**
***T*$_F$ - Fermi temperature**

$$E_F = \frac{\hbar^2 k_F^2}{2m_e}$$

$$T_F = \frac{E_F}{k_B}$$

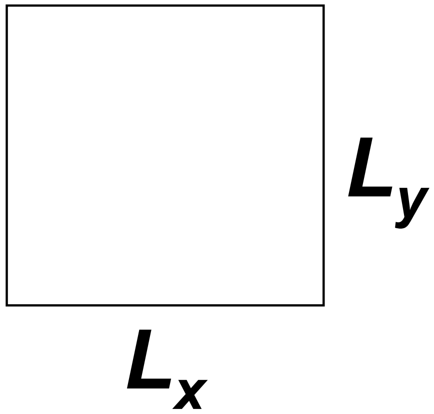
These values are determined by electron density N/L, not N or L

highest *occupied* state at *T* = 0 K

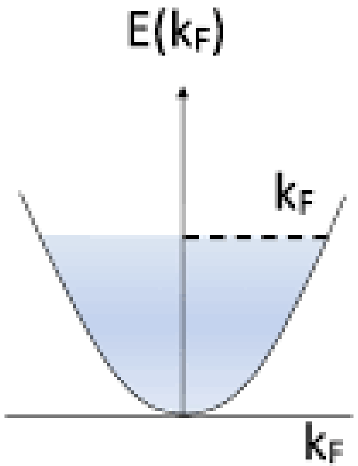
2D box

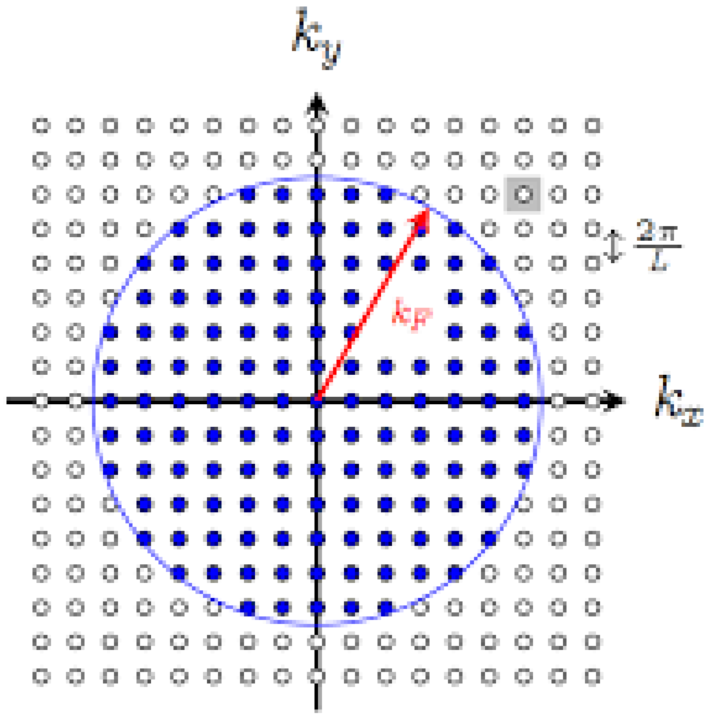
in a 2D box

$$k_x = \frac{2\pi n_x}{L_x}, k_y = \frac{2\pi n_y}{L_y}$$



$$A = L_x L_y$$





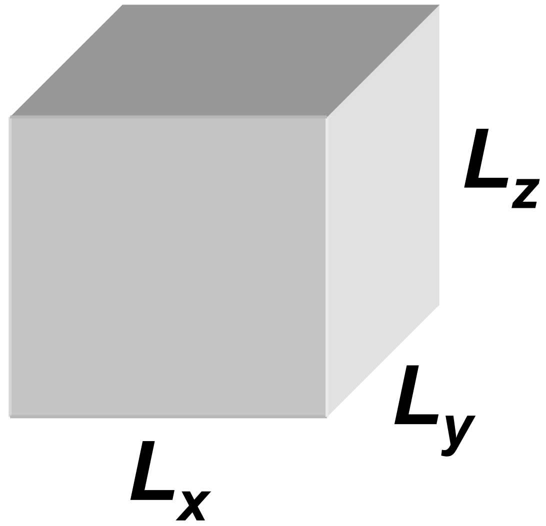
$$N = 2 \cdot \pi k_F^2 \cdot \frac{A}{(2\pi)^2}$$

2D Fermi circle (费米圆)

