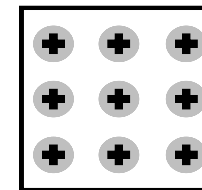
# Chapter 6. The Free-Electron Model

# Free electron model for electrons in metals

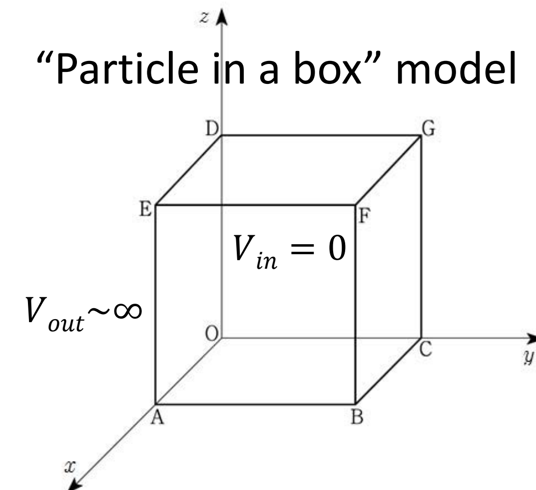
- It is sometimes found that the outmost valence electrons in a solid can be treated as if they are essentially free electrons, particularly in metals where outer-most valence electrons are not involved in chemical bonding.

  ex) metallic sodium has $1s^2 2s^2 2p^6 3s^1$, and the outermost 3s electron can be considered to be essentially free.



Positively charged ions are shielded by other electrons. $V \sim 0$ inside solid

“Particle in a box” model




- Almost-free electrons confined within the metal
  → The potential barrier to overcome for escape is the work function.

[Main questions in chapter 6]

1. What energies are allowed for the valence electrons in a metal?
2. What is the density of allowed states? How many states lie between $E$ and $E+dE$?
3. How are these states occupied by electrons at various temperatures?

# What energies are allowed?

Outside metal; $\psi \sim 0$,  inside metal; $-\frac{\hbar^2}{2m}\nabla^2\psi - E\psi = 0$ (Schrodinger eq.)

(separation of variables) $\psi(x,y,z) = X(x)Y(y)Z(z)$

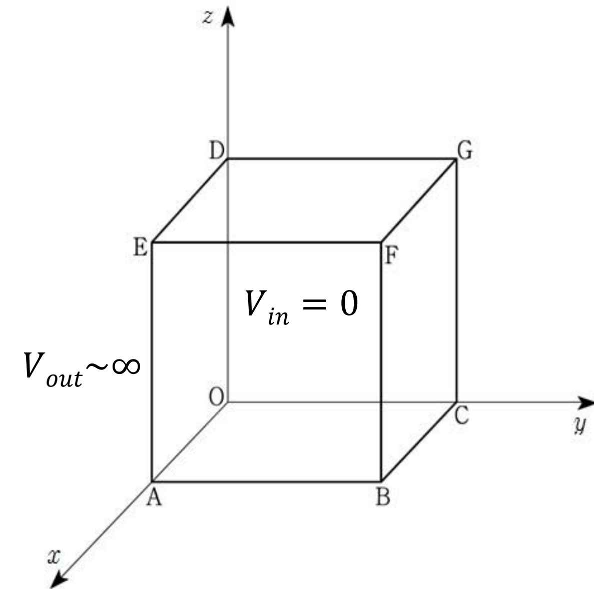
$$E = E_x + E_y + E_z$$

$$e.g. \quad \frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}E_x X = 0$$

$$X = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{n_x \pi x}{L}\right)$$

$$E_x = {n_x}^2 \frac{\hbar^2\pi^2}{2mL^2} \quad (n_x\text{:integer})$$

$$\psi_{n_x n_y n_z} = \left(\frac{2}{L}\right)^{\frac{3}{2}} \sin\frac{n_x \pi x}{L} \sin\frac{n_y \pi y}{L} \sin\frac{n_z \pi z}{L}$$




$$E_{n_x n_y n_z} = \frac{\hbar^2\pi^2}{2mL^2}({n_x}^2 + {n_y}^2 + {n_z}^2) = \left(\frac{\hbar^2}{2\mathrm{m}}\right)|\mathbf{k}|^2$$

with $\mathbf{k} = \mathbf{e}_1\left(\frac{n_x\pi}{L}\right) + \mathbf{e}_2\left(\frac{n_y\pi}{L}\right) + \mathbf{e}_3\left(\frac{n_z\pi}{L}\right)$

# What energies are allowed?

$$E_{n_x n_y n_z} = \frac{3.42 \times 10^{-15}}{L^2}({n_x}^2 + {n_y}^2 + {n_z}^2) \quad (eV)$$

Ground state: $E_{111} = \frac{3\hbar^2\pi^2}{2mL^2}$

$L \sim O\ (cm), E_{111} \sim 0, \Delta E \sim 0$

The ground state energy is effectively zero, and the distribution of energy states can be treated as ***quasi−continous*** since the differences between discrete states are so small

## Degeneracy

: Different state with different spatial distribution of probability density, but the same energy (single energy level)

