

# 2. Quantum Theory of Solids

## 2A. Free Electron Model

## 2B. Periodic Potential and Band Structure

## 2C. Lattice Vibration

(Bube Ch. 6)

In the hydrogen atom, the Schrödinger equation was exactly solved and full energy spectrum was obtained **without any approximation**. This is impossible for real solids where Avogadro's numbers of atoms and electrons coexist within the same system. Therefore, one has to introduce some level of **approximation or assumption** to come up **with a solvable model**. That is to say, **every model has limitations in explaining the experimental data**. When one theory fails, we can devise a more accurate one starting from the fundamental Schrödinger equation.

In this chapter, we begin with one of the simplest quantum model of solids that best applies to metals with conduction electrons originating from **s orbitals**, for instance **alkali metals** (Li:  $1s^2 2s^1$ , Na, ...) and **noble metals** (Cu, Ag:  $[Ar] 3d^{10} 4s^1$ , Au, .).

While the free electron model is highly successful in explaining many observations for metals, it **fails** dramatically for certain properties, most notably the existence of **positively charged hole carriers**. To explain this, we explicitly consider the **periodic potential** experienced by the electrons, and the resulting **energy structures as termed as the band structure**. The **band theory** is the most widely used model for explaining the electronic properties of solid materials. *Dispersion Relation*

From the engineering point of view, why we need a **theory** at all? Without theory, even though it may be approximate one, it will take **too much trial-and-error to engineer materials for the desired properties**.

*carpet bombing*

## **2A. Free Electron Model**

2A.1. Particle in a Box

2A.2. Fermi-Dirac Distribution

2A.3. Free-Electron Theory of Metals

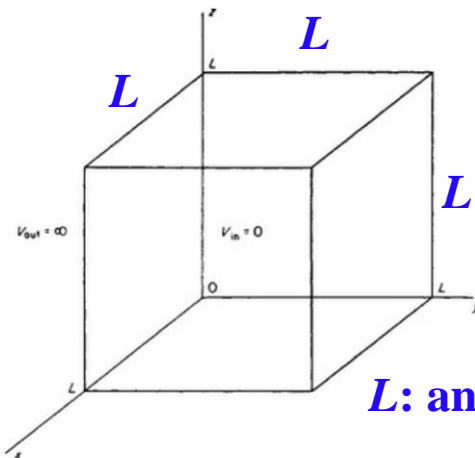
2A.4. Application of Free-Electron Model

# 2A.1. Particle in a Box

## Solution to Schrödinger Equation

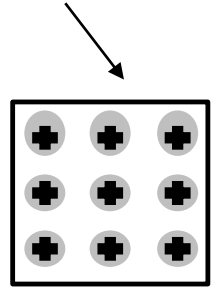
In some metals, outermost valence electrons in a solid can be treated as if they are **essentially free electrons**, particularly in metals where outer-most valence electrons are not much involved in chemical bonding. (Metallic sodium has  $1s^2 2s^2 2p^6 3s^1$ , and the outermost 3s electron can be considered to be essentially free.) The positive charges of nucleus are effectively screened by other freely moving electrons. (This does not apply to **transition metals**.) Therefore, **i) the potentials experienced by these valence electrons are very weak**, and so can be **approximated to be zero**. In addition, **ii) the repulsion between electrons is also well screened by other electrons**, so can be neglected.

Since the electrons are confined within the metal, we approximate the material surface as **infinite potential wells**. (In fact, it is rather a finite potential barrier with the height of the **work function**.) For convenience, the material is modeled as a cubic box with the length  $L$ .



**L: any length – No difference in nature**

Positively charged ions are shielded by other electrons.



$\bar{V} \sim 0$  inside solid

The mathematical expression of potential and boundary conditions are as follows:

$$V(x, y, z) = \begin{cases} 0 & ; 0 < x, y, z < L \\ \infty & ; \text{elsewhere} \end{cases}$$

Boundary conditions:  $\psi = 0$  on each face of the box.

Mathematically,

$$\psi(0, y, z) = \psi(L, y, z) = 0$$

$$\psi(x, 0, z) = \psi(x, L, z) = 0$$

$$\psi(x, y, 0) = \psi(x, y, L) = 0$$

$$\sigma = ne\mu = ne^2\tau/m^*$$

The Schrödinger equation is  $-\frac{\hbar}{2m}\nabla^2\psi(x,y,z) = E\psi(x,y,z)$

(From now on, the electron mass is  $m$  instead of  $m_{e.}$ ) We will see later that the electron mass within the solid is different from that in vacuum because of interactions with ions. This is called the **effective mass ( $m^*$ )**. The boundary condition in the rectangular form allows for separation of variables:  $\psi(x,y,z) = F(x)G(y)H(z)$ .

$$\frac{1}{F(x)}\frac{\partial^2 F(x)}{\partial x^2} + \frac{1}{G(y)}\frac{\partial^2 G(y)}{\partial y^2} + \frac{1}{H(z)}\frac{\partial^2 H(z)}{\partial z^2} = -\frac{2mE}{\hbar^2}$$
$$\Leftrightarrow \frac{d^2 F(x)}{dx^2} = C_x F(x), \quad \frac{d^2 G(y)}{dy^2} = C_y G(y), \quad \frac{d^2 H(z)}{dz^2} = C_z H(z)$$

Boundary conditions:  $\psi = 0$  on each face of the box.

$$\Leftrightarrow F(0) = F(L) = G(0) = G(L) = H(0) = H(L) = 0$$

If  $C_{x(y,z)}$  is a positive number, it cannot satisfy these boundary conditions. Therefore,  $C$ 's are negative numbers and  $F, G, H$  are linear combinations of sine and cosine

$$\rightarrow F(x) = A_x \sin \frac{n_x \pi x}{L} \quad G(y) = A_y \sin \frac{n_y \pi y}{L} \quad H(z) = A_z \sin \frac{n_z \pi z}{L}$$

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z = 1, 2, 3, \dots$$

$$\psi_{n_x, n_y, n_z}(x, y, z) = A \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \sin \frac{n_z \pi z}{L}$$

PPT 1-15

PPT 1-17

PPT 1-18

Normalization condition:  $\int_0^L \int_0^L \int_0^L |\psi|^2 dx dy dz = 1 \rightarrow A = \sqrt{\frac{8}{L^3}}$

$$\psi_{(n_x, n_y, n_z)}(x, y, z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

$$\underline{E_{(n_x, n_y, n_z)} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) = \varepsilon_1 n^2}$$

$(n_x, n_y, n_z)$ : quantum numbers.

### □ Degeneracy

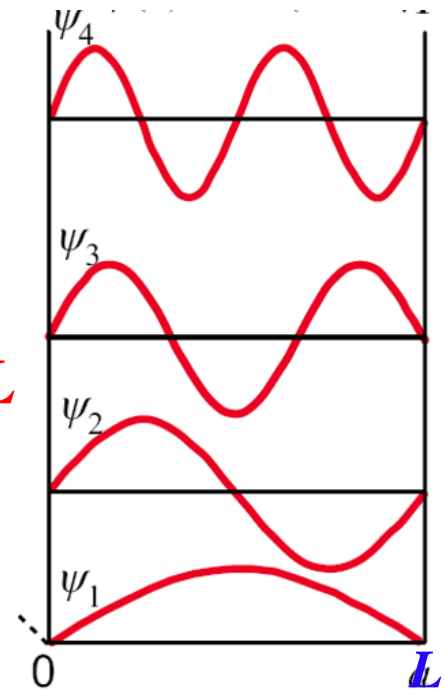
i)  $(n_x, n_y, n_z) = (1, 2, 3)$  or  $(1, 3, 2)$