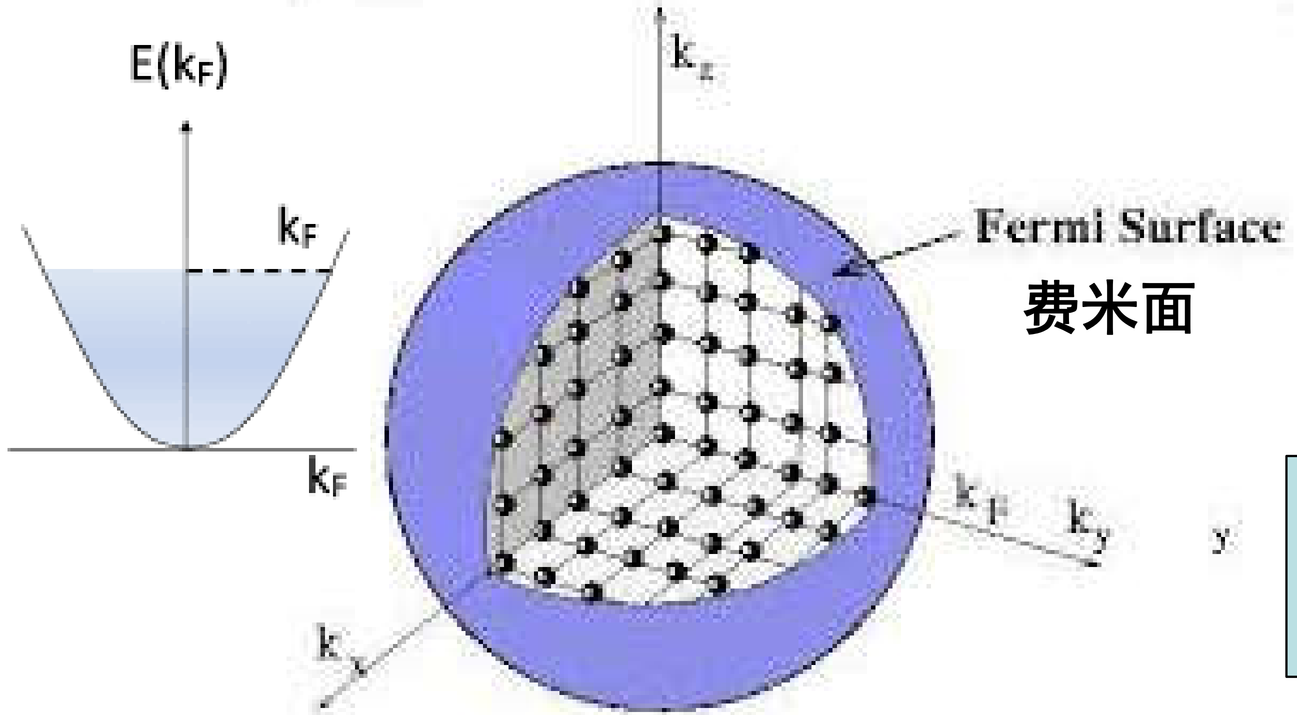
3D solid

in a 3D solid

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



$$\boxed{V = L_x L_y L_z}$$



$$N = 2 \cdot \frac{4\pi}{3} k_F^3 \cdot \frac{V}{(2\pi)^3}$$

3D Fermi sphere (费米球)

3D solid

$$N = 2 \cdot \frac{4\pi}{3} k_F^3 \cdot \frac{V}{(2\pi)^3}$$

in a 3D solid

$n = N/V$ - free electron density

k_F - Fermi wavevector
E_F - Fermi energy
v_F - Fermi velocity
T_F - Fermi temperature