Degenerate state $(n_x, n_y, n_z)$

$(1,1,1), (2,2,2)$ : not degenerate

Degeneracy: $E = 41\frac{\hbar^2\pi^2}{2mL^2}$

$(1,2,6), (1,6,2), (2,1,6), (2,6,1), (6,1,2), (6,2,1)$

$(3,4,4), (4,3,4), (4,4,3)$ 9 fold degenerate state

# The density of the allowed states as a function of E

*What is the Density of Allowed States as a Function of Energy?*

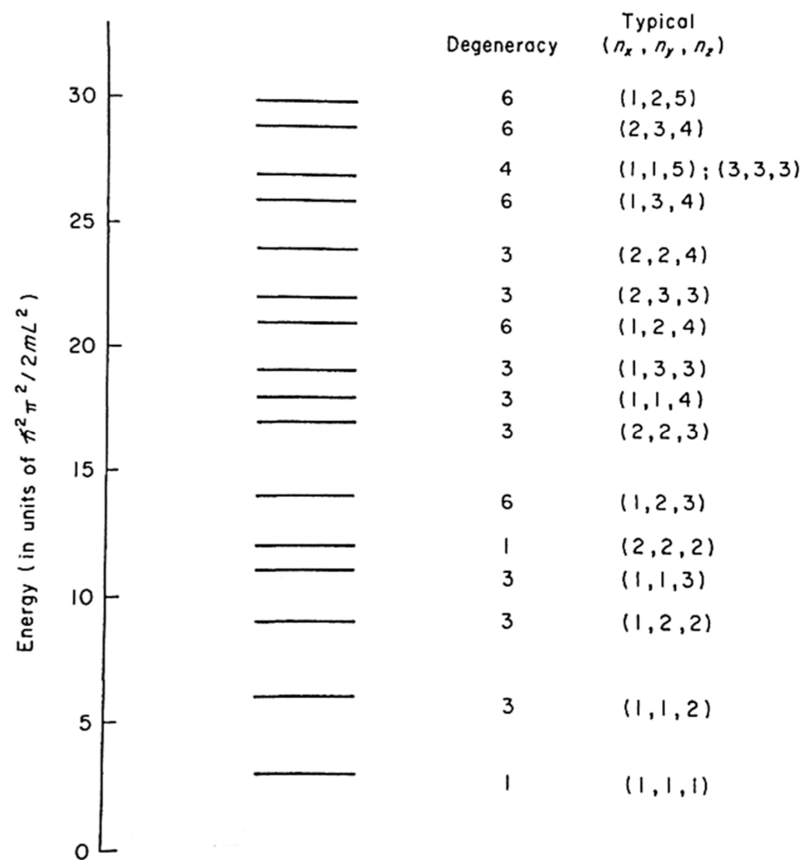



**FIG. 6.2** The lowest sixteen energy levels for a particle in a three-dimensional box, t with their degeneracy and typical quantum-number sets.

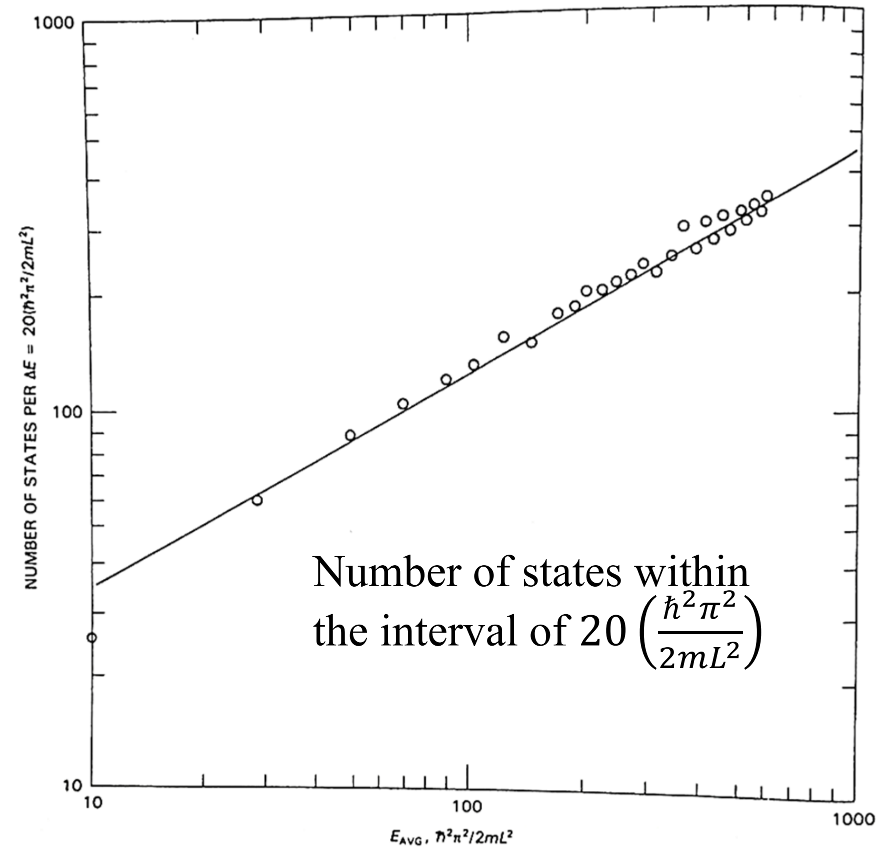



**FIG. 6.3** Number of states per energy interval vs energy for states in a three-dimensional box with $E \leq 600(\hbar^2\pi^2/2mL^2)$.

# The density of states as a function of $E$

How many states lie within a particular energy range, *e.g.*, the energy range between $E$ and $E+dE$?

Let $n(E)$ is the density of electron at energy $E$,

Then $n(E)=N(E)f(E)$

where, $N(E)$: density of allowed state, # of states between $E$ and $E+dE$

$f(E)$ : probability of occupation of a state

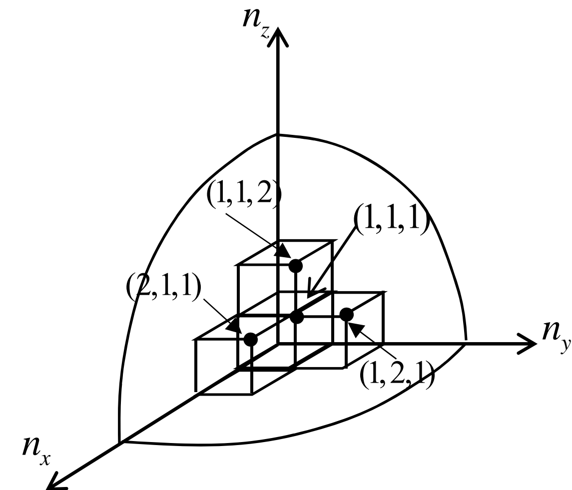
$\mathcal{N}(E)$: the total number of states with energy less than $E$

$$\mathcal{N}(E) = \int_0^E N(E)dE, \quad N(E) = \frac{d\mathcal{N}(E)}{dE}$$

How to count $\mathcal{N}(E)$?