▷ symmetry degeneracy

ii)  $(n_x, n_y, n_z) = (1, 1, 5)$  or  $(3, 3, 3)$

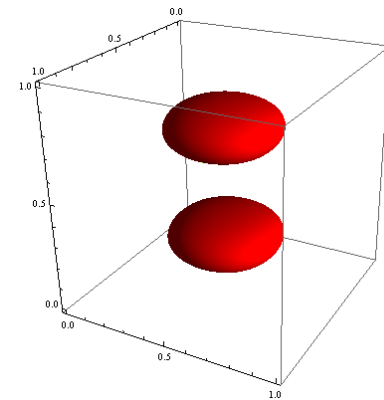
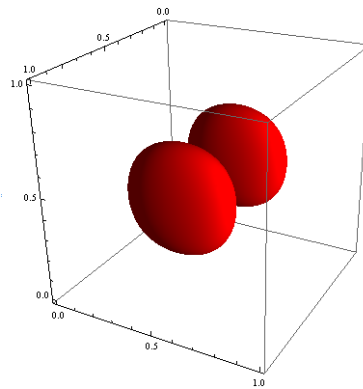
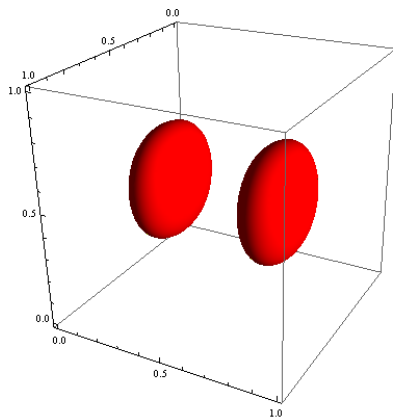
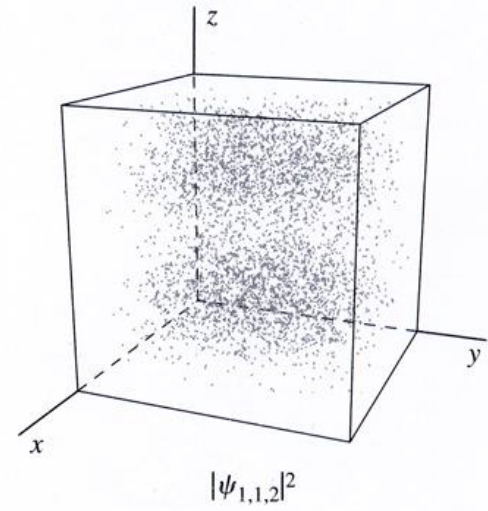
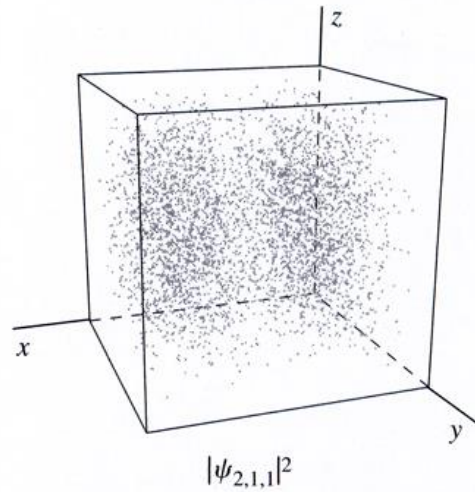
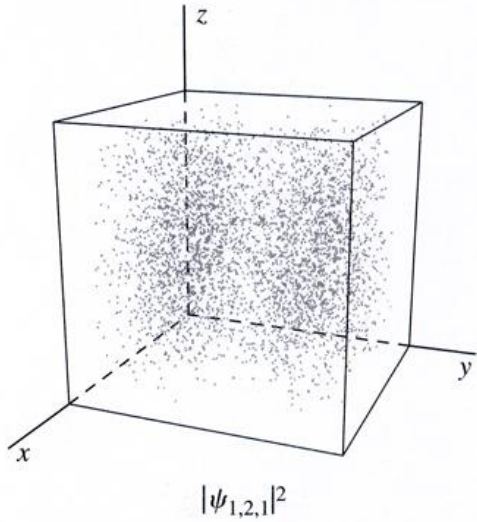
▷ accidental degeneracy

$$k = \pi n / L$$



Comments: When  $L$  is macroscopic, the energy spacing is so small that the particle may behave classically. This is the case when there is only a few electrons in the system such that wave functions do not overlap and we do not worry about the Pauli exclusion principle. (In fact, early scientists, notably Drude, treated electrons in metals as classical gas system and arrived at wrong results as well as correct ones.) However, when electrons are as dense as in metals (more than one electron per atom), the wave function overlaps significantly and one has to apply full quantum mechanics, at least the Pauli exclusion principle. This gives very different results from the classical approach, and is more true to the experiment.

Compare states with (1,2,1), (2,1,1), (1,1,2)

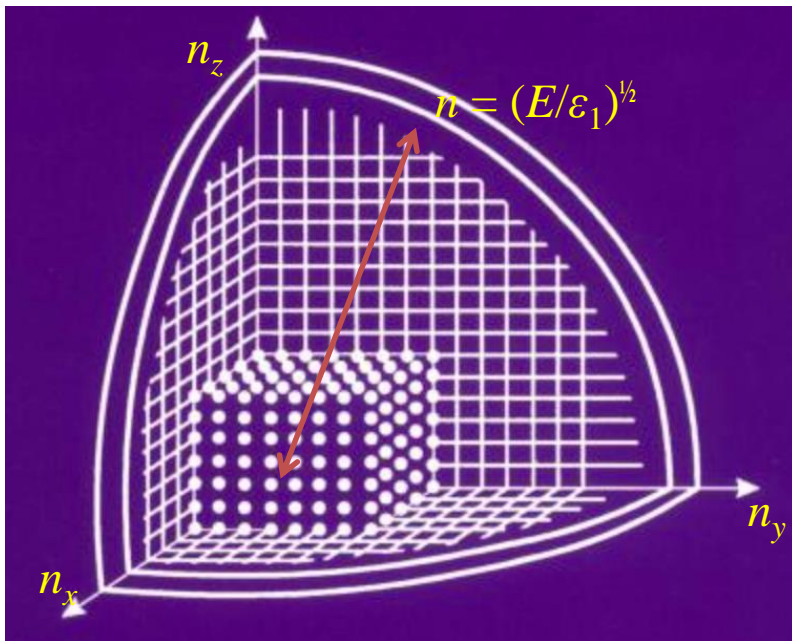


Isosurfaces

# Density of States (DOS)

For macroscopic samples ( $L > \mu\text{m}$ ), one needs a large number of states to occupy particles (on the order of Avogadro's number). In particular, it is of interest to know **how many states exist with a narrow energy range  $[E, E+dE]$**  because occupation number depends only on the energy. It is difficult to calculate this precisely but there is a good approximation which enable us to obtain the number of states.

In  **$(n_x, n_y, n_z)$  space**, each quantum state is represented as a point on the regular grid in the first octant. We first define  **$N(E)$  as the number of states with energy less than  $E$** . Since  $E = \varepsilon_1 n^2 = \varepsilon_1(n_x^2 + n_y^2 + n_z^2)$ ,  $N(E)$  is the number of mesh points within the sphere with the radius  $n = (E/\varepsilon_1)^{1/2}$ . This is **equivalent** to  $1/8 \times [\text{volume of sphere with radius } n]$  if we neglect errors from the boundary mismatch, which is negligible for large  $n$ .



***k Space***

$$N(E) = \frac{1}{8} \cdot \frac{4}{3} \rho n^3 = \frac{\rho}{6} \left( \frac{E}{\varepsilon_1} \right)^{3/2}$$

**3D**

$$k = \pi n / L$$

Number of states between  $E$  and  $E + dE$

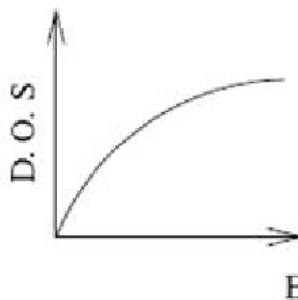
$$= N(E + dE) - N(E) = dE \frac{N(E + dE) - N(E)}{dE} = dE N'(E)$$

$N'(E)$  corresponds to the **density of states (DOS)  $D(E)$**  or **number of states per unit energy**.

$$D(E) = N'(E) = \frac{L^3}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E}$$

Since it is obvious that  $D(E)$  scales with the system **size of volume ( $L^3$ )**, sometimes  $D(E)$  is defined as per unit volume.

$$D(E) = \frac{1}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E}$$



**3D**  
**Free Electron Model**

## DOS per volume

(Considering only positive wavenumber  $k$  and spin-up)

If we consider spin degree of freedom,  $D(E)$  would be multiplied by two (some literature do this). But for the convenience of discussions in the section of Magnetic Properties, we implicitly assume this is DOS for **spin-up or spin-down**. This is to say,  $D(E) = D_{\uparrow}(E) = D_{\downarrow}(E)$ .

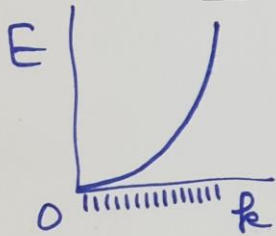


# Density of States (DOS) in Metals or Semiconductors

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m^* L^2} (n_x^2 + n_y^2 + n_z^2) = \frac{\hbar^2 (\rho_x^2 + \rho_y^2 + \rho_z^2)}{2m^*}$$

$$\lambda = \frac{2L}{n}$$

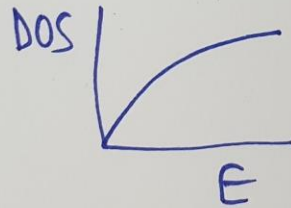
$$\rho = \frac{\pi n}{L}$$



quantized k space

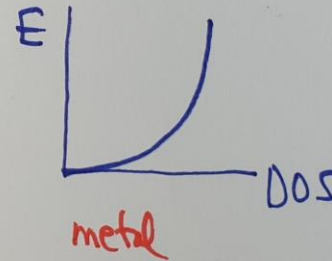
$$N(E) = \frac{V}{6} \left( \frac{E}{E_1} \right)^{3/2}$$

$0 \leq \text{energy} \leq E$

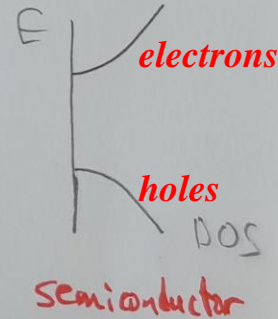


DOS  $\propto \sqrt{E}$   $D(E) = \frac{1}{4\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E}$

between  $E$  and  $E + dE$

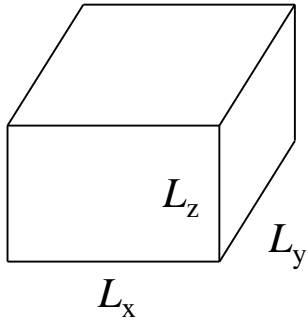


metal



semiconductor

Some materials have highly anisotropic geometries. These systems can also be approximated as **quantum well structure**. In order to accommodate anisotropy, we generalize the previous example to 3D quantum well with different cell lengths of  $L_x$ ,  $L_y$ , and  $L_z$  along each direction. It should be straightforward to solve this problem using the same technique of separation of variables.