$$k_F = (3\pi^2 n)^{1/3}$$

$$v_F = \frac{\hbar k_F}{m_e}$$

$$E_F = \frac{\hbar^2 k_F^2}{2m_e}$$

$$T_F = \frac{E_F}{k_B}$$

These values are determined by density n, not N or V

highest *occupied* state at $T = 0$ K

Density of States (DOS) 态密度

$g(k)$

DOS - number of energy states/levels in *k* space

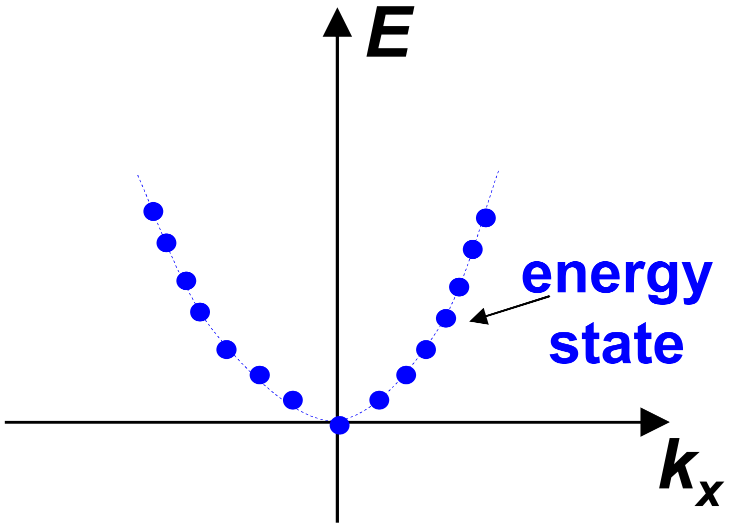
Ashcroft & Mermin, p.35

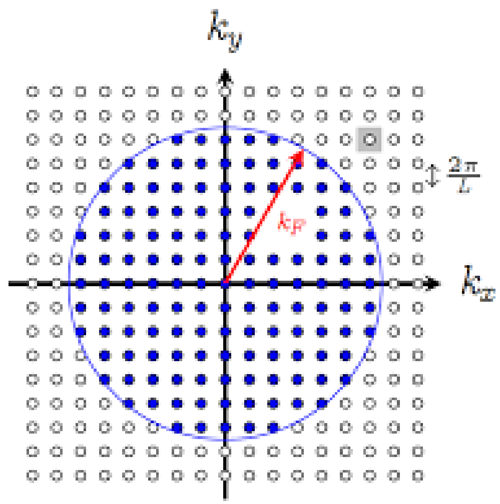
$$g(k) = 2\frac{L}{2\pi}$$

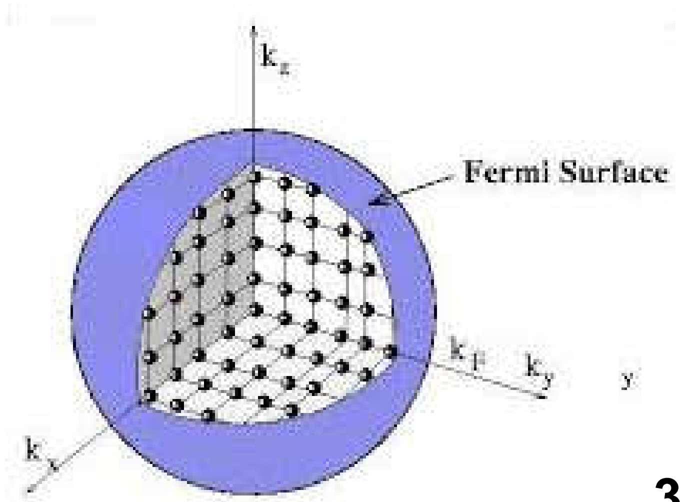
$$g(k) = 2\frac{A}{(2\pi)^2}$$

$$g(k) = 2\frac{V}{(2\pi)^3}$$

1D **2D** **3D**







Density of States (DOS) 态密度

$$g(E)=\frac{dn}{dE}$$

DOS - number of energy states/levels per unit energy in [*E*, *E+dE*], per unit volume