$$({n_x}^2 + {n_y}^2 + {n_z}^2) = \frac{2mL^2}{\hbar^2\pi^2}E$$

:equation of a sphere with radius of $\sqrt{\frac{2mL^2}{\hbar^2\pi^2}E}$




[n-space]
: one state ($n_x$, $n_y$, $n_z$) per unit volume

# The density of states as a function of $E$

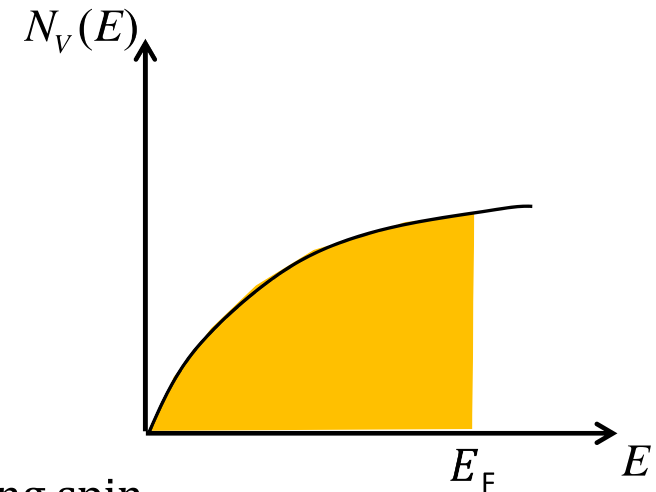
$\mathcal{N}(E)$: volume of the positive octant of the sphere with radius $R = \sqrt{\frac{2mL^2}{\hbar^2\pi^2}E}$

$$\mathcal{N}(E) = \frac{1}{8}\frac{4\pi}{3}\left(\frac{2mL^2}{\hbar^2\pi^2}E\right)^{\frac{3}{2}} = \frac{L^3}{6\pi^2}\left(\frac{2m}{\hbar^2}E\right)^{\frac{3}{2}}$$

$$= \frac{V}{6\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}E^{\frac{3}{2}} \quad (V = L^3)$$

$$N(E) = \frac{d\mathcal{N}(E)}{dE} = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}E^{\frac{1}{2}}$$

: Density of orbital states without considering spin

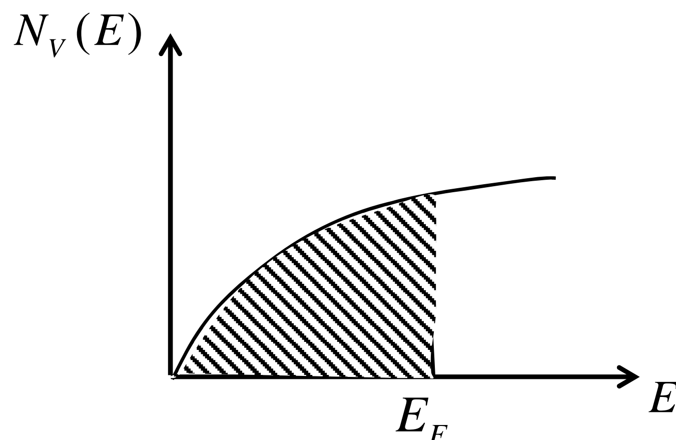



$N_v(E)$: the number of states per unit volume − "density of states"
$N(E) \times 2$ due to spin degeneracy

$$N_v(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}E^{\frac{1}{2}}$$

# Occupation probability: $f$(E)

At 0 K, we can expect that electrons will fill up the states, starting from the lowest energy first, until the last electron to be added has an energy $E_F$ which marks the occupied states from the higher-lying unoccupied states.




Fermi energy $E_f$
: The highest occupied electron state

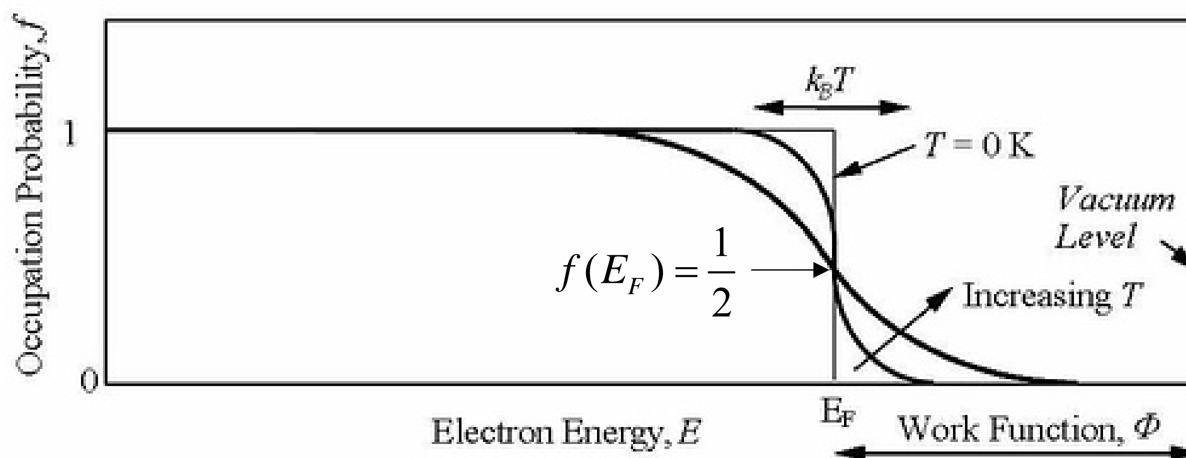
- Density of free electrons ($n$)

$$n = \int_0^{E_F} N_v(E)dE = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E_F{}^{\frac{3}{2}}$$

$$E_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{\frac{2}{3}} = \frac{\hbar^2 k_F{}^2}{2m} \qquad k_F = (3\pi^2 n)^{\frac{1}{3}}$$

# Occupation probability: $f(\mathrm{E})$

What is $f(E)$ for T > 0 K?
$E_F$ is a very slow function of temperature.