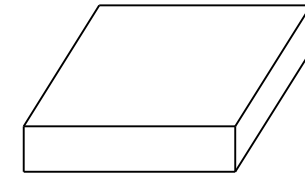
$$\psi_{(n_x, n_y, n_z)}(x, y, z) = \sqrt{\frac{8}{V}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right) \quad V = L_x L_y L_z$$

$$E_{(n_x, n_y, n_z)} = \frac{\pi^2 \hbar^2}{2m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \quad n_x, n_y, n_z = 1, 2, 3, \dots$$

# DOS in 2D

## homework

First, let's first consider 2-dimensional system in which **one length ( $L_z$ ) is nanometer scale** while the other two lengths are macroscopic. Examples are ultrathin metal layers or AlAs/GaAs heterostructures (**quantum well**). In this case, changing  $n_z$  will increase the energy in much bigger steps than changing  $n_x$  or  $n_y$ . Therefore, we can effectively fix  $n_z$  and obtain DOS by considering  $(n_x, n_y)$  in the two dimensional plane as we have done for three-dimensional case in the previous subsection. In this case, DOS per unit energy and unit area is given by:

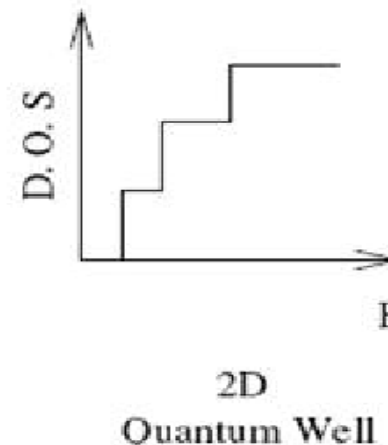
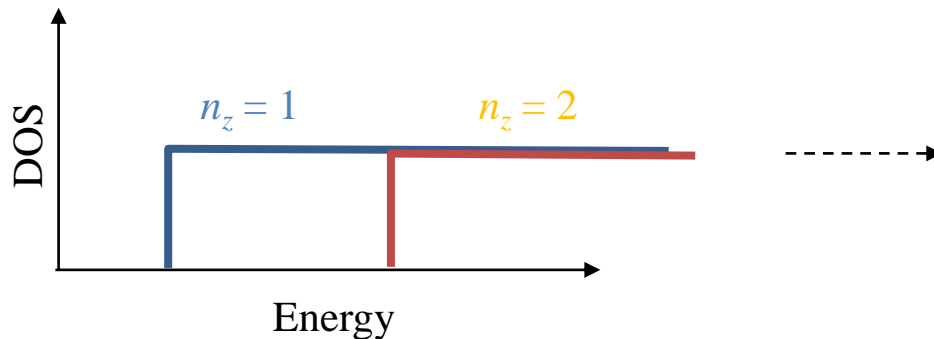


$$L_z \text{ (nm)} \ll L_x \text{ and } L_y \text{ (> } \mu\text{m)}$$

Quantum well

$$D(E) = \frac{m}{2\pi\hbar^2} : \text{constant} \quad (2D)$$

3D: PPT-2A-8



Free-Electron Model

States belong to a certain  $n_z$  are called subband.

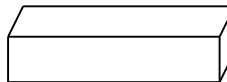
(Note that DOS for *graphene* is quite different.)

# DOS in 1D

Similarly, one can derive DOS for one-dimensional systems such as nanowire or carbon nanotubes.

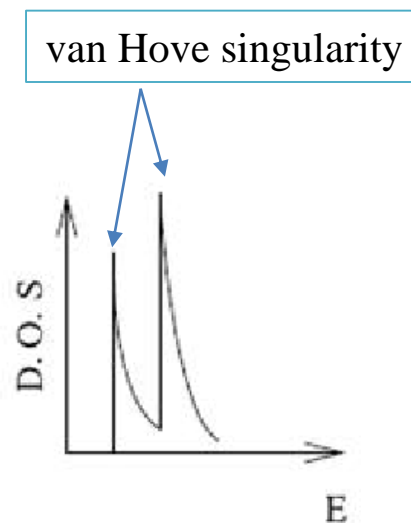
$$D(E) = \frac{\sqrt{2m}}{2\pi\hbar} E^{-1/2} \quad (1D)$$

The sharp peak at the beginning of each subband is called the van Hove singularity.  $E^{-1/2}$  behavior can be also understood from the 1D quantum well where the energy spacing increases with  $n$ .

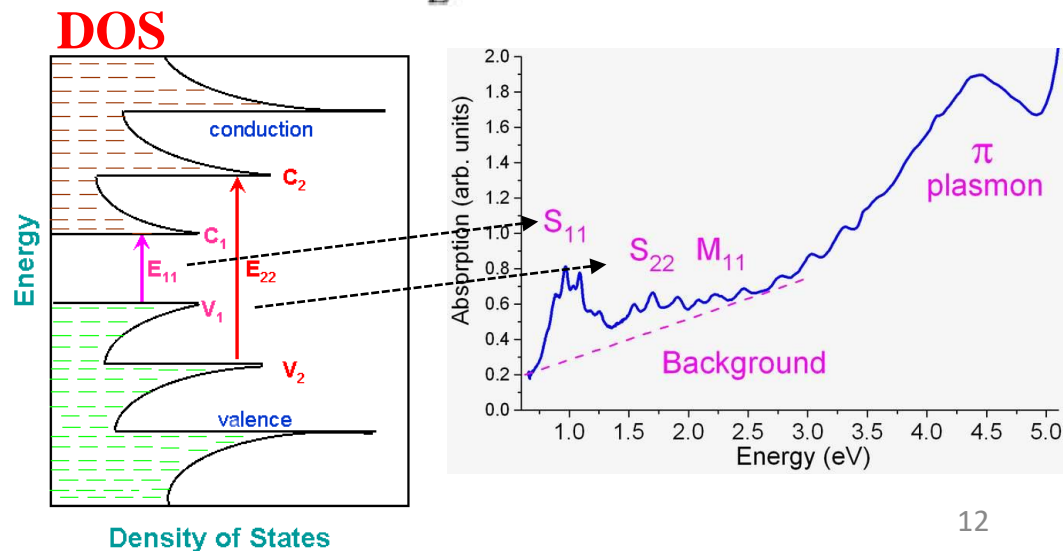
1D: 

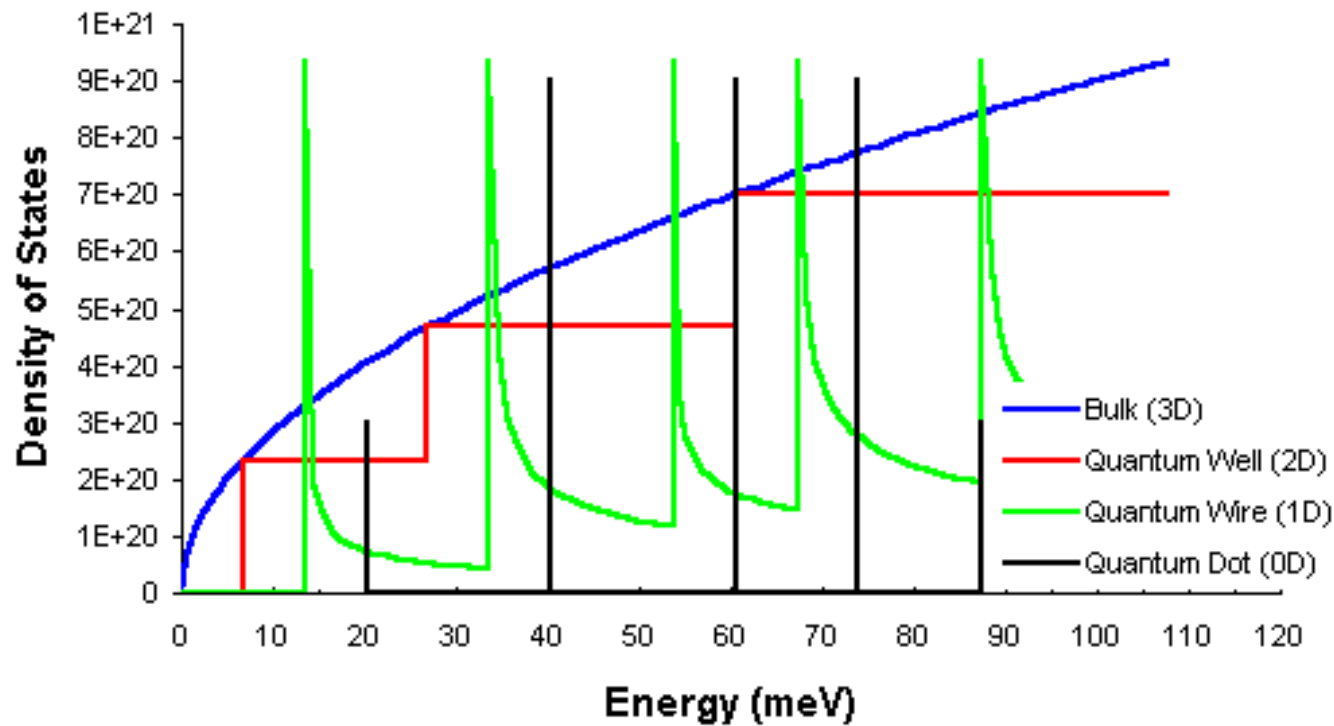
$$L_y, L_z \ll L_x$$

Nanowire or quantum wire



The van Hove singularity renders the quantum wire to display sharp absorption spectra. On the right is the example of semiconducting **carbon nanotube**. The electronic transition between singularities produce notable peaks in the absorption spectra.