$$k=(3\pi^2 n)^{1/3}$$

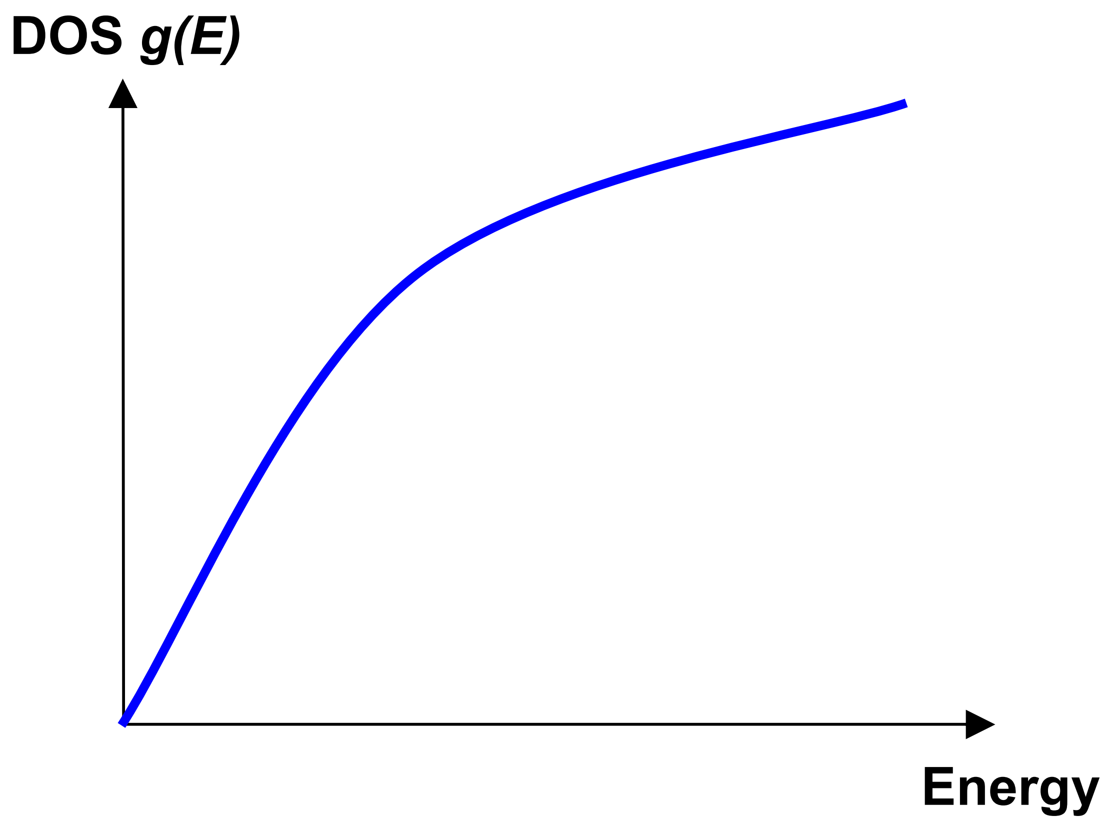
$$E=\frac{\hbar^2 k^2}{2m_e}$$

$$\rightarrow \quad n=\frac{1}{3\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} E^{3/2}$$

$$\rightarrow \quad g(E)=\frac{dn}{dE}=\frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} E^{1/2}$$

Density of States (DOS) 态密度

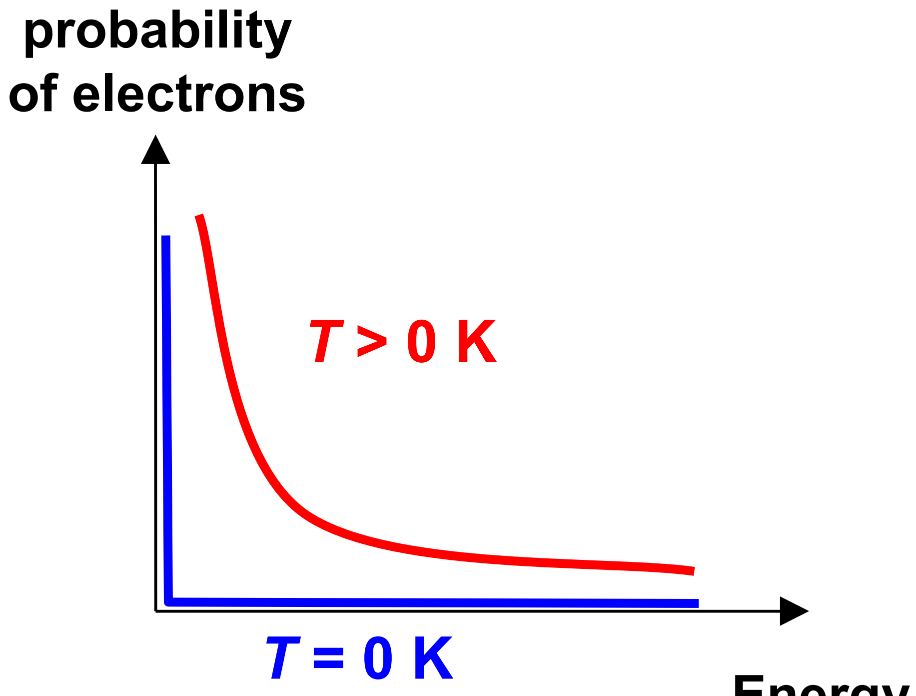
$$g(E) = \frac{dn}{dE} = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} E^{1/2}$$



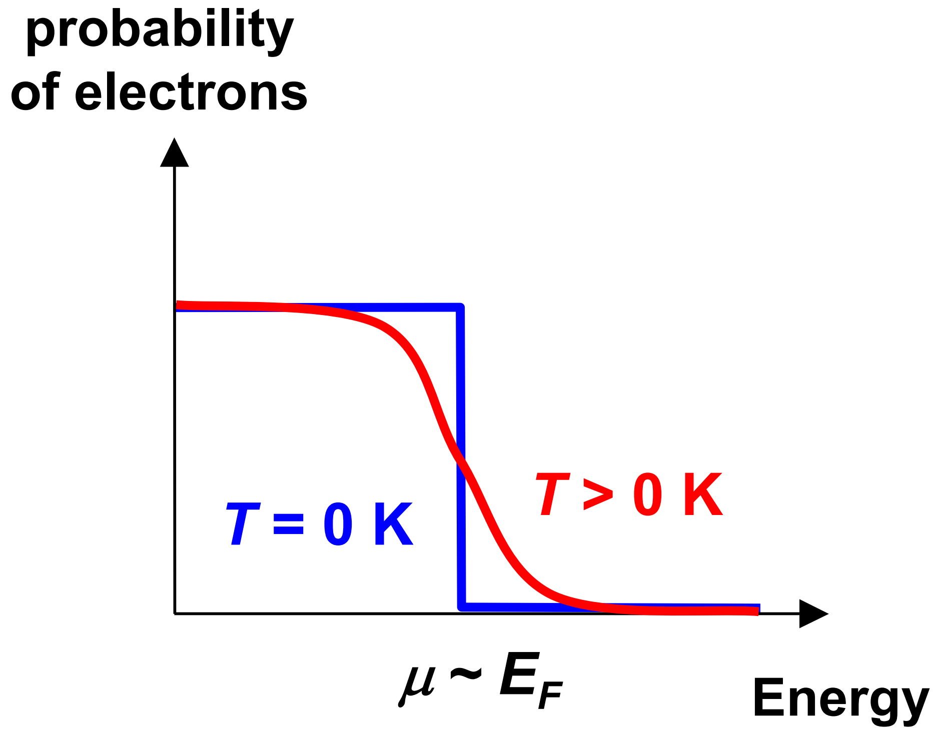
Q: How about in 1D and 2D?