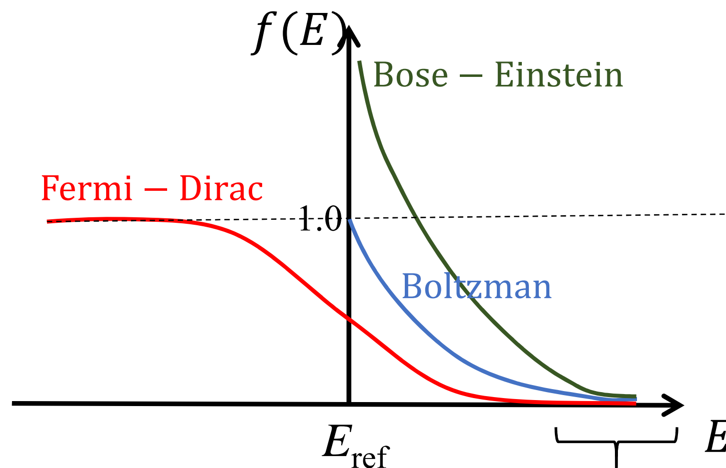



Requirements on $f(E)$
(1) For $E \ll E_F$, $f(E)=1$
(2) For $E \gg E_F$, $f(E) \sim 0$

$$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$$

[Fermi−Dirac distribution function]

# Occupation probability: distribution




$E_{ref} = 0$ for Boltzman & B–E

$E_{ref} = E_F$ for F–D

At large energies, three distributions are the same.

For Fermi function

$f(E)=1$ for $\mathrm{E} \ll \mathrm{E}_F$

$f(E)=\frac{1}{2}$ for $\mathrm{E} = \mathrm{E}_F$

$f(E)=0$ for $\mathrm{E} \gg \mathrm{E}_F$

For B-E distribution

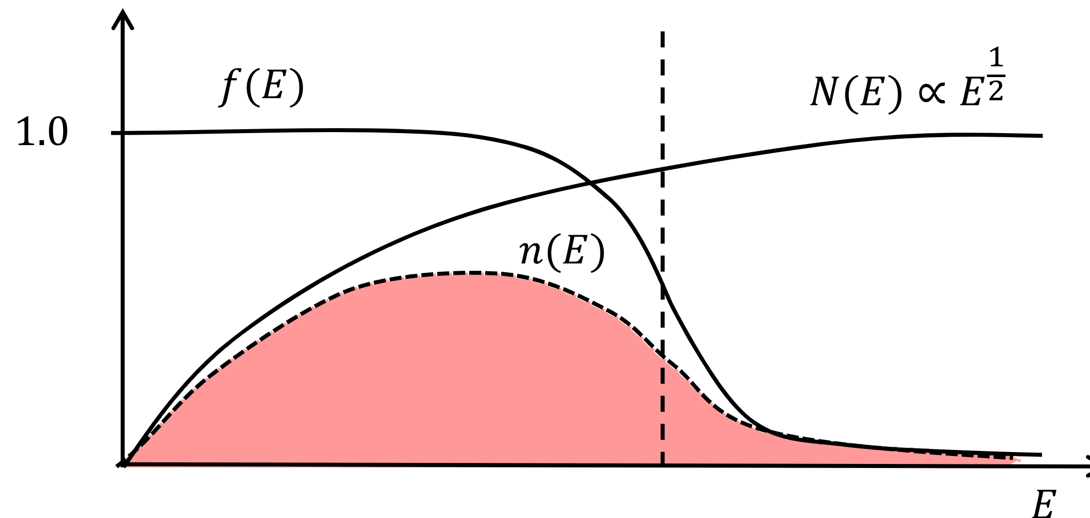
Infinite occupancy for phonons and photons with zero energy

# Density of occupied states

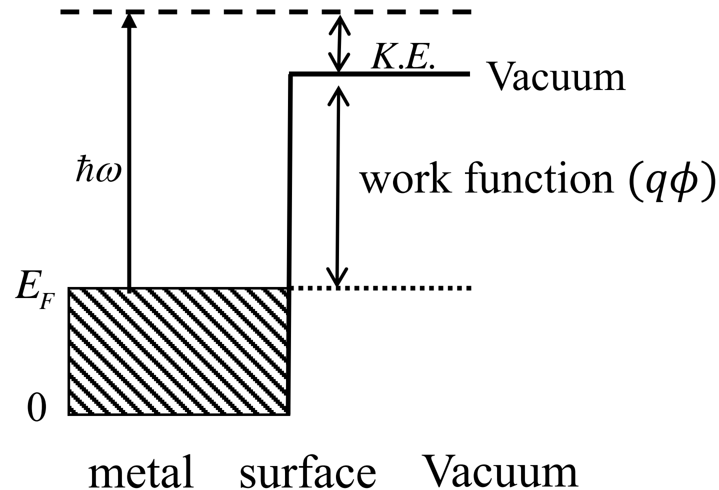
: every physically distinct distribution of N particles among various energy states in equally likely to occur.

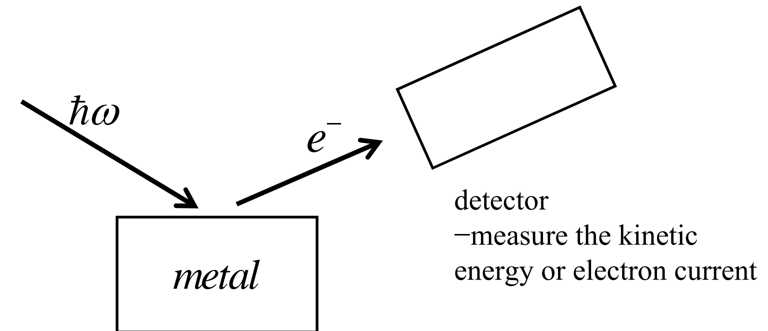
$$N_{\mathrm{v}}(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}} \qquad f(E) = \frac{1}{e^{(E-E_F)/kT}+1}$$

$$n(E) = f(\mathrm{E})\, N_{\mathrm{v}}(\mathrm{E}) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \frac{E^{\frac{1}{2}}}{e^{(E-E_F)/kT}+1}$$



# Photoemission




- To be emitted from the metal, electrons need to overcome the energy barrier, work function.

$$K.E. = \hbar\omega - V_\omega$$

- At low temperature, the minimum energy to produce photoemission is

$$\hbar\omega_{\min} = q\phi \qquad \lambda_{\max} = \frac{hc}{q\phi}$$

: Method for measurement of the work function of a metal surface

Note work function varies depending on the crystal face.