Very sharp and well defined energy levels in **0D quantum dots** allow for their usages in display applications.

(Samsung QLED TV – in fact it is not true QLED even though it makes use of quantum dots.)

# 2A.2. Fermi-Dirac Distribution

So far, we counted number of states that electrons can occupy. The actual occupation number of each state is given by thermodynamics. Classically, the Boltzmann distribution can be derived in which the occupation number (probability) is proportional to the Boltzmann factor  $\exp(-E/k_B T)$ . This is based on the assumption that every particle is distinguishable. This may look obvious, but in quantum mechanics or fundamentally you cannot distinguish two identical particles such as proton vs. proton, electron vs. electron, Si vs. Si, etc. (Remember that we considered this in calculating entropy in thermodynamics.)

For example, consider four identical particles ( $a, b, c, d$ ) in a hypothetical quantum well with only three energy levels  $0, \delta E,$  and  $2\delta E$ . Let's count the number of microstates with the total energy fixed to  $2\delta E$ .

When particles are distinguishable (classical):

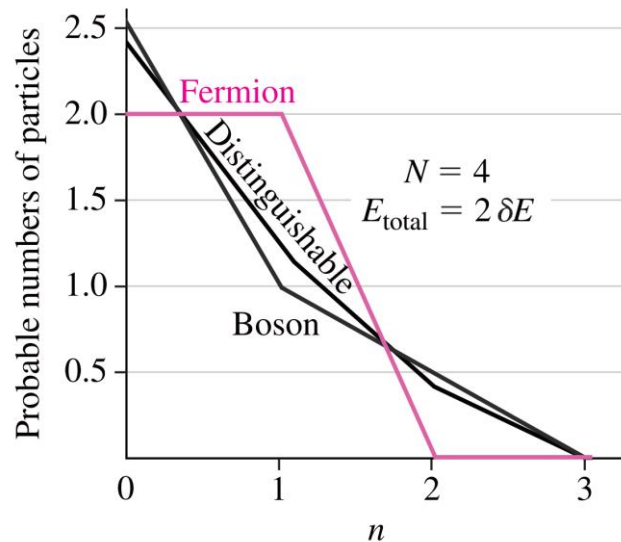
**TABLE 1** Ways of distributing energy  $2\delta E$  among distinguishable particles  $a, b, c, d$

$n$	Ways	Number of times $n$ appears (#)	Probability $P$ (#/40)	Probable number of particles ( $P \times 4$ )
2	$a \quad b \quad c \quad d$	4	0.1	0.4
1	$ab \quad ac \quad ad \quad bc \quad bd \quad cd$	12	0.3	1.2
0	$bcd \quad acd \quad abd \quad abc \quad cd \quad bd \quad bc \quad ad \quad ac \quad ab$	24	0.6	2.4
	Totals	40	1.0	4.0

Next, the particles are indistinguishable. In nature, there are two types of particles. **Fermions** with spin half-integer cannot occupy the same state if the spin is the same because of the Pauli exclusion principle. **Bosons** have integer spins and no limitations in the occupation number.

**TABLE 2** Ways of distributing energy  $2\delta E$  among four indistinguishable bosons and spin- $\frac{1}{2}$  fermions

$n$	Bosons				Fermions ( $s = \frac{1}{2}$ )			
	Ways	Number of times $n$ appears (#)	Probability $P$ (#/8)	Probable number of particles ( $P \times 4$ )	Ways	Number of times $n$ appears (#)	Probability $P$ (#/4)	Probable number of particles ( $P \times 4$ )
2	X	1	0.125	0.5		0	0.0	0
1	XX	2	0.250	1.0	XX	2	0.5	2
0	XXX XX	5	0.625	2.5	XX	2	0.5	2
	Totals	8	1.000	4.0	Totals	4	1.0	4



four identical particles  
three energy levels: 0,  $\delta E$ , and  $2\delta E$

The above discussion (four identical particles and three energy levels) can be extended

for the macroscopic systems with the **Avogadro number of particles**. By using the partition function for the **grand canonical ensemble**, the occupation number or occupation probability  $f(E)$ , which is the expected number of particles at a state with the energy of  $E$ , is obtained as follows:

$$f(E) = \begin{cases} \frac{1}{Be^{E/kT}} \propto e^{-E/kT} & \text{Boltzmann (distinguishable)} \\ \frac{1}{Be^{E/kT} - 1} = \frac{1}{e^{(E-\mu)/kT} - 1} & \text{Bose-Einstein (bosons)} \\ \frac{1}{Be^{E/kT} + 1} = \frac{1}{e^{(E-\mu)/kT} + 1} & \text{Fermi-Dirac (fermions)} \end{cases}$$

Here  $\mu$  is the **chemical potential** of the system (change in the Gibbs free energy when one particle is added to the system). For electrons, this is also called the **Fermi level or Fermi energy ( $E_F$ )**.

In all cases,  $B$  is determined by the total number of particles in the system. (For photons or vibrations, the particle number is not conserved so  $B = 1$ .)

All distributions monotonically decrease with the energy.

For Fermi-Dirac,  $f(E)$  cannot exceed 1 and is equal to  $\frac{1}{2}$  for  $E = E_F$ .

For Bose-Einstein,  $f(E)$  can be any positive number.

$$\text{chemical potential } \mu_i(T, p, n_j) = \left( \frac{\partial G}{\partial n_i} \right)_{T, p, n_j} \quad 16$$



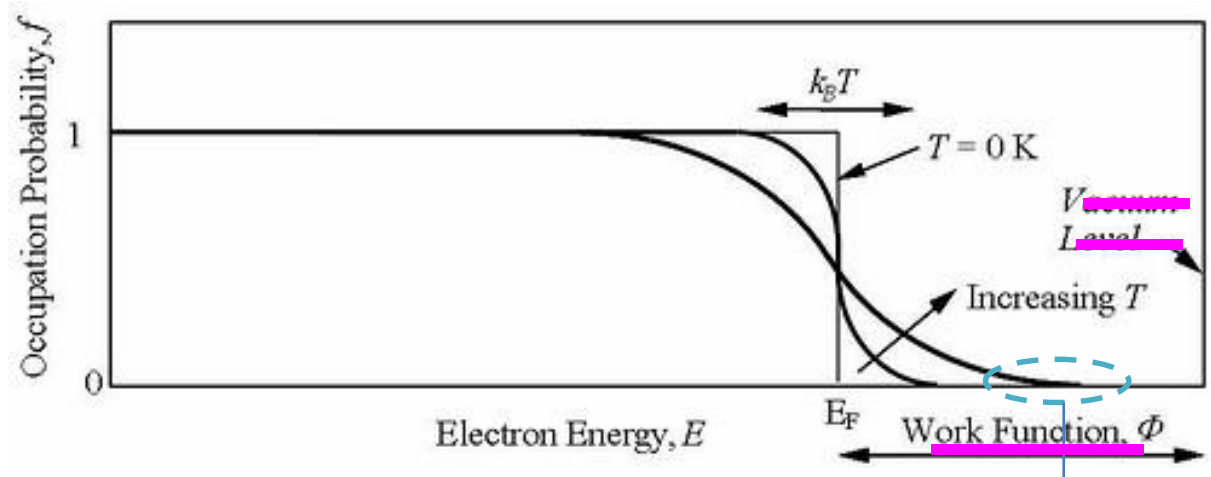
# 2A.2. Fermi-Dirac Distribution

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

At  $T = 0$  K:  $f(E) = 1$  for  $E < E_F$  and  $0$  for  $E > E_F$  : step function. (Can you understand why  $E_F$  corresponds to the chemical potential?)

As  $T$  increases,  $f(E)$  becomes gradually broadened. The broadening width is approximately  $k_B T$ , which is much smaller than  $E_F$  (see later).  $E_F(T)$  is determined by the total number of particles.

Since the distribution at usual  $T$  is almost the same as that at  $T = 0$  K,  $E_F(T) \approx E_F(0)$ .



**$E_F$  in Ag**  
 4.30 eV at 300 K  
 4.35 eV at 0 K

**$E_g$  in Si**  
 1.12 eV at 300 K  
 1.17 eV at 0 K

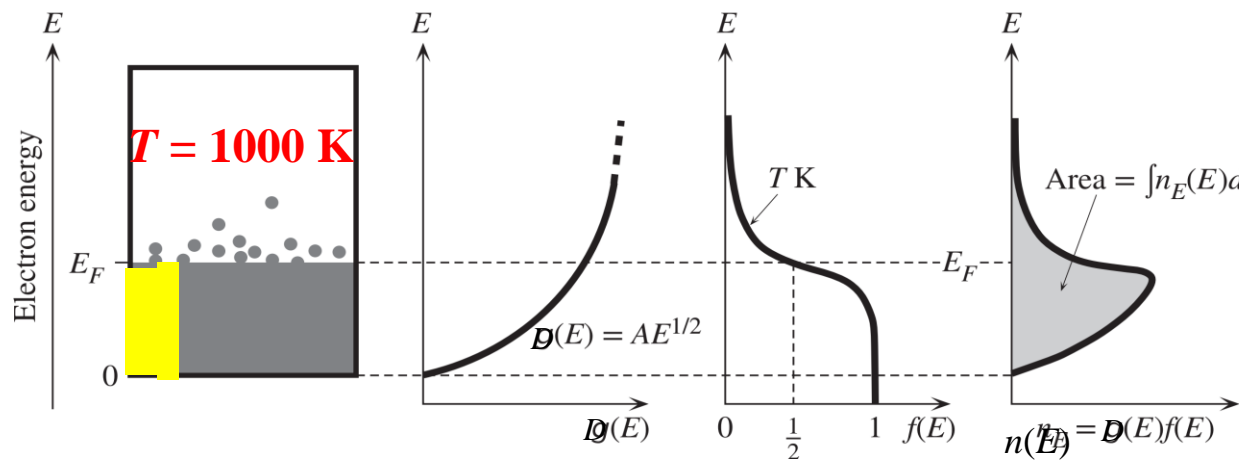
For  $E \gg E_F$ ,  $f(E)$  approach to  $e^{-E/k_B T}$   
 (Maxwell-Boltzmann distribution)