Distribution of Free Electrons

Drude Model
Maxwell–Boltzmann



Sommerfeld Model
Fermi–Dirac



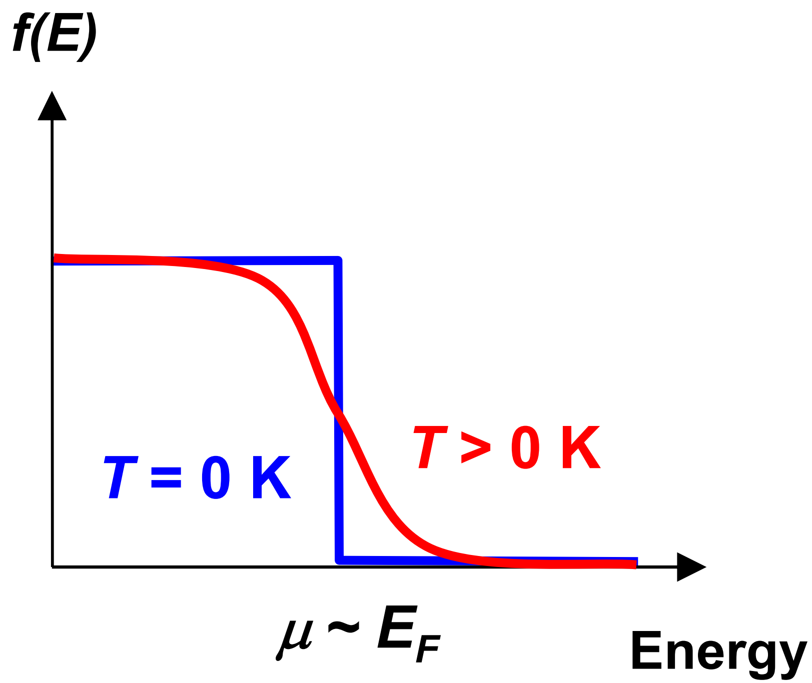
Electrons occupy higher levels of energy, even at 0 K

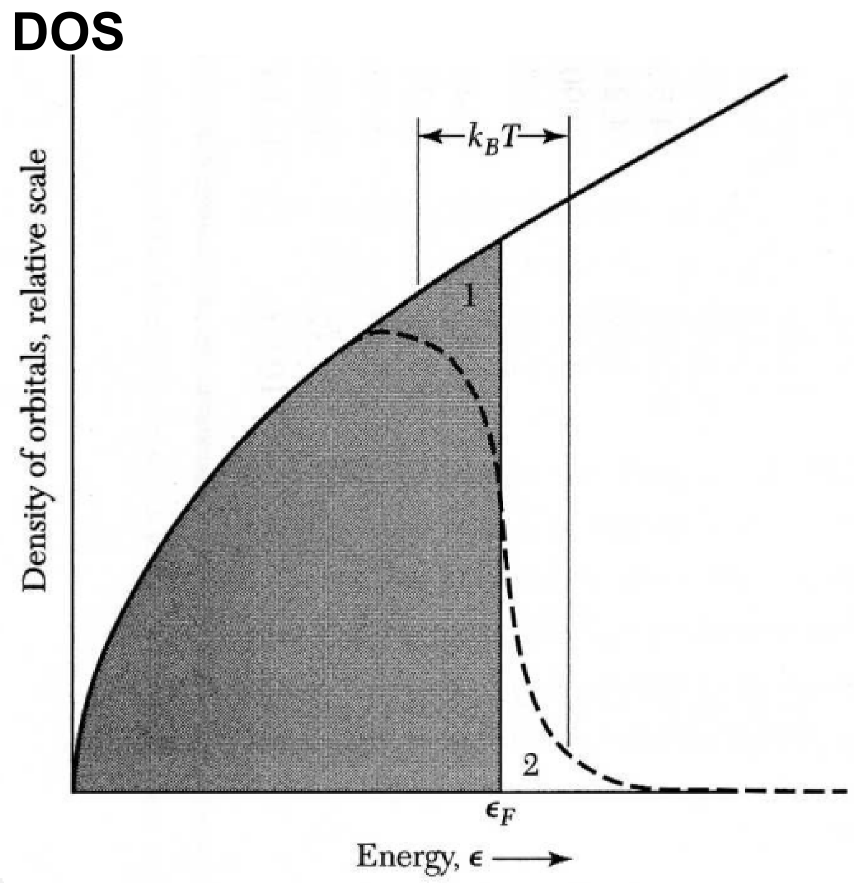
Density of Electrons

Density of electrons = DOS * probability

$$f(E)g(E)$$

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





When T > 0 K, some electrons are excited to higher states (from 1 to 2)

