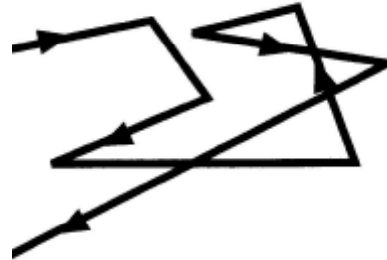
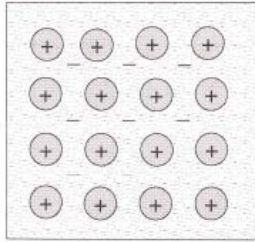


Two truths are told

## **3. ELECTRICAL CONDUCTIVITY**

# Kinetic Theory of Gases: Electron Gas

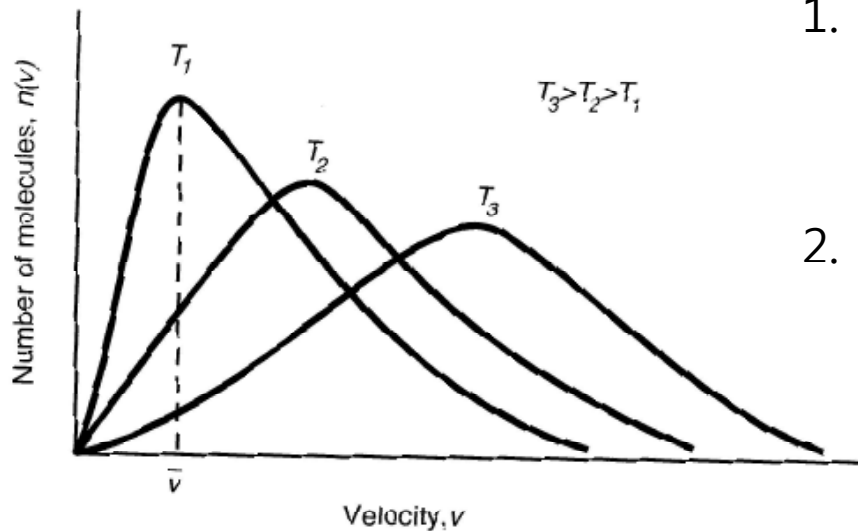


Maxwell-Boltzmann distribution

$$n(v) = Av^2 T^{-3/2} \exp(-Bv^2 / T) dv$$

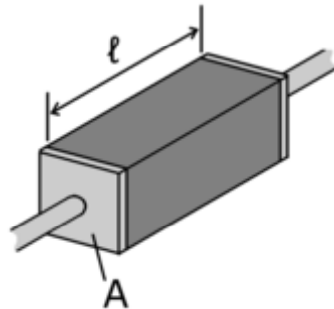
Assumptions for Drude Model:

1. Collisions btw electrons are neglected and the electrons undergo collision with the metal ions
2. The mean free path is governed by the lattice spacing in the crystal and independent of the electron's speed



**Figure 3.1** Maxwell-Boltzmann distribution of the electron velocities in a metal at different temperatures. Mean velocity =  $\bar{v}$ .

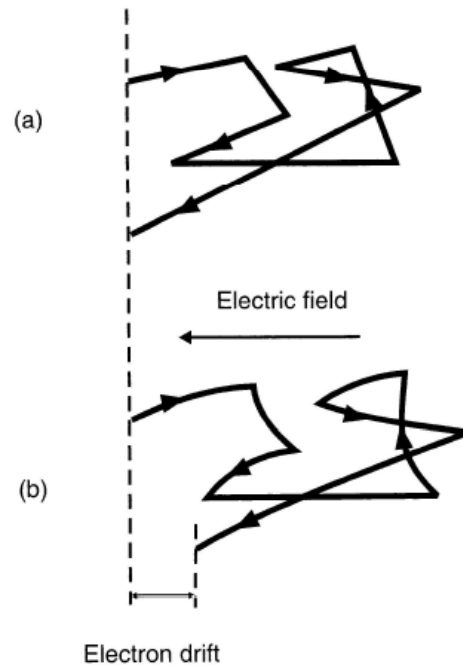
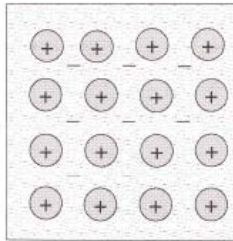
# Electrical Conduction: Drude Model



$$E = V / l \quad (\text{V/m})$$

$$J = I / A \quad (\text{A/m}^2)$$

$$\rho = RA / l \quad (\Omega\text{m})$$



1. Drude model: kinetic theory of gas

$$\frac{1}{2} m \bar{v}_t^2 = \frac{3}{2} k_B T$$

2. Avg. electron thermal velocity  $10^6 \text{ ms}^{-1}$

Mean free path: 10 nm

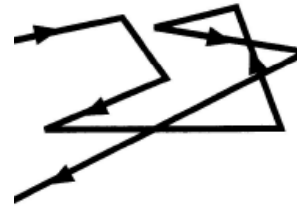
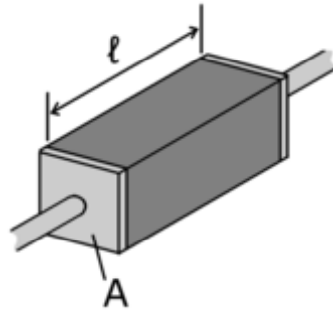
Let,  $\tau$  be the time of flight between collision

# Conductivity: Drude Model

$$E = V / l$$

$$J = I / A$$

$$\rho = RA / l$$



Let,  $\tau$  be the time of flight between collision

## Classical treatment (drift, scattering):

1. Force exerted on a single electron in a field:  $F = eE$
2. Acceleration experienced by the electron ( $a$ ):  $ma = eE$ , (by the Newton's law)
3. Average velocity in the electric field ( $\tau$ ):  $\bar{v}_d = \frac{e}{m} E \tau$

4. Current density ( $J=I/A$ ):

$$J = ne\bar{v}_d = \frac{ne^2\tau}{m} E$$

$$\therefore \sigma = \frac{ne^2\tau}{m}, \quad \rho = \frac{m}{ne^2\tau}$$

This is just the Ohm's law ( $V=RI$ ).

5. Drift mobility

$$\sigma = \frac{ne^2\tau}{m} = ne\mu, \quad \mu = \frac{e\tau}{m} = \frac{\bar{v}_d}{E}$$

6. Drift and diffusion:

$$J = ne\mu E + eD \frac{dn}{dx}$$

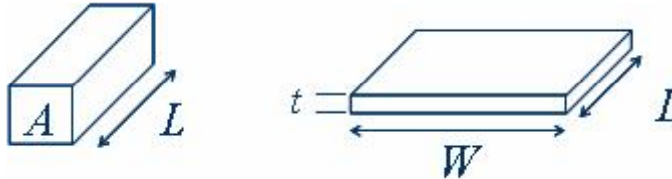
### Drift mobility values

Si single crystal:  $1500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

Pentacene:  $4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

C60:  $0.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

# Sheet Resistance



- Sheet resistance is applicable to two-dimensional systems where the thin film is considered to be a two dimensional entity. It is equivalent to resistivity as used in three-dimensional systems. When the term sheet resistance is used, the current must be flowing along the plane of the sheet, not perpendicular to it.