# Photoemission

(a) Rate of electron excitation by light

$$\frac{dn(x)}{dx} = C\exp(-\alpha x)$$

($\alpha$: absorption coefficient)

(b) Absorption coefficient is a function of the photon energy, $\hbar\omega$.
The photoemission current depends on the photon energy.

(c) Excitation of electrons can occur from the initial states at the Fermi energy or below.

(d) If electrons are scattered during excitation, there would be no emission.
(probability of not being scattered during traveling a distance $x$) = $\exp\left(-\frac{x}{x_0}\right)$
$x_0$: mean free path for scattering

(e) Electrons approaching the surface and to be photoemitted undergo reflection due to wave-like properties and change in kinetic energy at the surface.

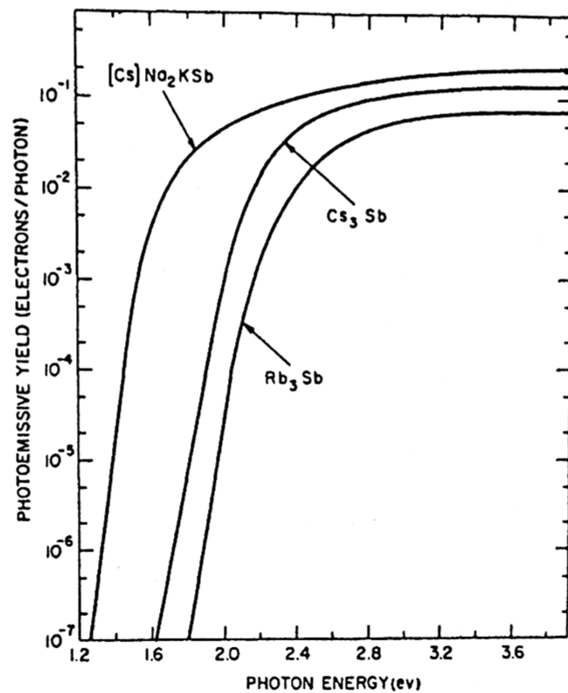
# Photoemission

ex) $q\phi \equiv V_{vacuum} - E_F$

$q\phi$ of metals: 1.8 $eV$ (cesium) ~ 4.8 $eV$ (nickel)

Cs　　Ni

700 nm　260 nm

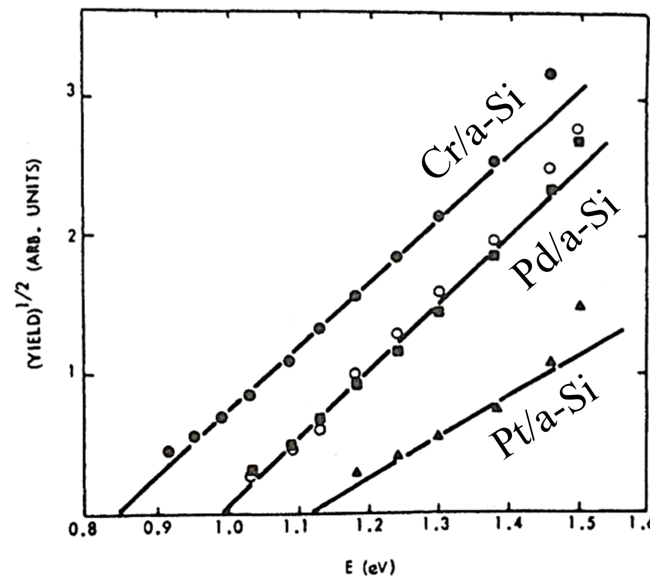


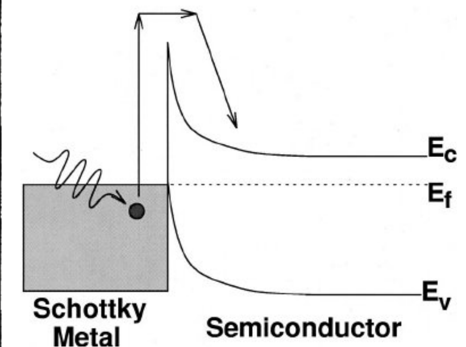

control of work function in intermetallic compounds

Internal photoemission

: In a contact between metal and another material, there is a barrier for photoemission.

Photoemission yield ~ (photon E – barrier height)$^2$



# Thermionic emission

- Emission of high energy electron corresponding to the high energy tail of the Fermi-distribution at high temperature.

For thermionic emission, $E_0 = \frac{1}{2} m {v_x}^2 \geq (E_F + q\phi)$

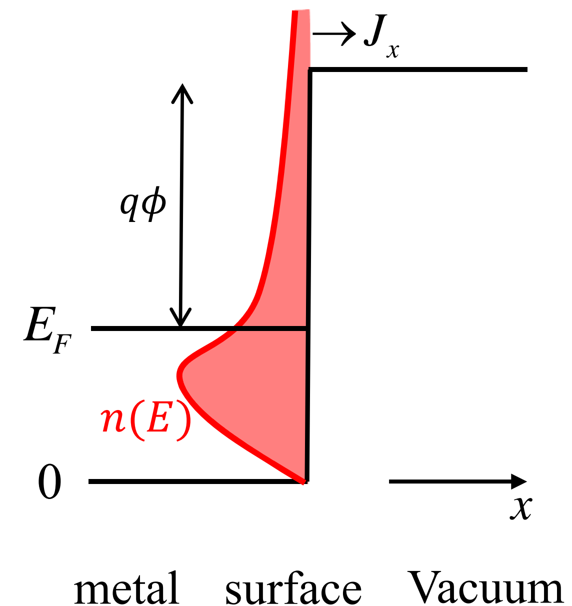
$\tilde{J}$ = (density of electrons with sufficient energy to pass into vacuum) × (velocity component in the x directon)

$$J_x = \int_{E_F + q\phi}^{\infty} q v_x dn = \int_{E_F + q\phi}^{\infty} q v_x n(E) dE$$

$$n(E)dE = f(E) N_v(E) dE$$

$$= \frac{8\pi m^3}{h^3} \frac{v^2 dv}{e^{(E - E_F)/kT} + 1}$$

$$(\because E = \frac{1}{2} m v^2, dE = m v dv)$$



# Thermionic emission

$4\pi v^2 dv$ (in spherical coordinate)$\sim dv_x dv_y dv_z$ (in courtesian coordinate)