State vs. Electron

energy state / level / orbital
能态 / 能级 / 轨道

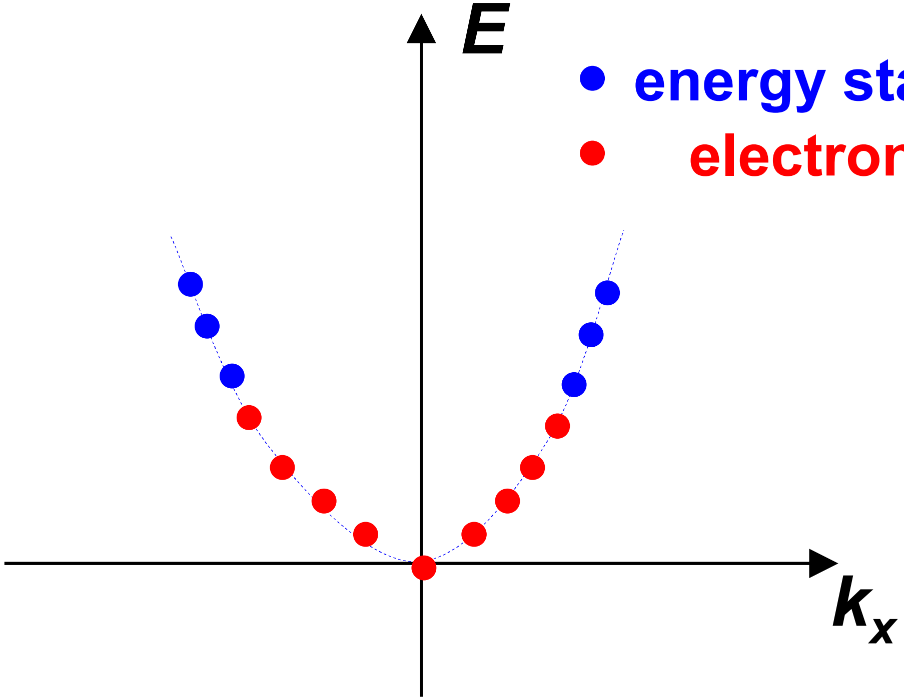
determined by space, lattice, environments, ...

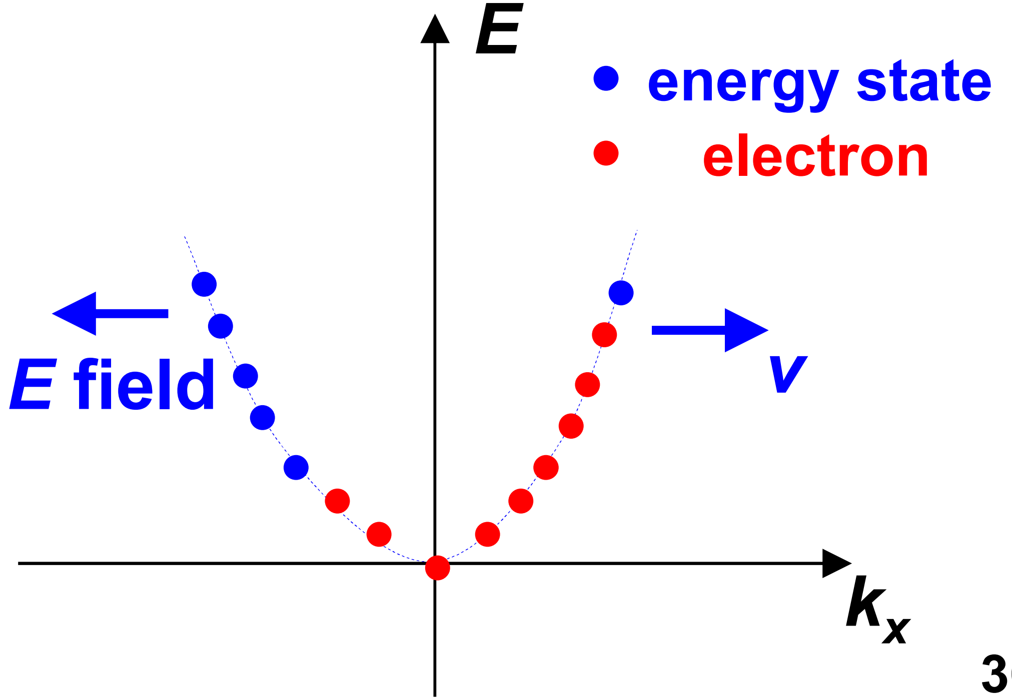
electron / phonon / ...
电子 / 声子 / ...