That is to say, when particles are sparse, the indistinguishability and Pauli-exclusion principle are not important.

$$\sigma = ne\mu = ne^2\tau/m^*$$

# 2A.3. Free-Electron Theory of Metals

In the preceding sections, we obtained the number of states (DOS:  $D(E)$ ) and how much to fill each state under the temperature  $T$  (Fermi-Dirac distribution:  $f(E)$ ). Thus, the number of electrons occupied per volume per energy is  $D(E) \times f(E)$ . Integrating this over the whole energy range should be equal to the **number of electrons per unit volume**, i.e., **electron density  $n$** , (provided that  $D(E)$  is defined per volume).



$$D(E) = \frac{1}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E}$$

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(Not including the spin degeneracy)

0 K

Since Fermi-Dirac does not change much at finite  $T$  ( $\ll E_F/k_B$ ), let's assume the zero temperature for simplicity. In this case,  $f(E)$  is 1 up to  $E_F(0)$  and 0 above.

$n = \text{electrons/volume}$   
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$$n = \int_0^{E_F} D(E) dE = \int_0^{E_F} 2 \times \frac{1}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E} dE = \frac{\sqrt{2}}{\pi^2} \left( \frac{m}{\hbar^2} \right)^{3/2} \int_0^{E_F} E^{1/2} dE = \frac{\sqrt{2}}{\pi^2} \left( \frac{m}{\hbar^2} \right)^{3/2} \frac{2}{3} E_F^{3/2}$$

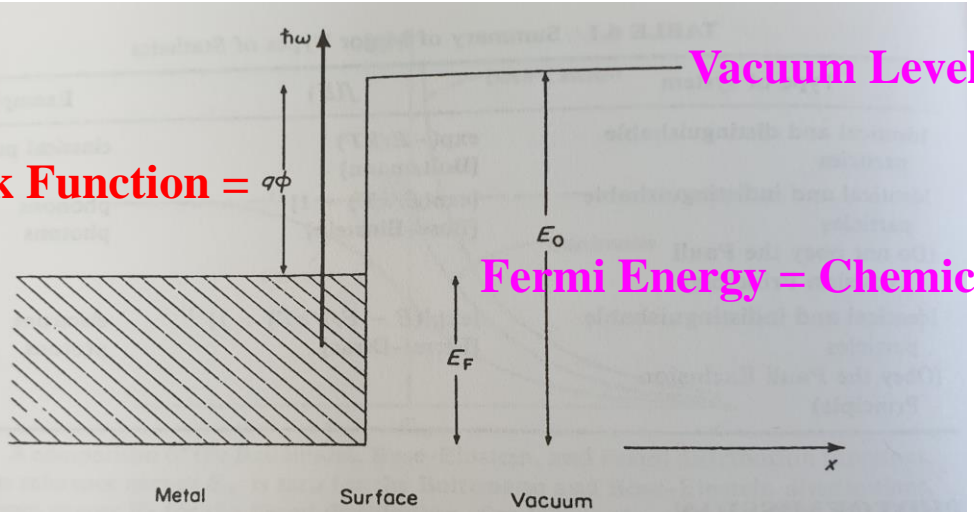
$$\rightarrow E_F(0) = \frac{\hbar^2}{2m} \left( 3\pi^2 n \right)^{2/3}$$

The factor 2 accounts for the spin degeneracy. 18

# Free-Electron Model

$T = 0 \text{ K}$

**Work Function =  $q\phi$**



**Vacuum Level**

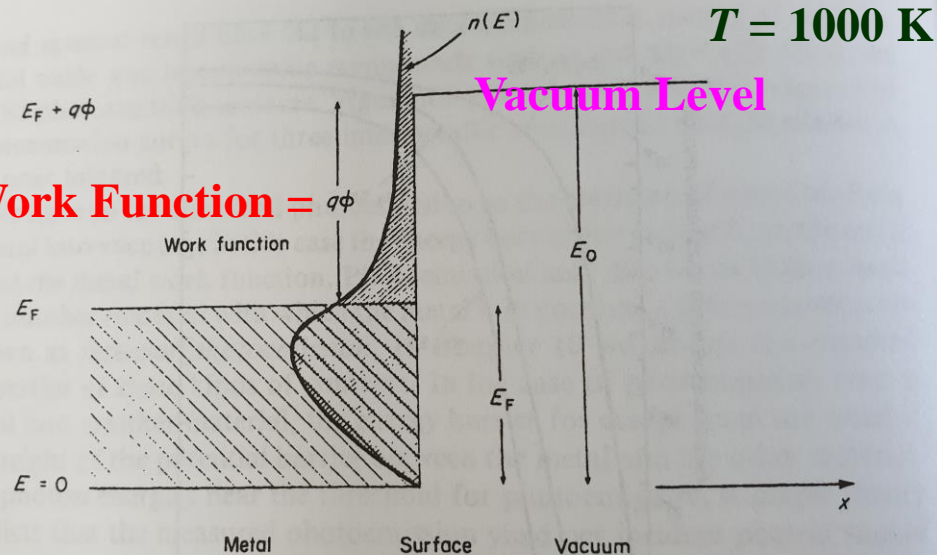
**Fermi Energy = Chemical Potential**

**FIG. 6.8** Free-electron model of a metal surface suitable for the discussion of photoemission processes. When the photon energy  $\hbar\omega$  is larger than the work function  $q\phi$ , photoemission of the photoexcited electron into vacuum is possible.

**Bube - Figs. 6.8 & 6.11**

**at  $T$  ???**

**Work Function =  $q\phi$**



$T = 1000 \text{ K}$

**Vacuum Level**

**FIG. 6.11** Free-electron model of a metal surface suitable for the discussion of thermionic emission processes. Electrons with energy greater than  $E_F + q\phi$  in the higher energy tail of the Fermi distribution can be emitted into vacuum.

Na: [Ne]3s<sup>1</sup>    Mg: [Ne]3s<sup>2</sup>    In: [Kr]4d<sup>10</sup>5s<sup>2</sup>5p<sup>1</sup>

To convert the Fermi level formula to be more explicit, we define the effective radius of free electrons ( $r_s$ ) from the mean volume per electron.

$$n = \text{electrons/volume}$$

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

The table on the right shows  $r_s$  for various metals using the nominal number of valence electrons ( $Z$ ) and crystal volume.

$$\text{Bohr radius: } a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \text{ \AA}$$

$$c\text{-Si} = 5.0 \times 10^{22} \text{ atoms/cm}^3$$

Table 1.1

FREE ELECTRON DENSITIES OF SELECTED METALLIC ELEMENTS<sup>a</sup>

$$r_s = 1 - 2 \text{ \AA}$$

ELEMENT	$Z$	$n$ ( $10^{22}/\text{cm}^3$ )	$r_s$ (Å)	$r_s/a_0$
Li (78 K)	1	4.70	1.72	3.25
Na (5 K)	1	2.65	2.08	3.93
K (5 K)	1	1.40	2.57	4.86
Rb (5 K)	1	1.15	2.75	5.20
Cs (5 K)	1	0.91	2.98	5.62
Cu	1	8.47	1.41	2.67
Ag	1	5.86	1.60	3.02
Au	1	5.90	1.59	3.01
Be	2	24.7	0.99	1.87
Mg	2	8.61	1.41	2.66
Ca	2	4.61	1.73	3.27
Sr	2	3.55	1.89	3.57
Ba	2	3.15	1.96	3.71
Nb	1	5.56	1.63	3.07
Fe	2	17.0	1.12	2.12
Mn (x)	2	16.5	1.13	2.14
Zn	2	13.2	1.22	2.30
Cd	2	9.27	1.37	2.59
Hg (78 K)	2	8.65	1.40	2.65
Al	3	18.1	1.10	2.07
Ga	3	15.4	1.16	2.19
In	3	11.5	1.27	2.41
Tl	3	10.5	1.31	2.48
Sn	4	14.8	1.17	2.22
Pb	4	13.2	1.22	2.30
Bi	5	14.1	1.19	2.25
Sb	5	16.5	1.13	2.14

<sup>a</sup> At room temperature (about 300 K) and atmospheric pressure, unless otherwise noted. The radius  $r_s$  of the free electron sphere is defined in Eq. (1.2). We have arbitrarily selected one value of  $Z$  for those elements that display more than one chemical valence. The Drude model gives no theoretical basis for the choice. Values of  $n$  are based on data from R. W. G. Wyckoff, *Crystal Structures*, 2nd ed., Interscience, New York, 1963.