Since $E - E_F \gg kT$

$$\frac{1}{e^{(E-E_F)/kt}+1} \rightarrow e^{-(E-E_F)/kT} = e^{E_F/kT} e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2kT}}$$

$$J_x = \int_{-\infty}^{\infty}\int dv_x dv_y \int_{\sqrt{\frac{2(E_F+q\phi)}{m}}}^{\infty} \frac{2m^3}{h^3} q v_x e^{E_F/kT} e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2kT}} dv_x$$

$$\int_{-\infty}^{\infty} e^{-\frac{mv_y^2}{2kT}} dv_y = \int_{-\infty}^{\infty} e^{-\frac{mv_z^2}{2kT}} dv_y = \left(\frac{2\pi kT}{m}\right)^{\frac{1}{2}}$$

$$\int_{\sqrt{\frac{2(E_F+q\phi)}{m}}}^{\infty} v_x e^{-\frac{mv_x^2}{2kT}} dx = \frac{kT}{m} e^{-(E_F+V_w)/kT}$$

$$\therefore J_x = \left(\frac{4\pi qm}{h^3}\right)(kT)^2 \exp\left(-\frac{q\phi}{kT}\right)$$

[Richardson Eq.]

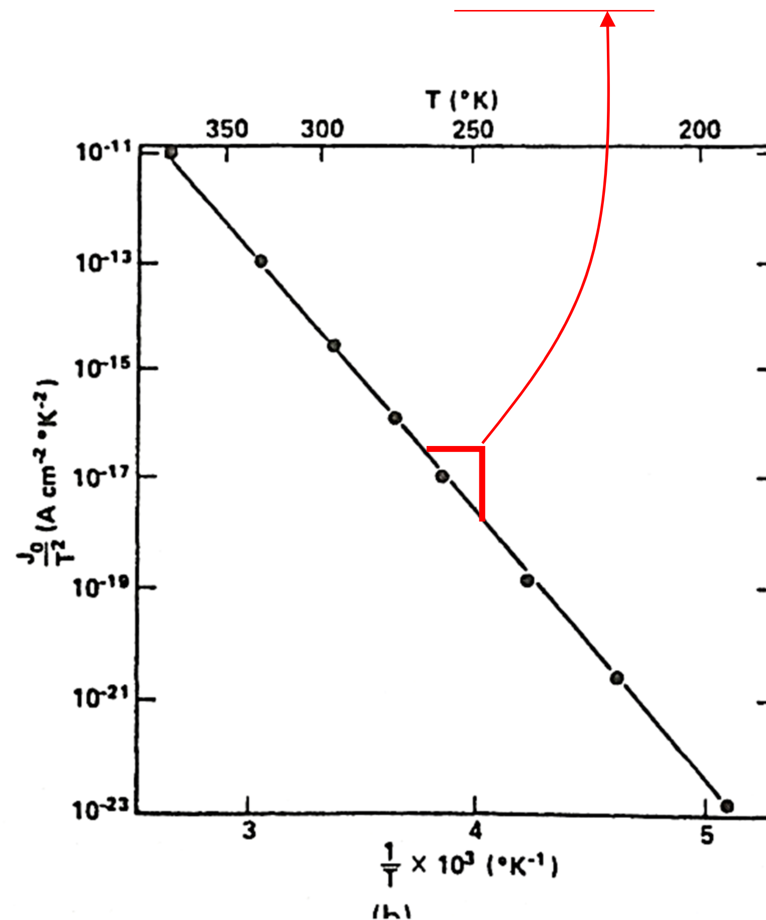
$$A = \left(\frac{4\pi qm}{h^3}\right)(kT)^2$$

(Richardson constant)

# Thermionic emission

From a plot of $\ln(\frac{J_x}{T^2})$ vs. $\frac{1}{T}$ from $J_x = \left(\frac{4\pi q m}{h^3}\right)(kT)^2 \exp(-q\phi/kT)$