Electrons in an Electric Field *E*

momentum 动量 $\boxed{p = mv = \hbar k}$

$$\boxed{\mathbf{F} = m\frac{d\mathbf{v}}{dt} = \hbar\frac{d\mathbf{k}}{dt} = -e\mathbf{E}} \rightarrow \boxed{\delta\mathbf{k} = -\frac{e\mathbf{E}}{\hbar}t}$$





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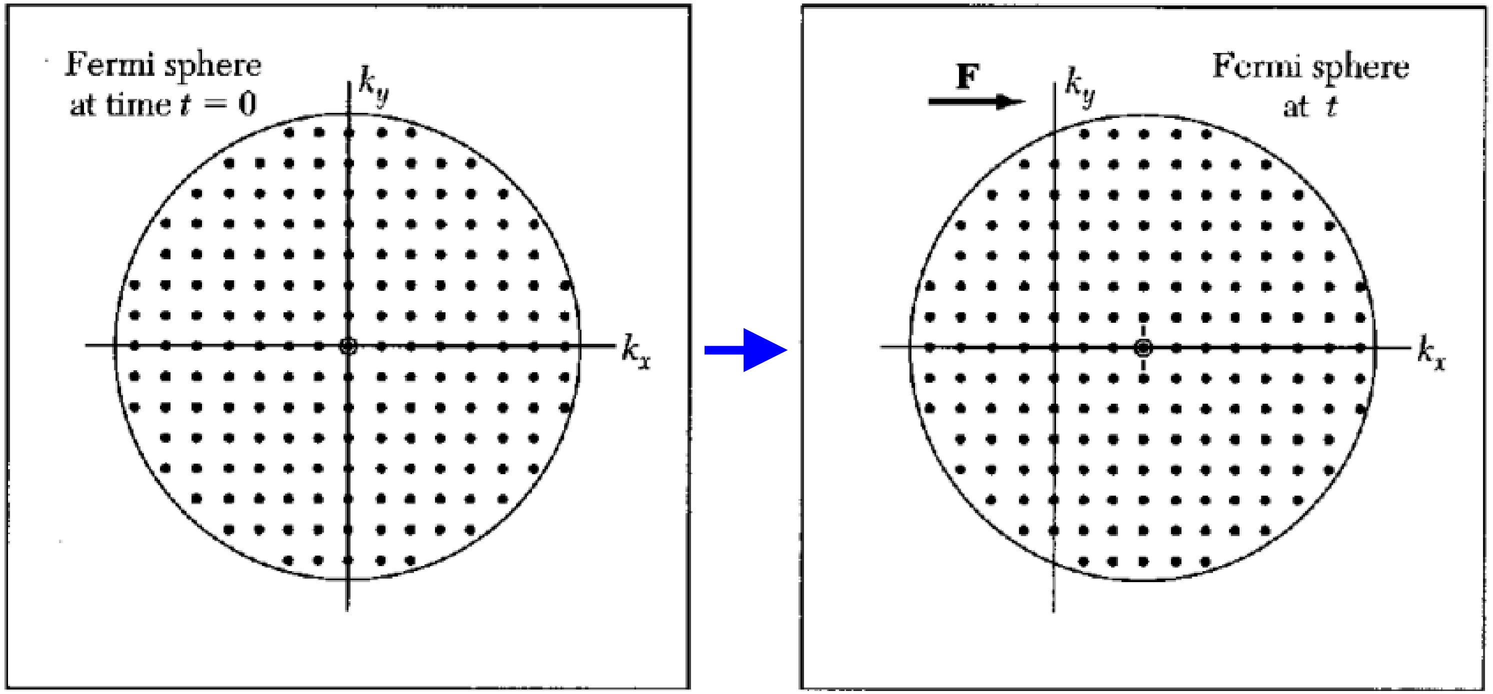

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collision time *t* = τ, the displacement δk is steady

$$\delta\mathbf{k} = -\frac{e\mathbf{E}}{\hbar}\tau \rightarrow v = \frac{\hbar\delta\mathbf{k}}{m} = -\frac{e\mathbf{E}}{m}\tau$$