- In a regular three-dimensional conductor, the resistance can be written as

$$R = \rho \frac{L}{A} = \rho \frac{L}{Wt}$$

- where  $\rho$  is the resistivity,  $A$  is the cross-sectional area and  $L$  is the length. The cross-sectional area can be split into the width  $W$  and the sheet thickness  $t$ .
- By grouping the resistivity with the thickness, the resistance can then be written as

$$R = \frac{\rho}{t} \frac{L}{W} = R_s \frac{L}{W}$$

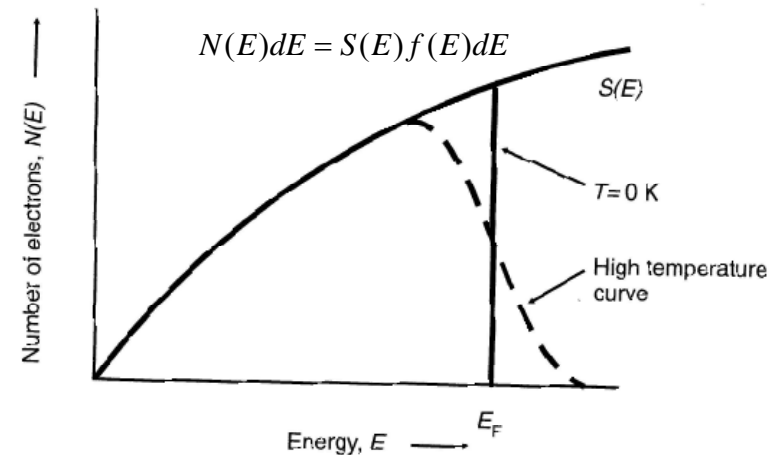
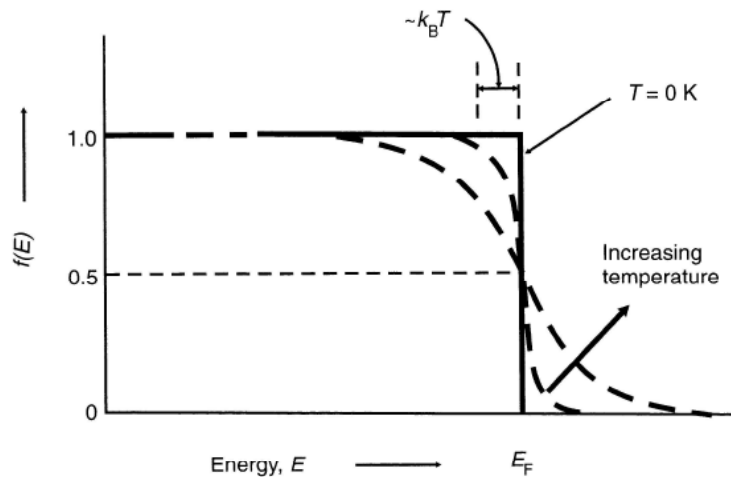
- $R_s$  is then the **sheet resistance**. Because it is multiplied by a dimensionless quantity, the units are ohms. The term ohms/square is sometimes (but not universally) used because it gives the resistance in ohms of current passing from one side of a square region to the opposite side, regardless of the size of the square. For a square,  $L = W$ . Therefore,  $R = R_s$  for any size square.

# Fermi Energy: Fermi-Dirac Quantum Statistics

- Sommerfeld 1928: Quantum mechanical approach
- Fermi-Dirac distribution function,  $f(E)$
- Fermi level ( $E_F$ ): energy at which the probability of electron occupancy is  $1/2$
- Density of state,  $S(E)$

$$f(E) = \frac{1}{\exp[(E - E_F)/k_B T] + 1}$$

$$S(E) = CE^{\frac{1}{2}}$$



**Figure 3.3** The Fermi-Dirac function  $f(E)$  at  $T = 0$  K and at  $T > 0$  K.

*Note that (1)  $k_B T$  is only 0.026 eV at 300 K, and (2)  $E_F$  of metal is several eV*

# Electromagnetic Waves

$$E = E_0 \cos(\omega t - kx)$$

$\omega = 2\pi\nu$  : angular freq. of the wave

$k = \frac{2\pi}{\lambda}$  : wave vector

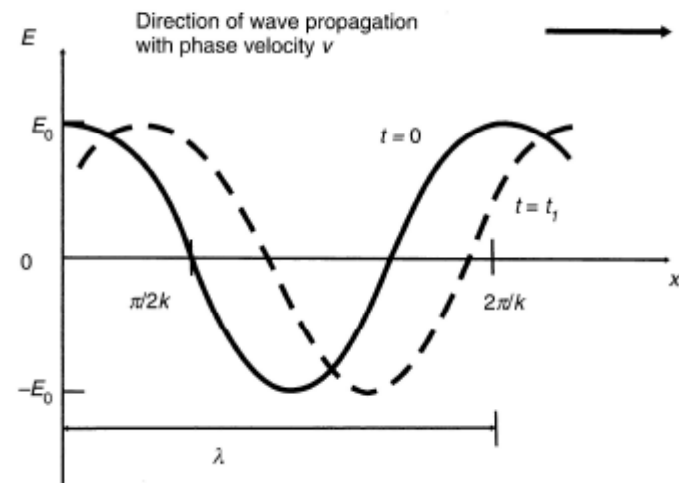
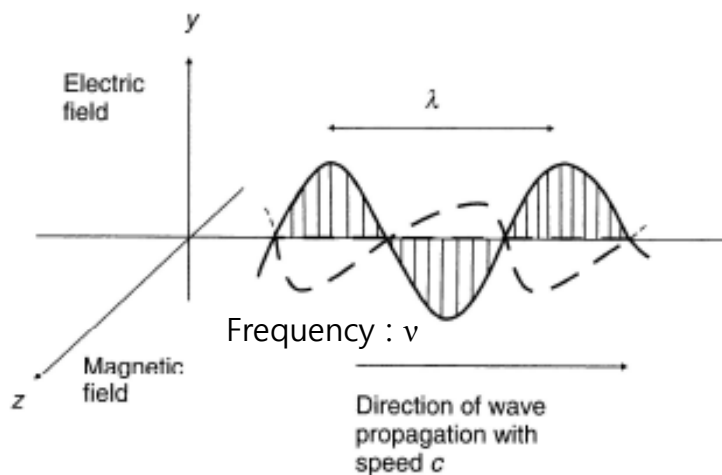
Phase velocity :