Straight line with a slope of $-q\phi/k$



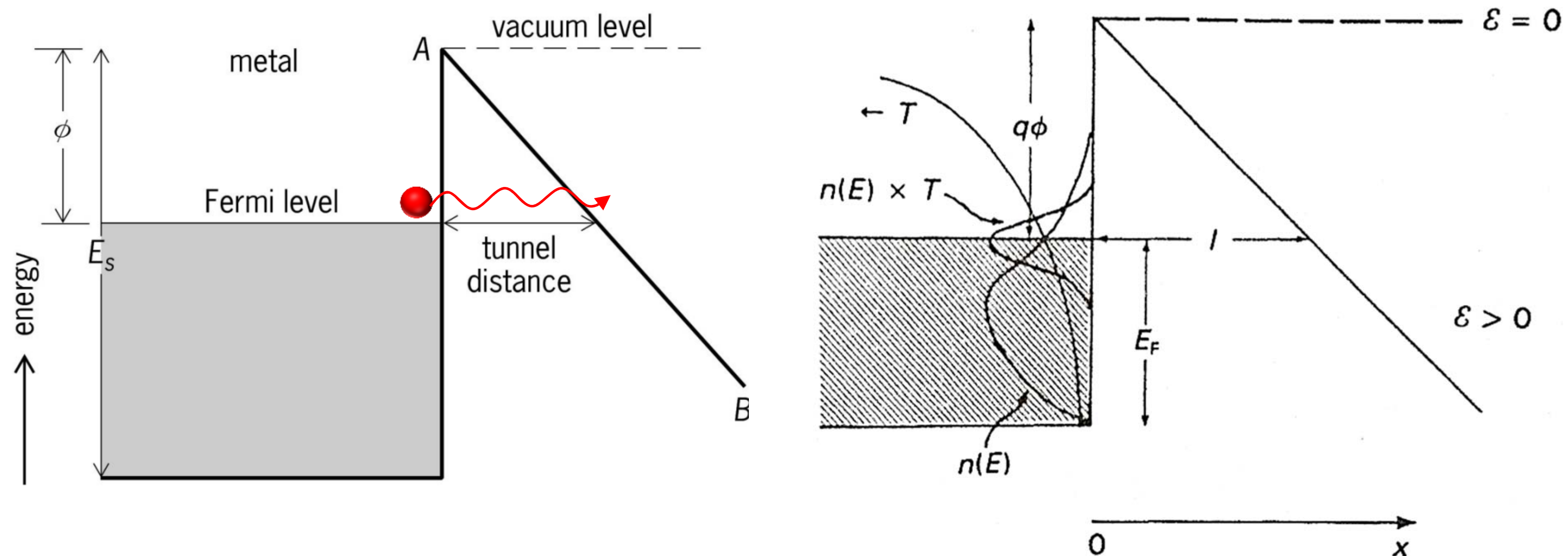

ex) contact between Pd and a-Si
The slope gives an effective barrier height of 0.97 eV, which is similar to the barrier measured by photoemission.

# Field emission

- Field-induced electron emission from metals
- The mechanism: quantum mechanical tunneling
- The rate of emission ∝ $n(E) \times T(E)$

  $n(E)$: the density of occupied states at a given $E$

  $T(E)$: tunneling transmission coefficient at the same $E$



# Field emission

- Rate of emission ~ (density of occupied states at given E)

  × (tunneling transmission coeff.)
- Total emission $= \int_E$ (the rate of emission)$dE$
- Most of the emission, however, comes from state close to $E_F$

  For high energy, n(E) ↓, T(E) ↑

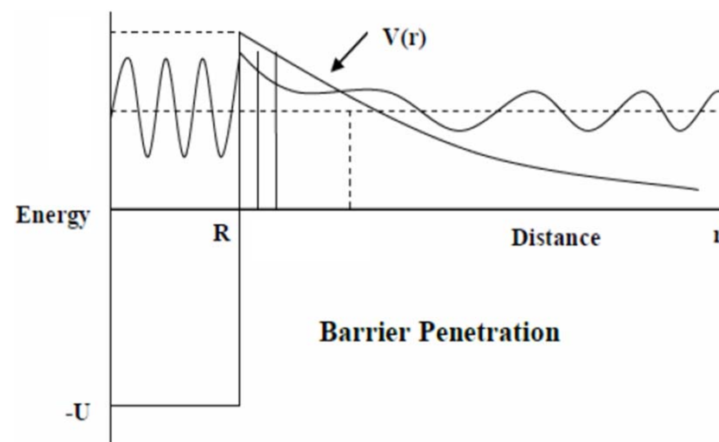
  For low energy, n(E) ↑, T(E) ↓

  $\varepsilon = -\nabla\phi = -\frac{d\phi}{dx}$

  ($\phi$: potential, $\varepsilon$: electric field)

  $\phi = -q\varepsilon_x$ for const. $\varepsilon$

  : In electric field, potential energy varies with distance $x$ from the surface




- A traveling wave moving in the $+x$ direction approaching the barrier from the left would be attenuated in passing "through" the region of the barrier

# Field emission

- Approximate tunneling probability T is given by Wentzel−Kramers−Brillouin

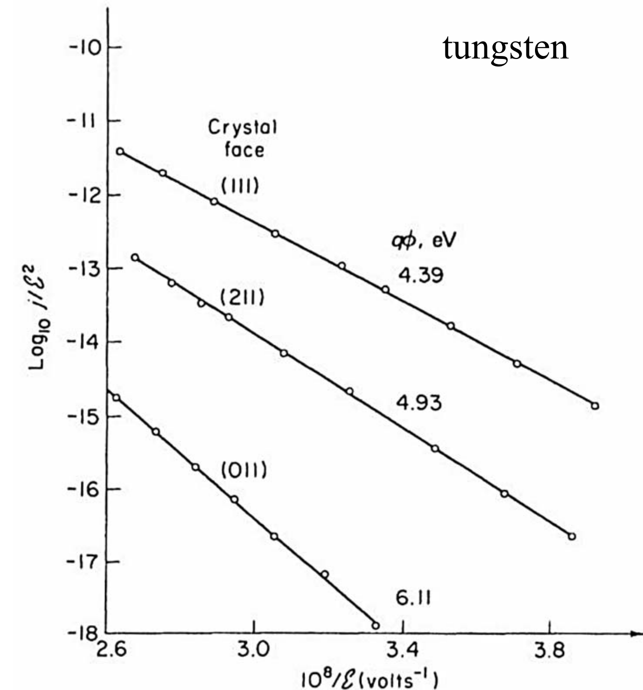
$$T = \exp\left(-\frac{2}{\hbar}\int_0^d \{2m(V_0 - E)\}^{\frac{1}{2}} dx\right) \text{ [WKB model]}$$

$(V_0 - E)$: effective barrier height, $d$: barrier width

Considering the tunneling at the Fermi level,

$$V_0 - E = q\phi\left(1 - \frac{x}{l}\right),\ d = l$$

$$\therefore T(E_F) = \exp\left(-\frac{4}{3\hbar}(2mq)^{\frac{1}{2}}\frac{\phi^{\frac{3}{2}}}{\varepsilon}\right)$$