The zero temperature  $E_F(0)$  can be expressed by  $r_s$  and  $a_0$  as follows:

$$E_F(0) = \frac{\hbar^2}{2m} (3\pi^2 n)^{\frac{2}{3}} = \frac{\hbar^2}{2m} \left( \frac{9\pi}{4} \right)^{\frac{2}{3}} \frac{1}{r_s^2}$$

$$= \frac{\hbar^2}{2ma_0^2} \left( \frac{9\pi}{4} \right)^{\frac{2}{3}} \frac{1}{(r_s/a_0)^2} = \frac{50.1 \text{ eV}}{(r_s/a_0)^2}$$

Table 2.1

**FERMI ENERGIES, FERMI TEMPERATURES, FERMI WAVE VECTORS, AND FERMI VELOCITIES FOR REPRESENTATIVE METALS<sup>a</sup>**

ELEMENT	$r_s/a_0$	$E_F$	$T_F$	$k_F$	$v_F$
Li	3.25	4.74 eV	$5.51 \times 10^4$ K	$1.12 \times 10^8 \text{ cm}^{-1}$	$1.29 \times 10^8 \text{ cm/sec}$
Na	3.93	3.24	3.77	0.92	1.07
K	4.86	2.12	2.46	0.75	0.86
Rb	5.20	1.85	2.15	0.70	0.81
Cs	5.62	1.59	1.84	0.65	0.75
Cu	2.67	7.00	8.16	1.36	1.57
Ag	3.02	5.49	6.38	1.20	1.39
Au	3.01	5.53	6.42	1.21	1.40
Be	1.87	14.3	16.6	1.94	2.25
Mg	2.66	7.08	8.23	1.36	1.58
Ca	3.27	4.69	5.44	1.11	1.28
Sr	3.57	3.93	4.57	1.02	1.18
Ba	3.71	3.64	4.23	0.98	1.13
Nb	3.07	5.32	6.18	1.18	1.37
Fe	2.12	11.1	13.0	1.71	1.98
Mn	2.14	10.9	12.7	1.70	1.96
Zn	2.30	9.47	11.0	1.58	1.83
Cd	2.59	7.47	8.68	1.40	1.62
Hg	2.65	7.13	8.29	1.37	1.58
Al	2.07	11.7	13.6	1.75	2.03
Ga	2.19	10.4	12.1	1.66	1.92
In	2.41	8.63	10.0	1.51	1.74
Tl	2.48	8.15	9.46	1.46	1.69
Sn	2.22	10.2	11.8	1.64	1.90
Pb	2.30	9.47	11.0	1.58	1.83
Bi	2.25	9.90	11.5	1.61	1.87
Sb	2.14	10.9	12.7	1.70	1.96

<sup>a</sup> The table entries are calculated from the values of  $r_s/a_0$  given in Table 1.1 using  $m = 9.11 \times 10^{-28}$  grams.

$$k_B = 8.617 \times 10^{-5} \text{ eV/K}$$

$$h = 4.1357 \times 10^{-15} \text{ eV} \cdot \text{s}$$

$$c = 10^{10} \text{ cm/s}$$

$$-\frac{\rho}{a} < k \leq \frac{\rho}{a}$$

Note in the right table that  $E_F$  is typically **several eVs**. The Fermi temperature ( $T_F = E_F/k_B$ ) is much higher than usual temperatures.

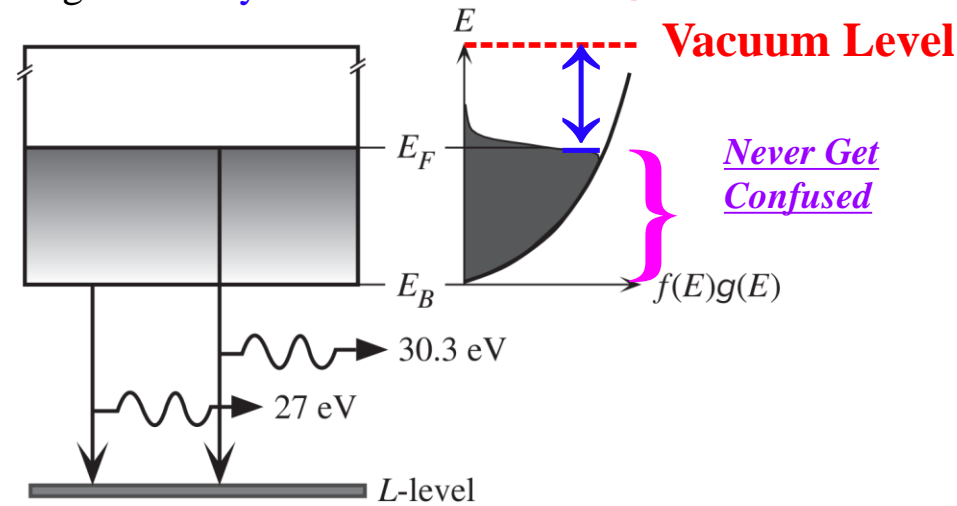
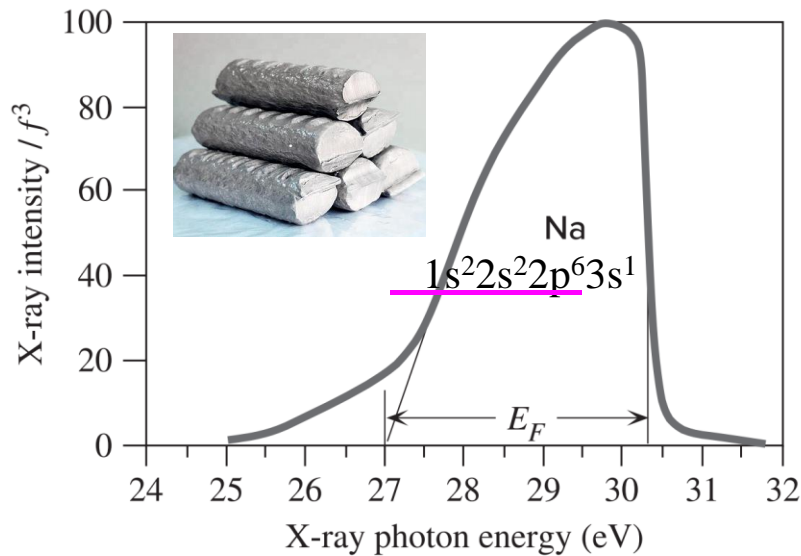
The **Fermi velocity** ( $v_F$ ) is the group velocity of the free electron at the Fermi level:

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

We will see in the next chapter that the electrical conduction is mediated by mostly electrons at the Fermi level. Therefore, the Fermi velocity can be regarded as the velocity of the **charge carrier (~1% of light velocity)**.

The Fermi level can be measured experimentally using soft x-ray emission.

**Fig. 6.8**



On this page,  $g(E) = D(E)$

**Figure 4.31** Emission of soft X-rays from a sodium sample that is bombarded by electrons (in a suitable high vacuum). An impinging electron knocks out an electron from an inner core shell ( $L$ -level). A conduction electron falls down and fills this space and emits an X-ray photon. The X-ray emission intensity is proportional to the number of conduction electrons available,  $f(E)g(E)$ , and to  $hf^3$ , a quantum mechanical transition probability. The vertical axis has been scaled to make the peak 100 percent.

† Data extracted from Cady, W.M. and Tombouljian D.H., *Physical Review* 59, 381, 1941, Table 1.

Experimental  $E_F = 30.3 - 27 = 3.3$  eV vs. Theoretical  $E_F = 3.24$  eV

- Total energy of free electrons (per volume)

$$E_{\text{tot}} = \int_0^{\infty} E n(E) dE = \int_0^{E_F} \underline{E D(E) dE} = \frac{\sqrt{2}}{\pi^2} \left( \frac{m}{\hbar^2} \right)^{3/2} \int_0^{E_F} E^{3/2} dE = \frac{\sqrt{2}}{\pi^2} \left( \frac{m}{\hbar^2} \right)^{3/2} \frac{2}{5} E_F^{5/2} = \frac{3}{5} E_F(0) n$$

DOS  
ppt-2A-18

(Including the spin degeneracy)

- Average energy per electron:  $\underline{E_{\text{av}} = \frac{3}{5} E_F(0)}$

# Finite Temperature

How about finite temperatures? I emphasize that the previous **results for 0 K are still valid for most temperatures**. Nevertheless, we here focus on the small change induced by the temperature. The following relation still holds:

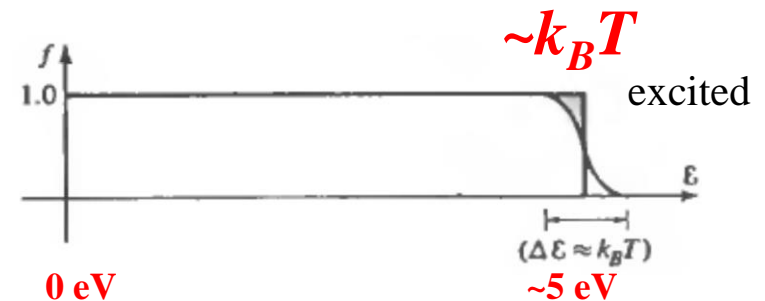
$$n = \int_0^\infty n(E) dE = \int_0^\infty D(E) f(E) dE = \frac{\sqrt{2}}{\pi^2} \left( \frac{m}{\hbar^2} \right)^{3/2} \int_0^\infty E^{1/2} \frac{1}{e^{(E-E_F)/k_B T} + 1} dE$$

The right-hand side depends on  $E_F$ , and  $E_F$  that satisfies the equality is the Fermi level at the given temperature.