to follow the first x-cut phase of  $-\frac{\pi}{2}$

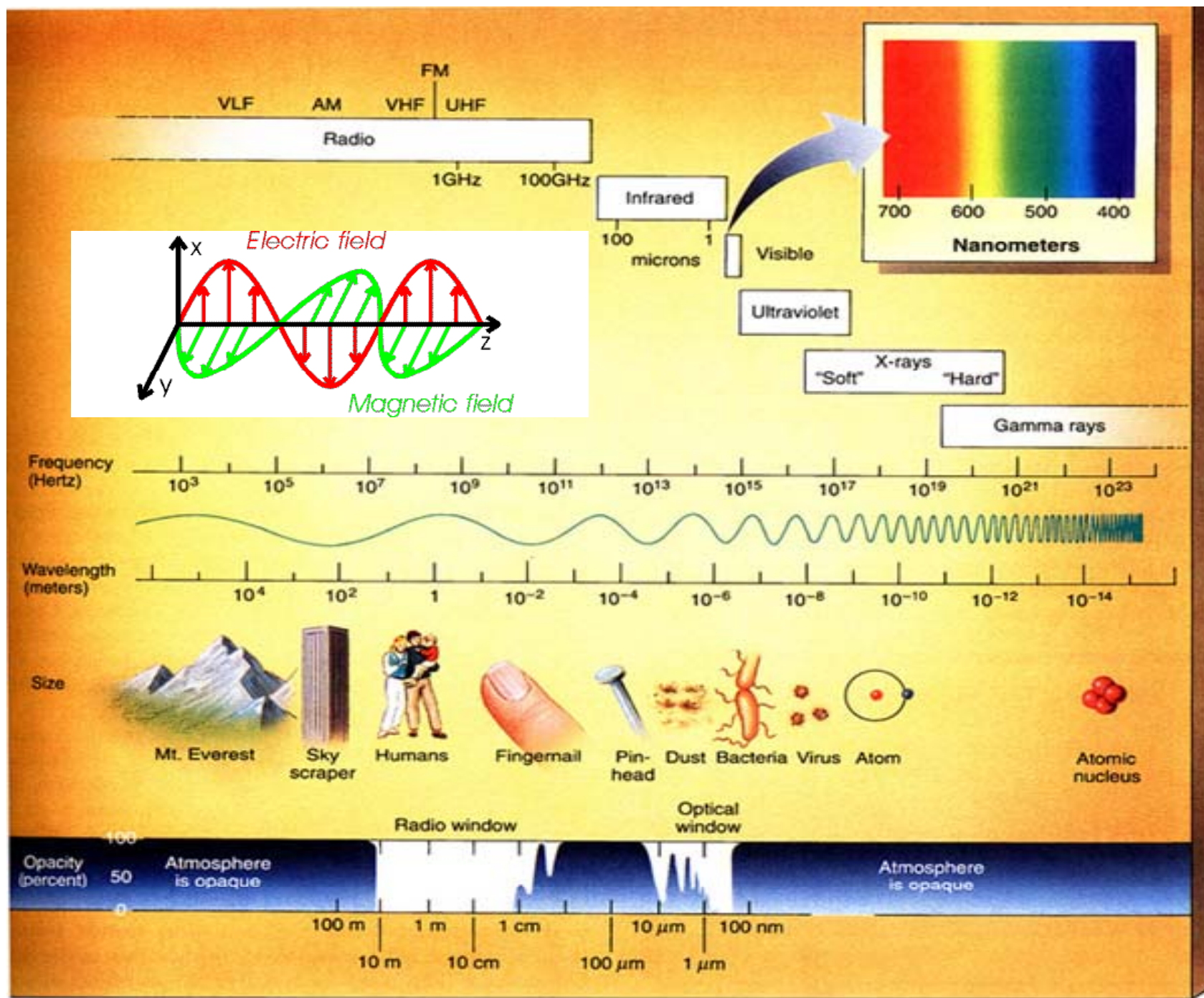
$(\omega t - kx) = -\frac{\pi}{2}$ , which gives

$x = (\pi / 2k) + (\omega t / k)$ , thus moving at the **phase velocity**( $v$ ) of

$$v = \frac{\omega}{k}$$



For EM wave, phase velocity  $v = \omega/k = \lambda\nu = c$ , ( $3.00 \times 10^8 \text{ ms}^{-1}$ )



# Photons as Particles: Group Velocity

- Photoelectric effect, Einstein 1905: Light as the 'energy packet' or 'quanta'
- Wave-particle duality can be better understood by realizing that the electron can be represented by a combination of several wave trains having slight different freq. and wave number.
- Group velocity ( $v_g$ ): speed at which the wave packet propagates

$$\Psi_1 = \sin[kx - \omega t] \quad (2.7)$$

and

$$\Psi_2 = \sin[(k + \Delta k)x - (\omega + \Delta\omega)t]. \quad (2.8)$$

Superposition of  $\Psi_1$  and  $\Psi_2$  yields a new wave  $\Psi$ . With  $\sin \alpha + \sin \beta = 2 \cos \frac{1}{2}(\alpha - \beta) \cdot \sin \frac{1}{2}(\alpha + \beta)$  we obtain

$$\Psi_1 + \Psi_2 = \Psi = \underbrace{2 \cos\left(\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x\right)}_{\text{Modulated amplitude}} \cdot \underbrace{\sin\left[\left(k + \frac{\Delta k}{2}\right)x - \left(\omega + \frac{\Delta\omega}{2}\right)t\right]}_{\text{Sine wave}}. \quad (2.9)$$

$$v_g = \frac{d\omega}{dk}$$

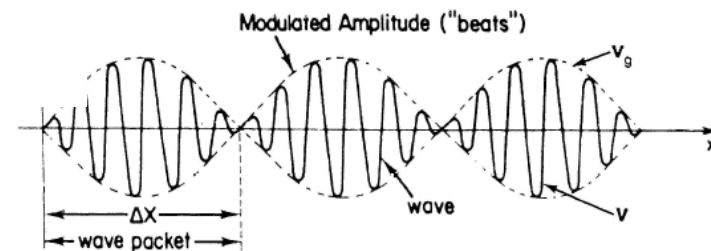


Figure 2.1. Combination of two waves of slightly different frequencies.  $\Delta X$  is the distance over which the particle can be found.

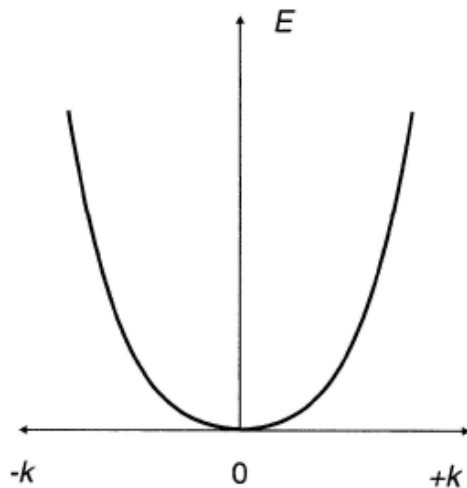
*R. E. Hummel, 3<sup>rd</sup> ed*

# Schrödinger Equations:

$$H\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

- 1-D Free Electron:  $V=0$



*Equation*

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

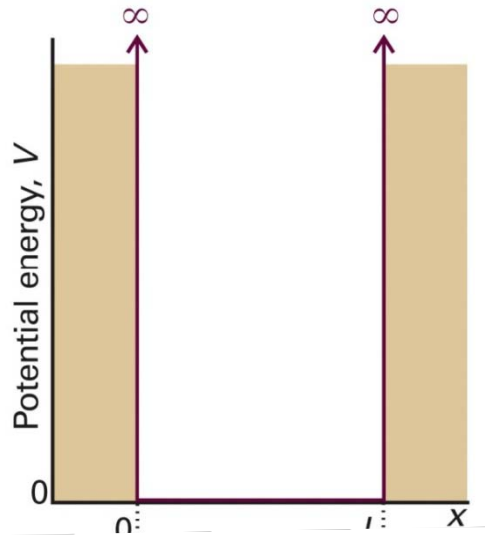
*Eigenfunctions*

$$\psi(x) = A \exp(jkx) \text{ or } \psi(x) = B \exp(-jkx)$$

*Eigenenergies*

$$E = \frac{\hbar^2 k^2}{2m} \quad (\text{note that } p = \hbar k)$$

# Particle in a Box

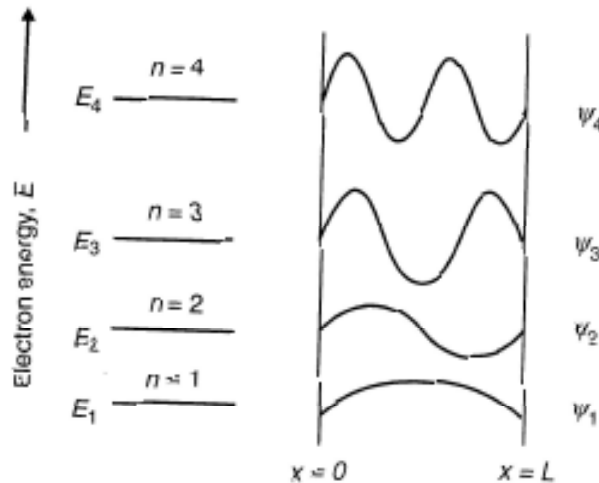


$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$$

$$\psi = Ae^{ikx} + Be^{-ikx}, E = \frac{k^2\hbar^2}{2m}$$

Boundary Conditions:

$$\Psi(0) = \Psi(L) = 0$$



i.e.  $\Psi_n = C \sin\left(\frac{n\pi}{L}x\right), n = 1, 2, 3, \dots \text{quantums}$

$$E_n = \frac{k^2\hbar^2}{2m} = \frac{n^2\hbar^2\pi^2}{2mL^2} = \frac{n^2h^2}{8mL^2}$$

*Note the ground state energy when  $n=1$*

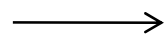
# Heisenberg's Uncertainty Principle

$$\Delta x \Delta p_x \geq h$$

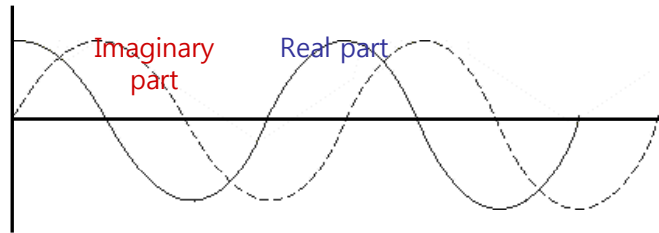
$$\Delta E \Delta t \geq h$$

$$\psi = Ae^{ikx}$$

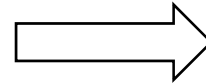
$$e^{ikx} = \cos kx + i \sin kx$$



$p = k\hbar$  momentum described exactly! What about the position?



Very uncertain in position



$$\begin{aligned} \psi^* \psi &= (Ae^{ikx})^* (Ae^{ikx}) \\ &= A^2, \text{const. independent of } x \end{aligned}$$

To make the location better-defined, you need to have momentum uncertainty by superposing several waves with different  $k$  values.

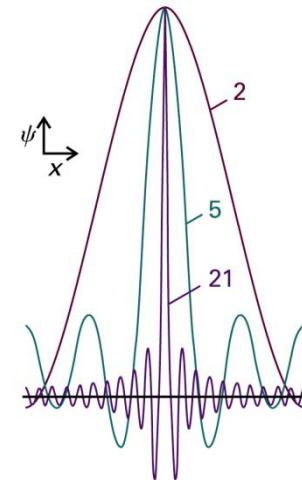
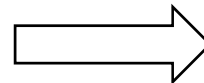
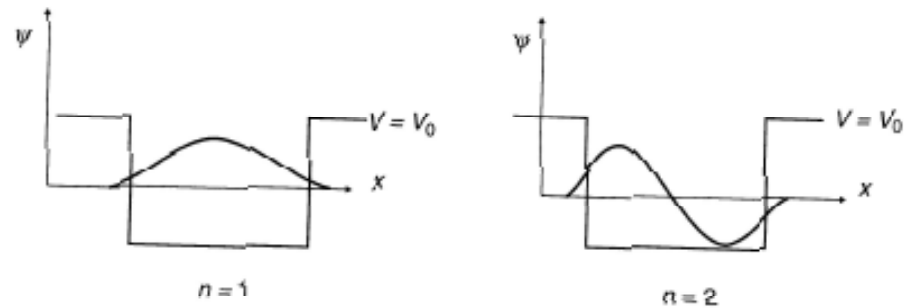
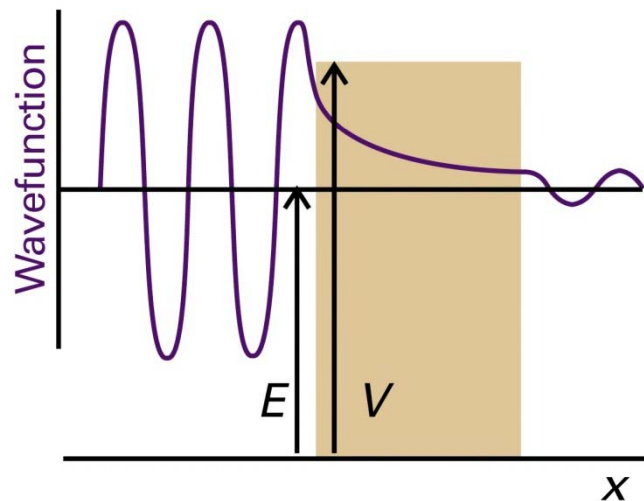


Figure 8-31  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

# Quantum Mechanical Tunnelling

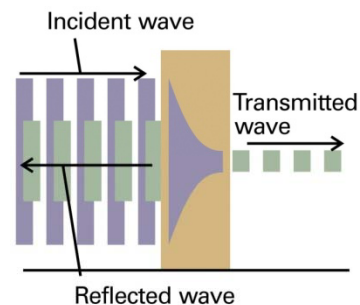


**Figure 3.11** Wavefunctions for  $n = 1$  and  $n = 2$  are superimposed on a one-dimensional well of finite height. Penetration of the wavefunctions outside the well represent quantum mechanical tunnelling.



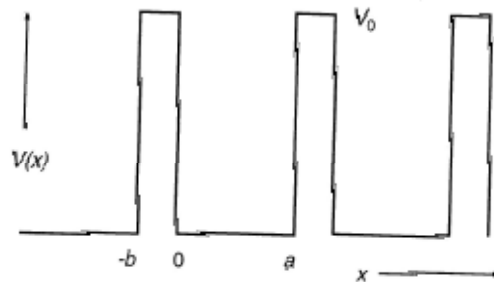
**Figure 9-9**  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

## Finite height potential barrier ( $V$ )



**Figure 9-10**  
Atkins Physical Chemistry, Eighth Edition  
© 2006 Peter Atkins and Julio de Paula

# Kronig-Penny Model in 1930

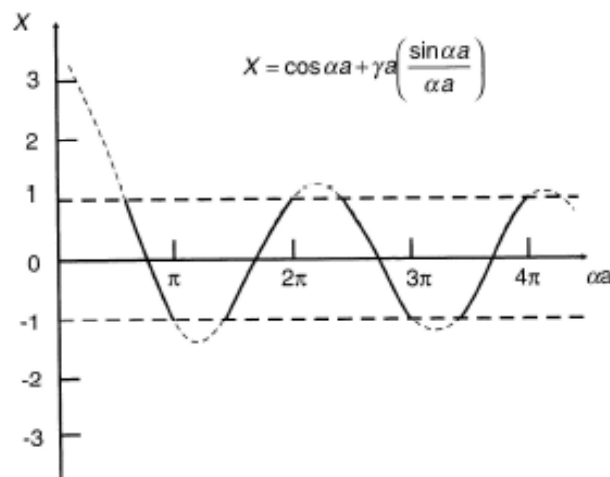


$$E = \frac{\hbar^2 \alpha^2}{2m} \quad \text{note that } \alpha \text{ replaces } k \text{ of free electron case}$$