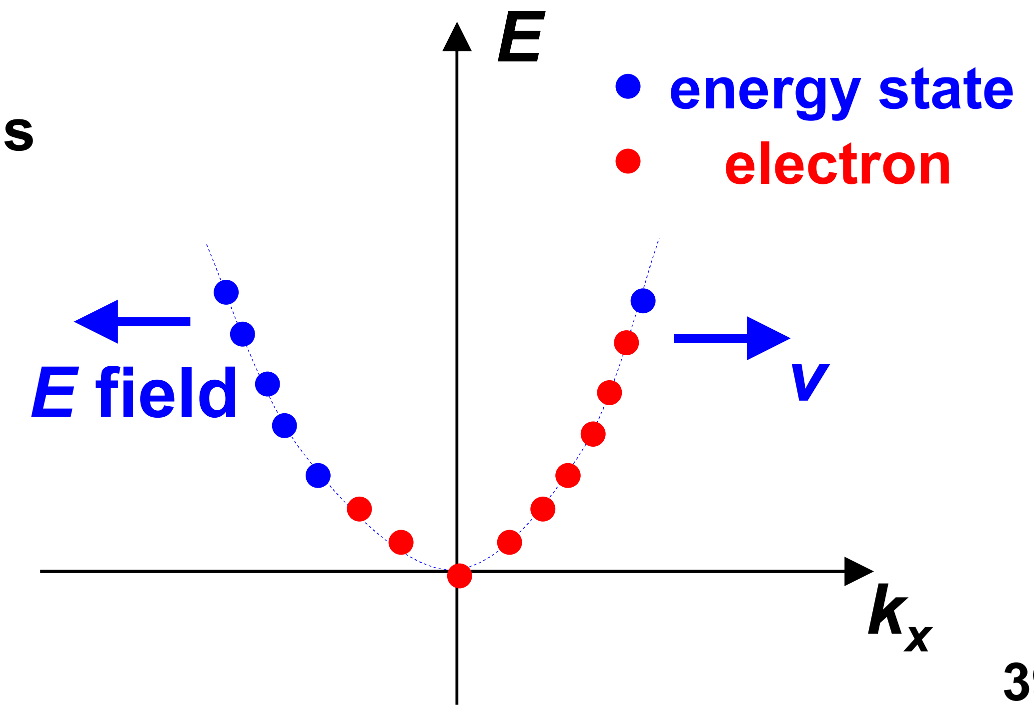
$$\rightarrow \mathbf{j} = -ne\mathbf{v} = \frac{ne^2\tau}{m}\mathbf{E} = \sigma\mathbf{E}$$

Ohm's law

Electron Conductivity - Revisit

- Electrons are in different energy states, therefore have different velocities and energies. Under *E* field, there are more electrons moving in the opposite direction.
- Mobility μ and relaxation time τ are average values for all the free electrons
- only σ is meaningful for metals

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



Success of The Sommerfeld Model

- **Ohm's Law**
- **Electronic conductivity** σ
- **Thermal conductivity of electrons**
- **Electronic heat capacity**

Failures of The Sommerfeld Model

It *cannot* explain

- Electronic / Thermal properties of some other metals
- Hall effect / Hall coefficient
- Insulators / Semiconductors
- ...

The Free Electron Models

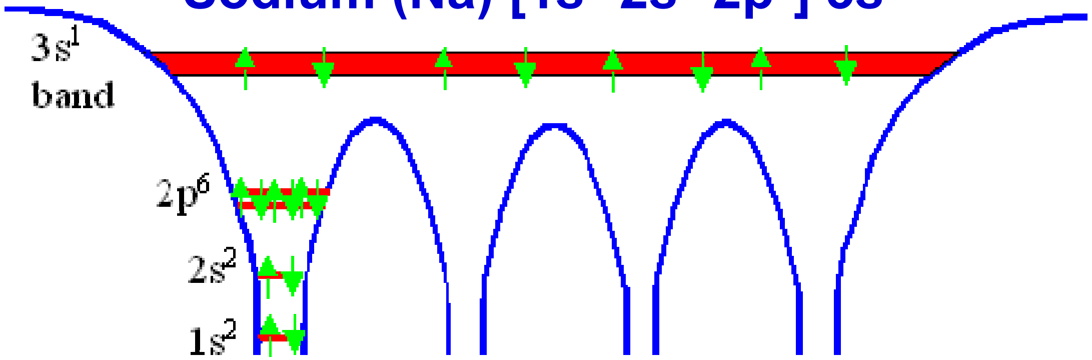
- The Drude Model: 1900s
- The Sommerfeld Model: 1920s

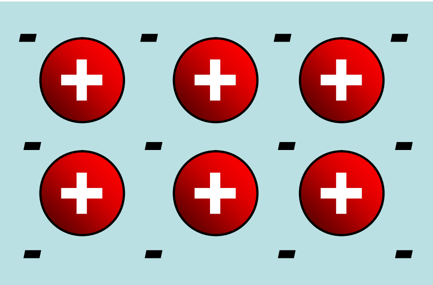
- What are missing?
  - Material and atom structures
  - Potentials of positive ions
  - Localized electrons
  - ...

P. Drude
1863–1906

A. Sommerfeld
1868–1951

Sodium (Na) [$1s^2$ $2s^2$ $2p^6$] $3s^1$





positive ions
+
electron cloud

Thank you for your attention