The closed form of  $\int n(E) dE$  does not exist at finite temperatures. Instead, one can exploit the fact that the F-D distribution is affected only near the Fermi level and expand F-D function in a Taylor series. This procedure is called the Sommerfeld expansion, and please refer to Ashcroft & Mermin pp 45 for the detailed derivation. The results to the lowest order of  $(kT/E_F(0))$  are as follows:

$$E_F(T) = E_F(0) \left[ 1 - \frac{\rho^2}{12} \left( \frac{k_B T}{E_F(0)} \right)^2 \right] \quad E_{\text{tot}}(T) = E_{\text{tot}}(0) \left[ 1 + \frac{5\rho^2}{12} \left( \frac{k_B T}{E_F(0)} \right)^2 \right]$$

The temperature dependence of  $E_{\text{tot}}$  can be understood by considering the change in the F-D distribution in the right figure. The **excited electrons range over the  $\Delta\varepsilon \sim k_B T$** , and so their **number is  $\sim D(E_F) k_B T$** . The energy increase of each excited electron is also  $\sim k_B T$ . Therefore, the increase in  $E_{\text{tot}}$  is  $\sim D(E_F)(k_B T)^2$ , which is in fact very similar to the exact expression in the above.



Since  $E_F(0) \gg k_B T$  ( $kT/E_F(0) = T/T_F \sim 0.01$ ), the temperature dependence is very small. Nevertheless, the temperature dependence of  $E_{av}$  and so  $E_{tot}$  leads to the electronic part of the heat capacity ( $C_e$ ) that originates from free electrons.

$$C_e = \frac{\partial E_{tot}}{\partial T} \mu T$$

The **heat capacity** at normal temperatures is mainly contributed by the lattice vibration or phonons. We will see at the end of this chapter that the lattice component of the heat capacity ( $C_L$ ) is proportional to  $T^3$  **at low temperatures**. Therefore,  $C_e$  becomes significant at low temperatures:

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

*lattice      metallic*  
*(electronic)*

**Bube Eq. (6.37)**

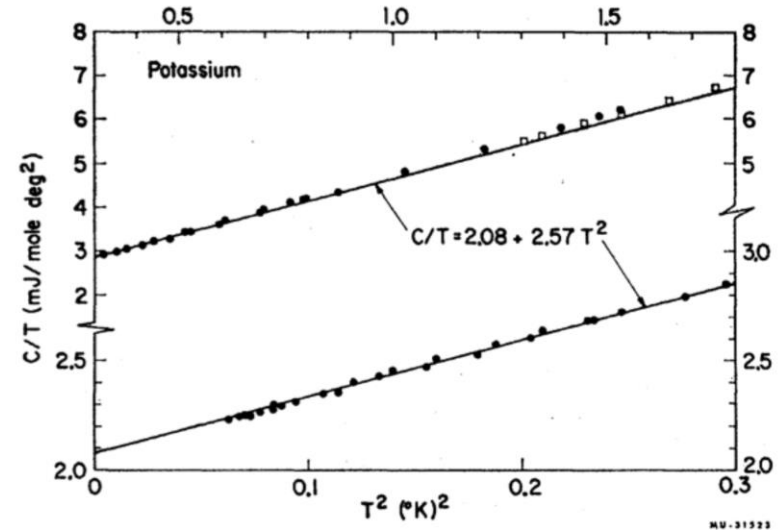


FIG. 1.  $C/T$  versus  $T^2$  for potassium.  $\square$ : liquid-helium cryostat;  $\bullet$ : adiabatic demagnetization cryostat.



## 2A.4. Application of Free Electron Model

[Henceforth, Boltzmann constant is  $k$  instead of  $k_B$ .]

### Thermionic Emission

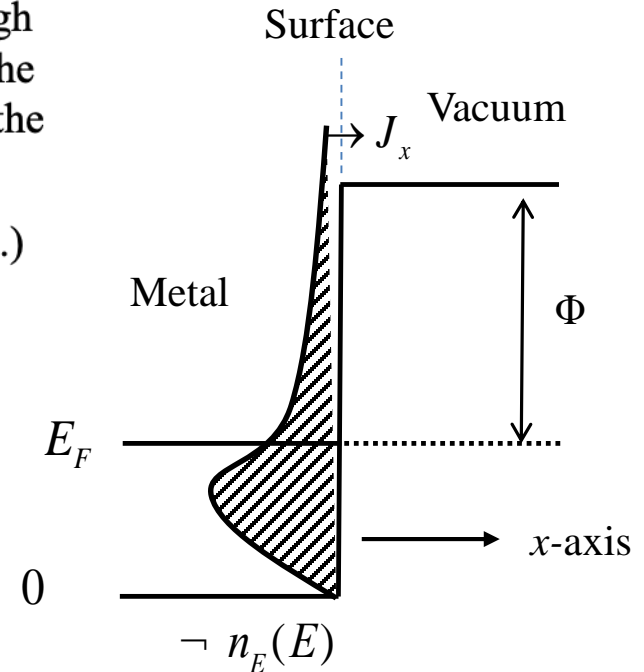
**Thermionic emission** means the emission of high energy electron corresponding to the high energy tail of the Fermi-distribution at high temperatures. When the surface is normal to  $x$ -axis, electrons with the kinetic energy along the  $x$ -axis bigger than  $E_F + \Phi$  can escape from the surface. That is to say,  $\frac{1}{2}mv_x^2 \geq (E_F + \Phi)$  for thermionic emission. (Note that in the free electron model, there are only kinetic energies.) In order to count electrons that meet this condition, we first change variable from  $E$  to  $v$  using  $E = \frac{1}{2}mv^2$

$$n(E)dE = D(E)f(E)dE = \frac{\sqrt{2}}{\pi^2} \left( \frac{m}{\hbar^2} \right)^{3/2} \frac{E^{1/2} dE}{e^{(E-E_F)/kT} + 1}$$

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

This is the number of electrons with the speed between  $v$  and  $v+dv$ . The contribution to the current density out of the surface,  $J_x$ , is obtained by multiplying  $-ev_x$  to each electron and integrate over the whole range satisfying  $\frac{1}{2}mv_x^2 \geq (E_F + \Phi)$ . Noticing that  $4\pi v^2 dv$  in the spherical coordinate corresponds to the volume element when the integrand is isotropic, it should be replaced by  $dv_x dv_y dv_z$  in the rectangular coordinate.

$$J_x = \frac{-2em^3}{h^3} \int_{\sqrt{2(E_F+\Phi)/m}}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{v_x dv_x dv_y dv_z}{e^{(E-E_F)/kT} + 1}$$



When  $E > E_F + \Phi$ ,  $E - E_F \gg kT$  and  $f(E)$  follows the Boltzmann distribution.

$$\begin{aligned}
 J_x &= -\frac{2em^3}{h^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\exp\left[-\frac{(E - E_F)}{kT}\right]}{\sqrt{2(E_F + F)/m}} v_x dv_x dv_y dv_z \\
 &= -\frac{2em^3}{h^3} \exp\left[\frac{E_F}{kT}\right] \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\exp\left[-\frac{m}{2kT}(v_x^2 + v_y^2 + v_z^2)\right]}{\sqrt{2(E_F + F)/m}} v_x dv_x dv_y dv_z
 \end{aligned}$$

This gaussian integration can be evaluated analytically. The result is the **Richardson equation**.

$$J_x = -\frac{4\rho emk^2}{h^3} T^2 \exp\left(-\frac{F}{kT}\right) = B_0 T^2 \exp\left(-\frac{F}{kT}\right) \quad B_0 = 4\pi emk^2/h^3 = 1.20 \times 10^6 \text{ A m}^{-2} \text{ K}^{-2}$$

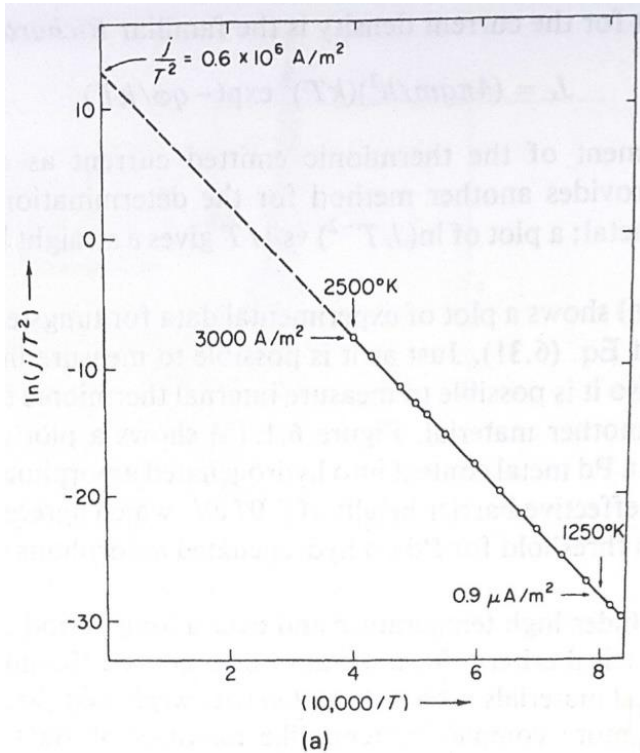
: Richardson constant

(Here we neglect the minus sign for convenience.)

The Richardson formula indicates a linear relationship between  $J_x/T^2$  and  $1/T$ . The slope is equal to  $-\Phi/k$ .