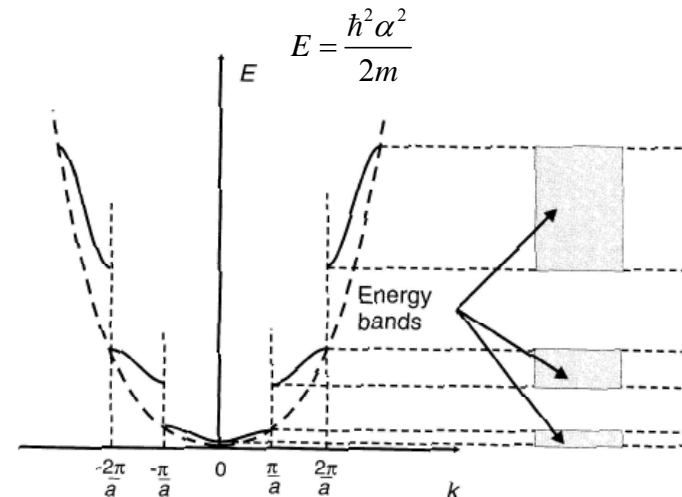
$$\cos ka = \cos \alpha a + \gamma a \left( \frac{\sin \alpha a}{\alpha a} \right) \quad \text{note that } \alpha \text{ gets } k \text{ when } \gamma \text{ is very low}$$