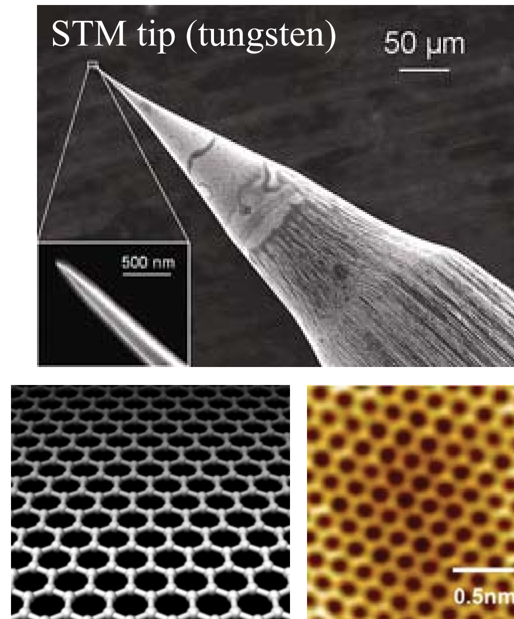

- From integration over the whole distribution of $n(E) \times T(E)$

$$J \sim \varepsilon^2 \exp\left(-\frac{4}{3\hbar}(2mq)^{\frac{1}{2}}\frac{\phi^{\frac{3}{2}}}{\varepsilon}\right)$$

Plot of $\ln\frac{J}{\varepsilon^2}$ vs. $\frac{1}{\varepsilon}$ $\Rightarrow$ straight line with slope of $\phi^{\frac{3}{2}}$

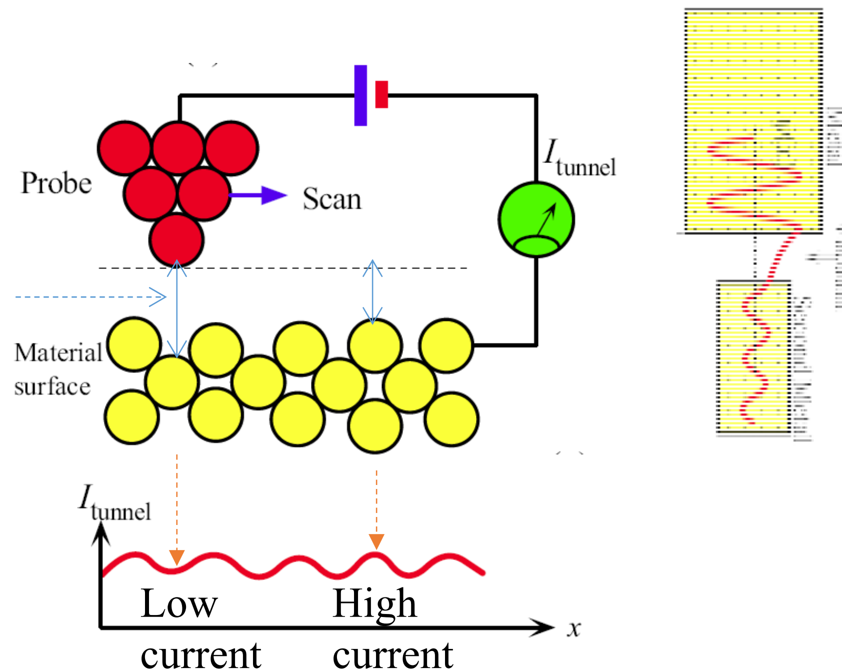
note: J is independent of temperature

## Scanning tunneling microscope (STM)

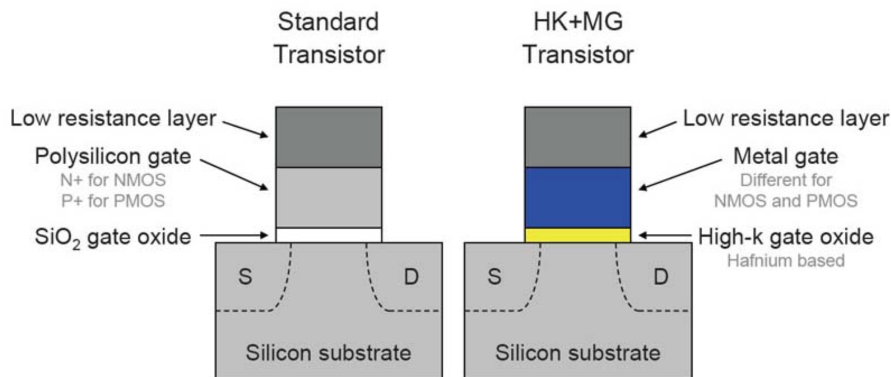



Graphene

Tunneling distance




## Leakage current in nanoscale transistor




The size of the transistor constantly scales down. At the same time, the thickness of gate oxide - an insulator separating the gate electrode and channel layer - also becomes thinner. When the thickness of the oxide is only a few nanometers, the tunneling current through the gate oxide becomes sizeable, which induces failure of the devices. To resolve this issue, the industry (pioneered by Intel) changed the material for the gate oxide from $SiO_2$ to $HfO_2$ that has high dielectric constant. So, we can decrease the oxide thickness while maintaining the capacitance.

# Heat capacity

- A significant contribution to the heat capacity comes from the free electrons present in the metals in addition to the lattice vibration.

  ex) semiconductor and insulator – lattice vibration

  metal – free electrons significantly contribute to the heat capacity

- The contribution of lattice vibrations:

  Phonon E

  Density of lattice vibrational states

  $$C_L = \partial U_L / \partial T$$

  $$U_L = \int_0^{\omega_D} U_L(\omega) d\omega = \int_0^{\omega_D} \hbar\omega [\exp\{(\hbar\omega/kT\} - 1]^{-1} N_L(\omega) d\omega$$

  $$C_L \propto T^3$$

- The contribution of free electrons

  $$C_e = \partial U_e / \partial T$$

  $$U_e = \int_0^{\infty} U_e(E) dE = \int_0^{\infty} E f(E) N_v(E)\, dE$$

  $C_e \propto T$ for low T

- At low temperature,

  $$C = C_L + C_e = AT^3 + BT$$

  Plot of $\frac{C}{T}$ vs. $T^2$ $\Longrightarrow$ slope = A and intercept = B