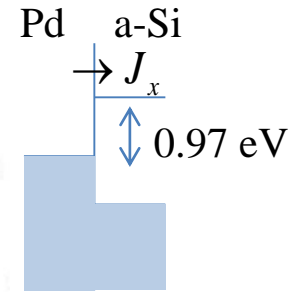
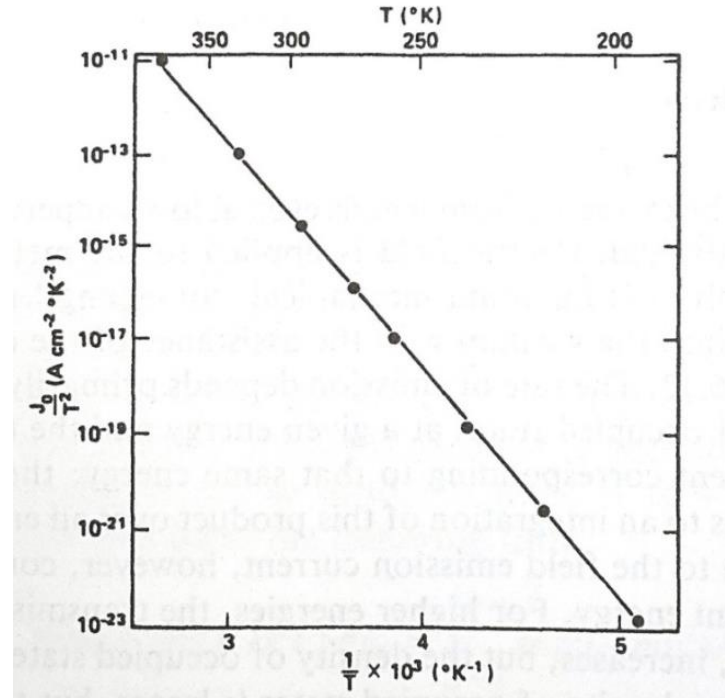
$$\ln\left(\frac{J_x}{T^2}\right) = \ln B_0 - \frac{F}{kT}$$

Thermionic emission from W into vacuum.



Note that the thermionic emission becomes significant only at very high temperatures. The wave nature of electron indicates that some electrons reflect back from the surface. Because of this, the measured  $B_0$  is about half of the Richardson constant. The work function estimated by the slope is about 4.4 eV.

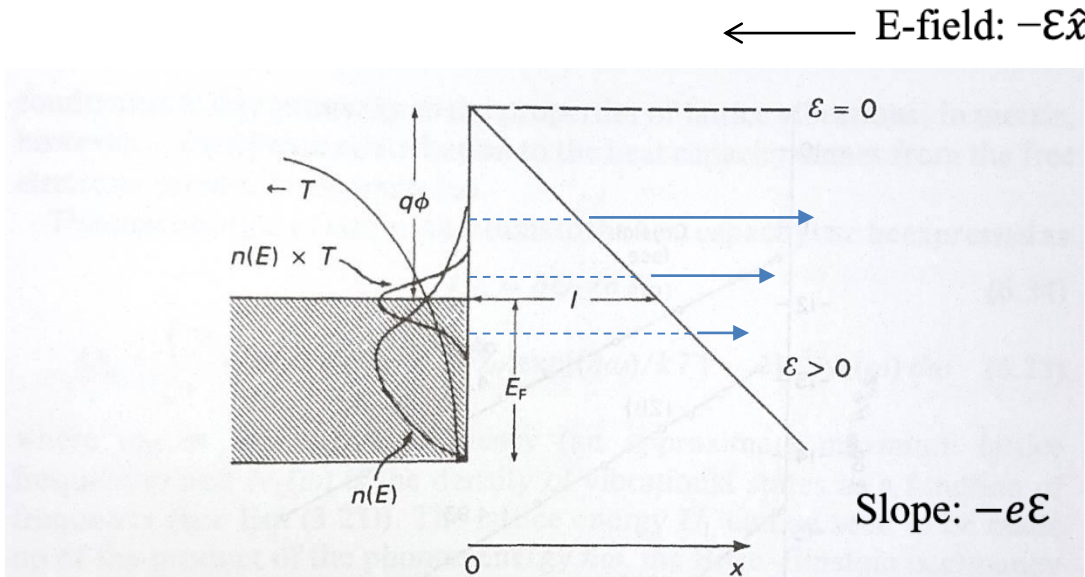
Thermionic emission from Pd into a-Si.



The thermionic emission also occurs internally between materials. The slope gives an effective injection barrier of 0.97 eV from Pd to a-Si. The injection barrier plays an important role in I-V characteristics and thermionic emission is a useful tool to measure it.

Field Emission

Another way to extract electrons from metals is using the quantum-mechanical tunneling effect. When an electric field is applied on the surface of metal (electric field pointing into the metal), a downward potential develops outside the surface. Therefore, emission by electron tunneling becomes possible, which is called the **field emission**. As we have learned in the previous chapter, the tunneling probability or transmission coefficient ( $T(E)$ ) strongly depends on the energy and tunneling length (barrier width). Multiplying  $n(E)$  and  $T(E)$  gives the tunneling current that has a sharp peak around  $E_F$ .



**FIG. 6.13** Free-electron model of a metal surface suitable for the discussion of field emission processes. The tunneling transmission coefficient  $T$  increases exponentially with  $E$  as the effective barrier height and width decrease with increasing  $E$ , but the density of occupied states available for tunneling  $n(E)$  decreases rapidly above the Fermi energy. The result is that the product of  $T$  and  $n(E)$  has a maximum near the Fermi energy.

The transmission coefficient through a general shape of potential can be obtained by generalizing the result on the square barrier.

$$T(E) \sim \exp\left(-\frac{\sqrt{8m(V_0 - E)}}{\hbar} a\right)$$

$$T(E) \sim \exp\left(-\int_0^d \frac{\sqrt{8m(V(x) - E)}}{\hbar} dx\right)$$

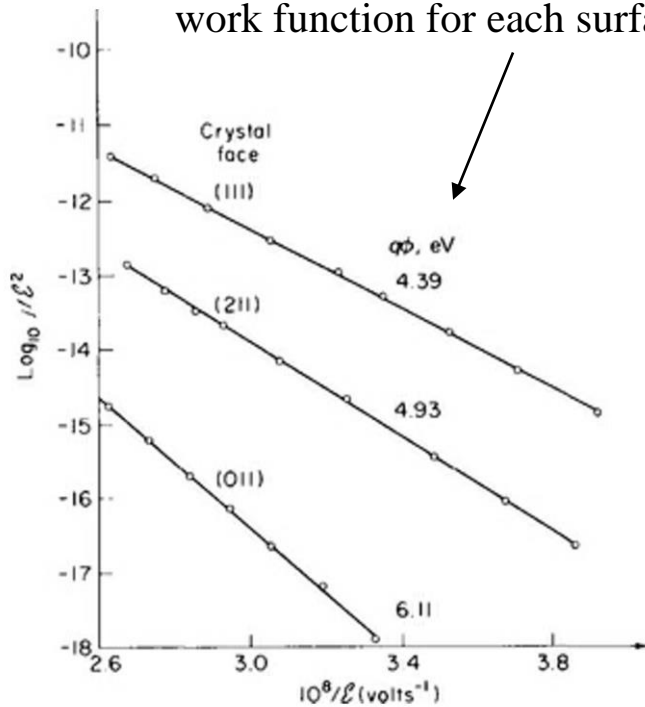
This is called the **WKB** (Wentzel-Kramers-Brillouin) **approximation** and is valid when  $V(x)$  is a slowly varying function. The triangular potential in the previous figure is given by  $V(x) = -e\mathcal{E}x + E_F + \Phi$ . For  $E = E_F$ ,  $V(x) - E = \Phi \left(1 - \frac{e\mathcal{E}x}{\Phi}\right)$  and the WKB approximation yields the following transmission coefficient:

$$T(E_F) \cong \exp\left(-\frac{4}{3\hbar e} \sqrt{2m} \frac{\Phi^{3/2}}{\mathcal{E}}\right)$$

A more complete treatment involving integration over the whole distribution  $n(E)T(E)$  yields a preexponential factor proportional to  $\mathcal{E}^2$ . Therefore, the current density from field emission is

$$J \sim \mathcal{E}^2 \exp\left(-\frac{4}{3\hbar e} \sqrt{2m} \frac{\Phi^{3/2}}{\mathcal{E}}\right) \rightarrow \ln\left(\frac{J}{\mathcal{E}^2}\right) = \frac{a}{\mathcal{E}} + b \quad \text{Fowler-Nordheim equation}$$

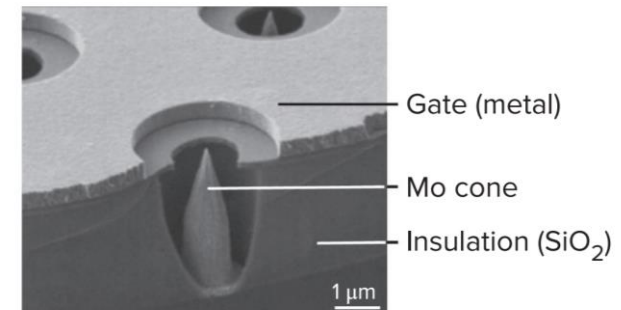
From the slope, one can estimate the work function for each surface.



- Field emission from different surfaces of tungsten.

Note that field emission has a very weak dependence on the temperature. Since it does not require high-temperature heating, the field emission is also called the cold emission.

In order to obtain meaningful field emission currents, the electric field at the surface should be at least 1 V/nm. To enable such large fields, sharp tip structures are fabricated such that fields are concentrated at the tip owing to the field enhancement effect. (This is similar to a lightning rod.)



The above microtips are used for the display applications (called the field emission display).

## Problems from Chap. 2A

**6-30 (a)/(b)/(c)/(d)**      **2,250 Å light**

**6-31**

**6-32 (a)/(b)/(c)**