and that it becomes 'particle in a box' when  $\gamma$  is very large

$$\gamma = \frac{mV_0 b}{\hbar^2} \quad \text{strength of the barrier}$$

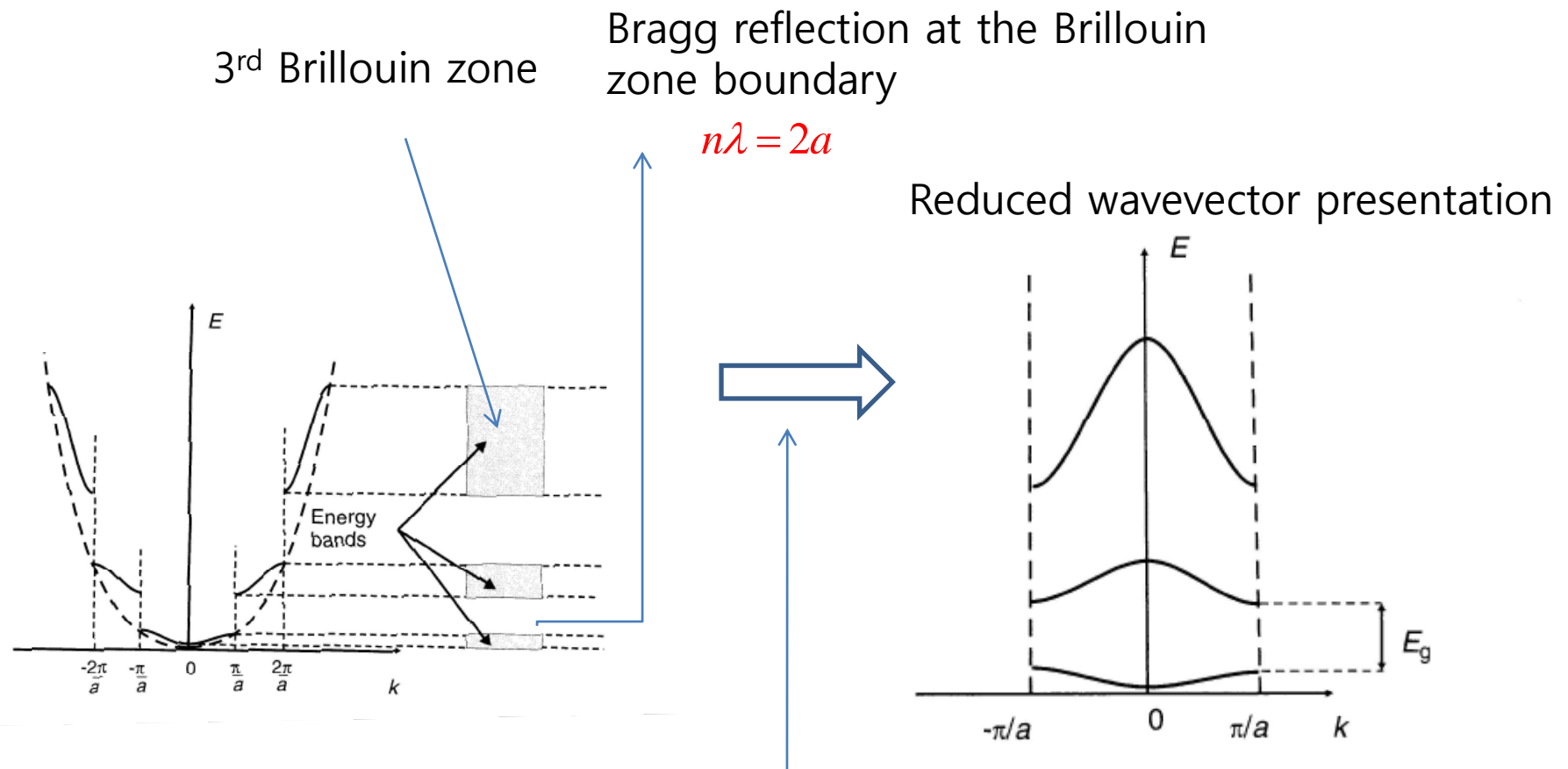


Allowed values of  $\cos ka$



Allowed range of  $\alpha$  gives allowed range of  $E$

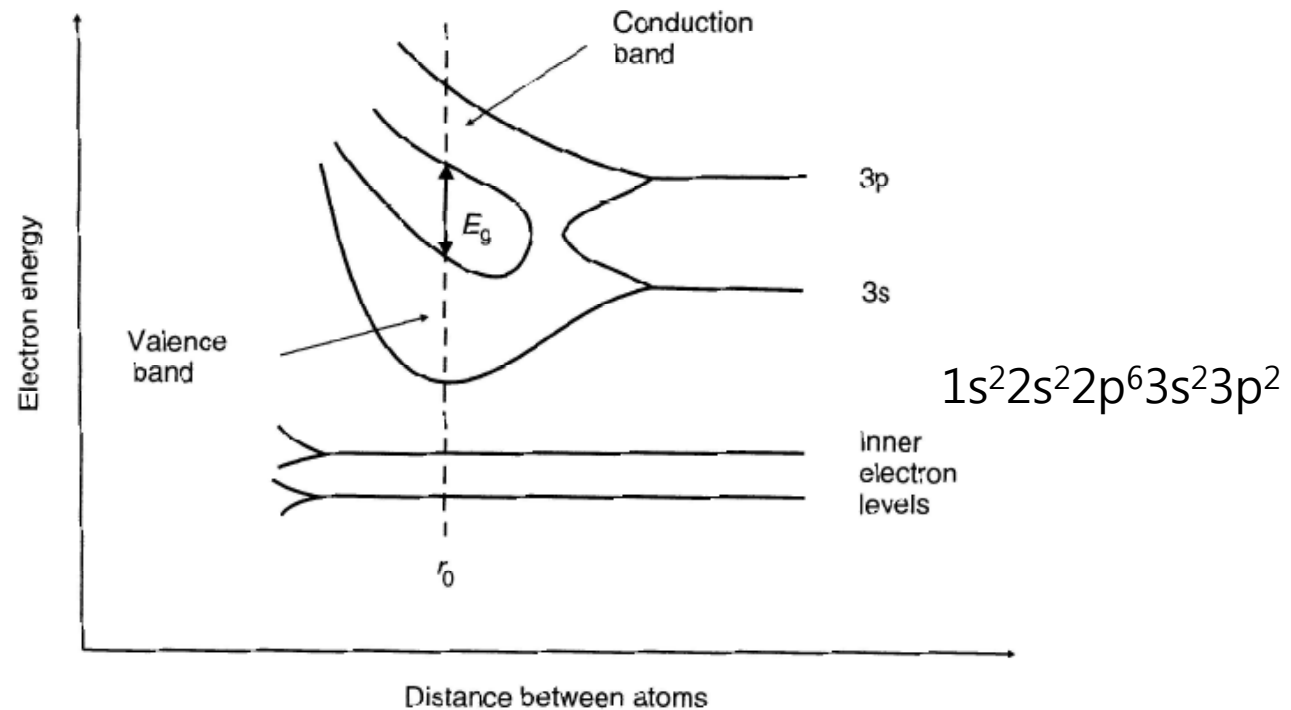
# Brillouin zone & Bragg Reflection



Because the same  $\alpha$  and thus  $E$  is obtained, for  $k$  and  $(k+2\pi na)$

$$\cos ka = \cos \alpha a + \gamma a \left( \frac{\sin \alpha a}{\alpha a} \right)$$

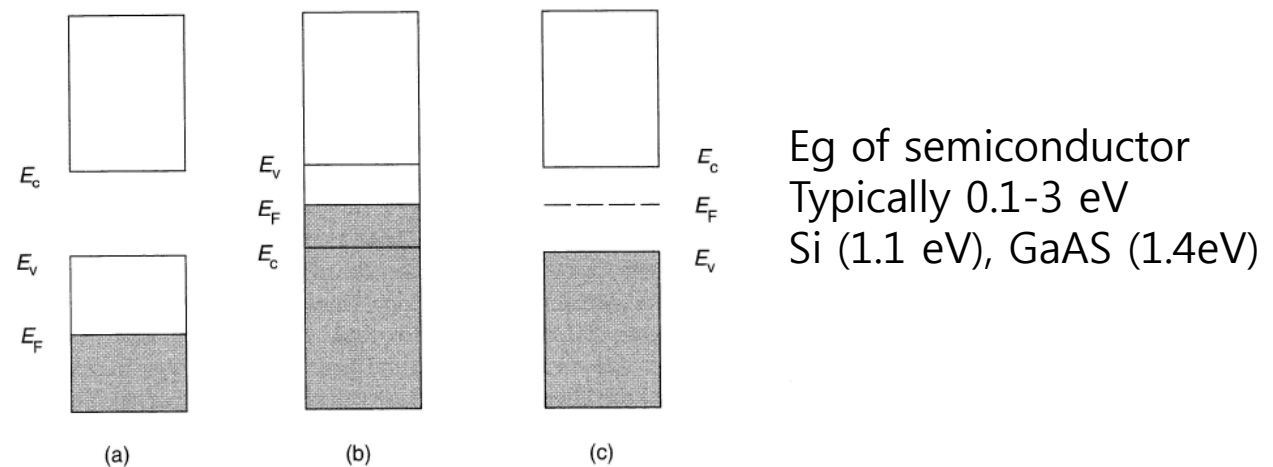
# Band Formation : Si crystal



**Figure 3.16** Energy levels in silicon as a function of interatomic spacing. The inner electron levels are completely filled with electrons. At the actual atomic spacing of the crystal  $r_0$  the electrons in the 3s subshell and the electrons in the 3p subshell undergo  $sp^3$  hybridization and all are accommodated in the lower valence band, while the upper conduction band is empty. The energy separation is the band gap  $E_g$ .

How many atoms in 1 kg of silicon?  $10^{26}$  atoms --- Energy level splitting of the same number

# Metal, Semiconductor, Insulator



**Figure 3.17** Possible energy band structures of crystalline solids. (a) Energy gap between the conduction and valence bands. The valence band is partly filled. (b) Overlapping valence and conduction bands. (c) Energy gap between the valence and conduction bands. The valence band is completely filled. Parts (a) and (b) represent the band structures of metals and (c) is the band structure for an insulator.  $E_v$  = top of valence band;  $E_c$  = bottom of conduction band;  $E_F$  = Fermi energy.

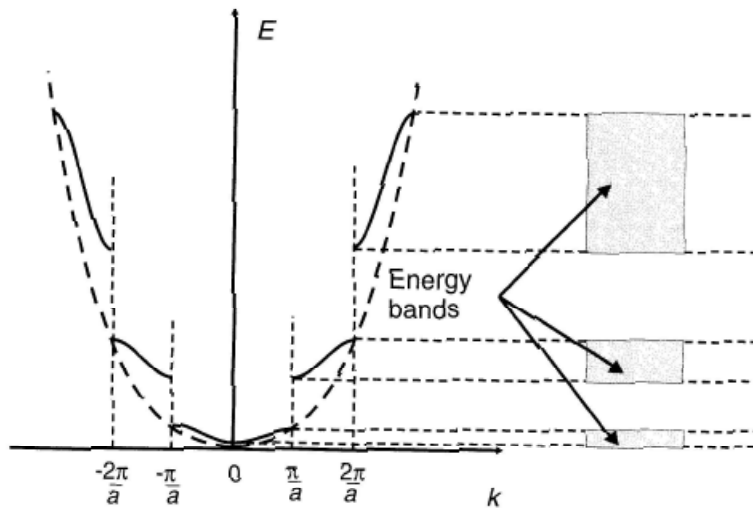
- Process of electronic conduction: valence band electron takes the energy from the field and change its energy state, i.e. move to a higher lying energy level: partly-filled band is able to conduct but fully-filled band is not.
- Semiconductor: increasing conductivity with T and/or light illumination

# Electrons and Holes

To describe the electron in a valence band much like the free electron but with modified mass ( $m^*$ ), we can put

$$E = \frac{\hbar^2 k^2}{2m^*} \rightarrow \frac{d^2 E}{dk^2} = \frac{\hbar^2}{m^*} \rightarrow m^* = \frac{\hbar^2}{d^2 E / dk^2}$$

Curvature of E-k curve determines the effective mass.



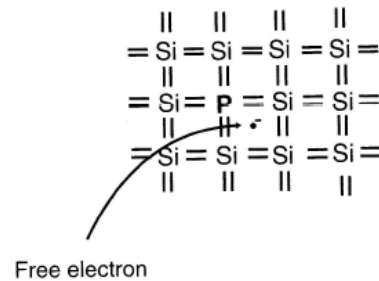
$m^*$  is positive at the bottom but negative at the top of the valence band

Negative  $m^*$  means the reversal of the momentum upon application of electric field

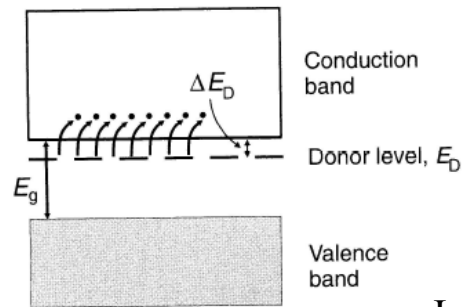
Therefore use of the 'hole' with positive charge and positive effective mass is convenient

# Doping

n-doping: P, As, Sb, Bi;  
Increasing  $E_F$

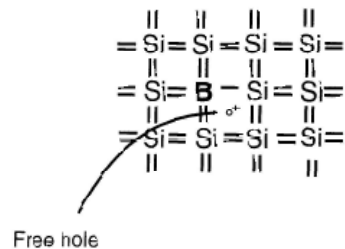


(a)

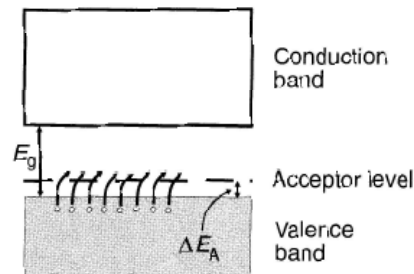


(b)

p-doping: B, Al, Ga, In  
Decreasing  $E_F$



(a)



(b)

*Extrinsic carrier generation*

$$n_e = BT^{\frac{3}{4}} \exp\left(\frac{-\Delta E_D}{2k_B T}\right)$$

and goes to  $n_e = ND$  at sufficiently high  $T$

$$\Delta E_D \approx 0.05 \text{ eV}$$

$$k_B T = 0.025 \text{ eV}$$

*Intrinsic carrier generation*

$$n_i = AT^{\frac{3}{2}} \exp\left(\frac{-E_g}{2k_B T}\right)$$

$$E_g = 1.1 \text{ eV}$$

$$k_B T \approx 0.025 \text{ eV}$$

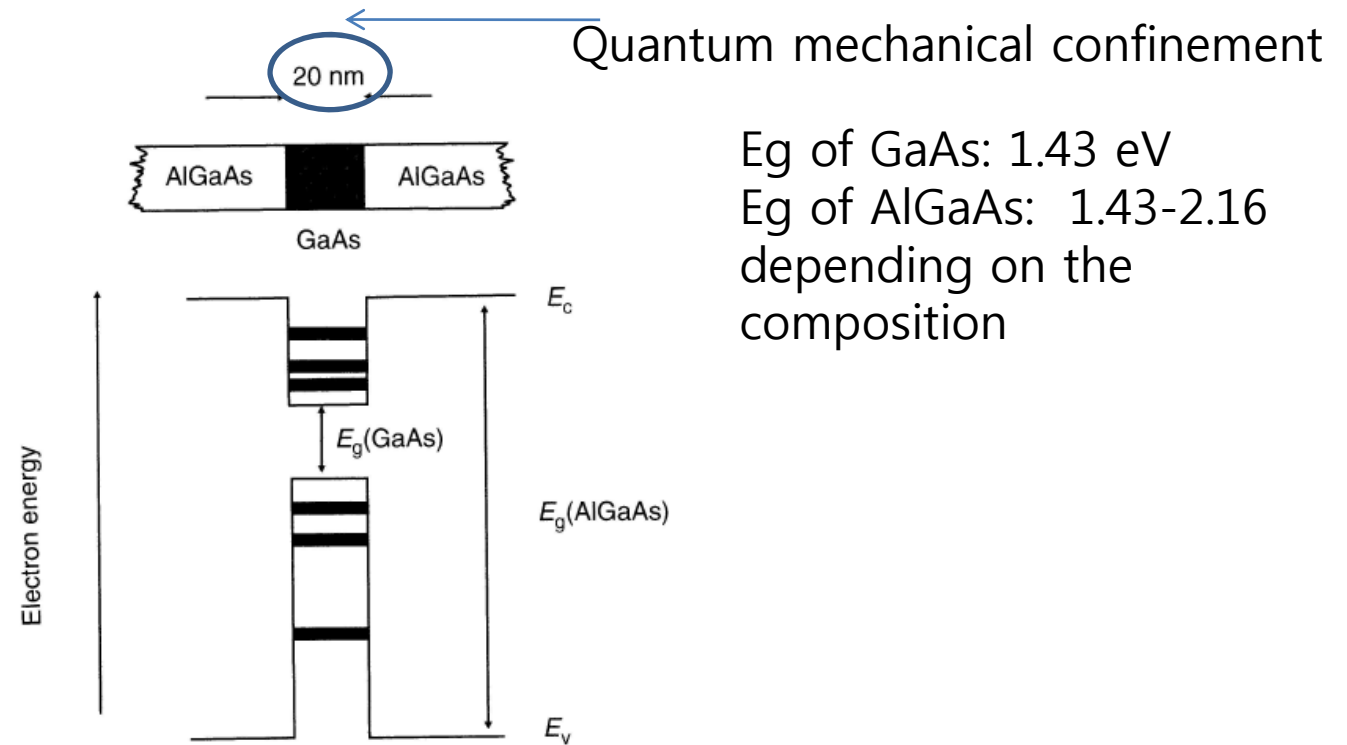
$$\Delta E_A \approx 0.05 - 0.16 \text{ eV}$$

$$k_B T = 0.025 \text{ eV}$$

Localized energy levels within band gap

1. Trap: temporary removal (trap) of carriers
2. Recombination center: permanent removal of carriers

# Quantum Wells



**Figure 3.23** Example of a quantum well. Discontinuities in the conduction and valence band edges in the case of a thin layer of GaAs sandwiched between layers of wider band gap AlGaAs. Quantum states are formed in the valence and conduction bands of the GaAs.

# Molecular Electronics

## Lecture for Public

Prof. Soo Young Park

September 5, 2008

VOD

[http://www.sciencetouch.net/sub/sub2\\_1.php](http://www.sciencetouch.net/sub/sub2_1.php)

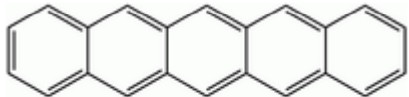

YTN 'Science TV' Broadcasting

<http://www.sciencetv.kr/>

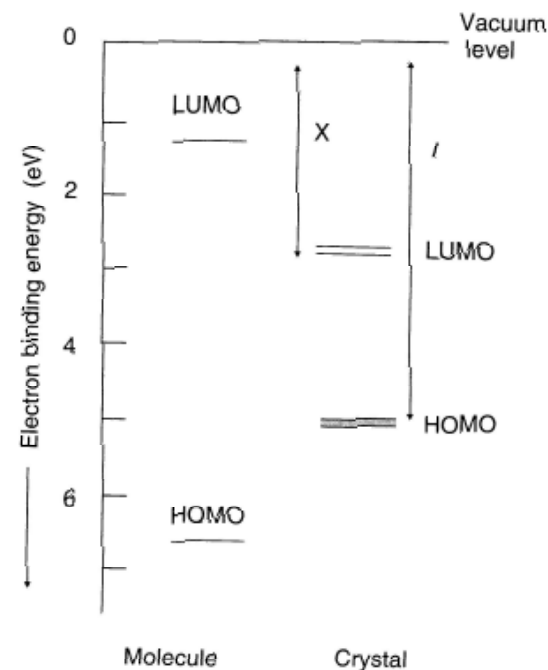
On air 10:00 am and 10:30pm, September 26 (Fri), 2008



# Pentacene: Organic Semiconductor


Pentacene	
	
IUPAC name	Pentacene
Identifiers	
CAS number	[135-48-8]
PubChem	24886995
SMILES	<a href="#">[show]</a>
Properties	
Molecular formula	C <sub>22</sub> H <sub>14</sub>
Molar mass	278.36 g/mol
Appearance	Dark powder
Melting point	> 300 °C; sublimes at 372-374 °C
<div>  <p>photograph of pentacene crystals</p> </div>	

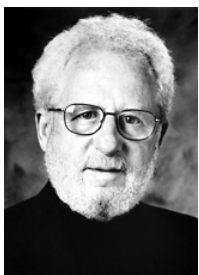
- Hole drift mobility:  $5.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$
- HOMO: highest occupied molecular orbital
- LUMO: lowest unoccupied molecular orbital
- What is the origin of the different HOMO/LUMO values in gas and crystal?
- Note the small band width of HOMO and LUMO



**Figure 3.27** Electronic energy levels associated with pentacene. The levels on the left are for free molecules in the gaseous state and those on the right are for the crystal.  $I$  = ionization energy;  $\chi$  = electron affinity [4].

# Polyacetylene: Conducting Polymer

 [http://nobelprize.org/nobel\\_prizes/chemistry/laureates/2000/presentation-speech.html](http://nobelprize.org/nobel_prizes/chemistry/laureates/2000/presentation-speech.html)



Chemistry

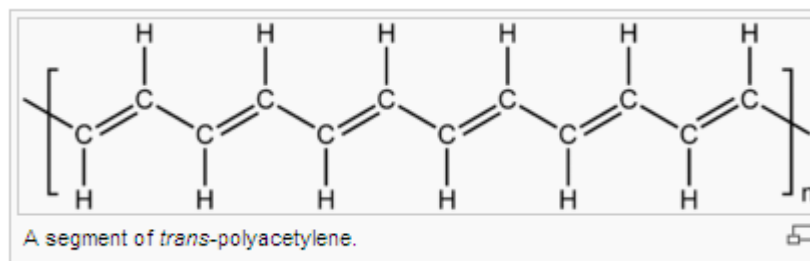


## The Nobel Prize in Chemistry 2000

### Presentation Speech

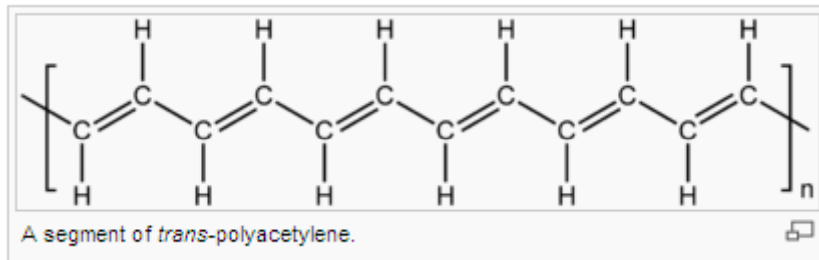
Presentation Speech by Professor Bengt Nordén of the [Royal Swedish Academy of Sciences](#),  
December 10, 2000.

*Translation of the Swedish text.*

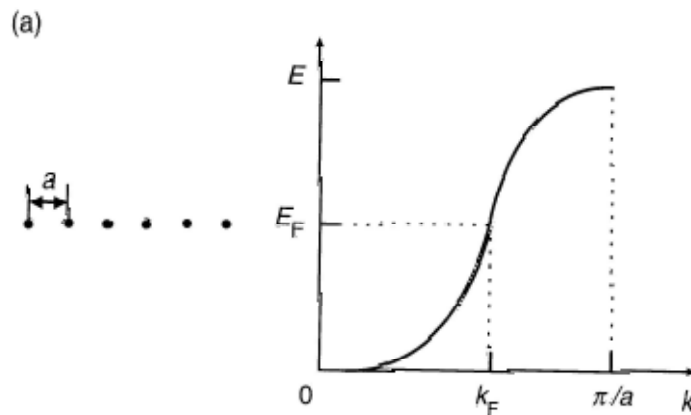


- **Homework #1:** Read the Nobel prize presentation speech and do the web search for polyacetylenes. Report on the polyacetylene history, facts, and future: 5 pages of A4 in English due 29 September.

# Polyacetylene: 1-D Kronig-Penney Model



- N atoms with separation 'a' : no bond alternation: Kronig-Penney Model
- $E_g$  is expected to vanish with increasing N to give the half-filled metallic band



$$E_n = \frac{\hbar^2 \pi^2 n^2}{2m(Na)^2}$$

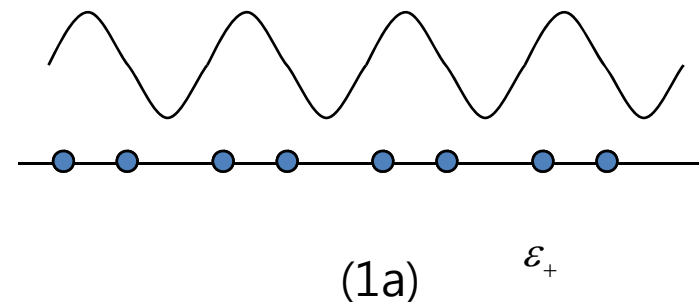
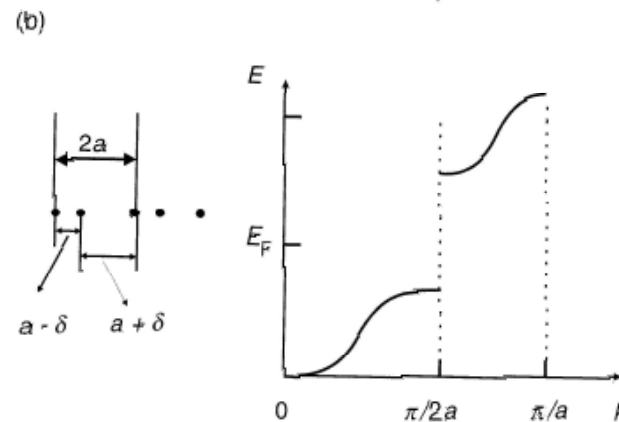
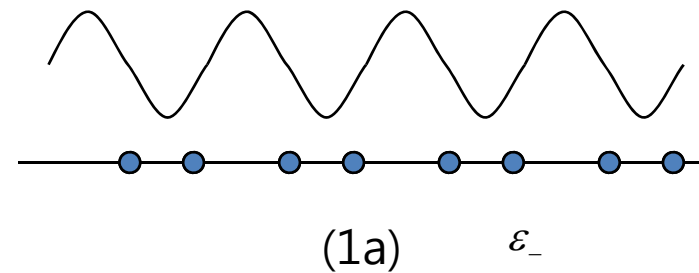
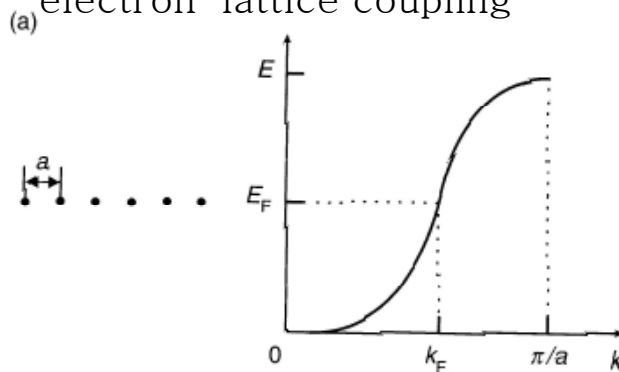
$$E_{HOMO} = \left(\frac{N}{2}\right)^2 \left[ \frac{\hbar^2 \pi^2}{2m(Na)^2} \right]$$

$$E_{LUMO} = \left(\frac{N}{2} + 1\right)^2 \left[ \frac{\hbar^2 \pi^2}{2m(Na)^2} \right]$$

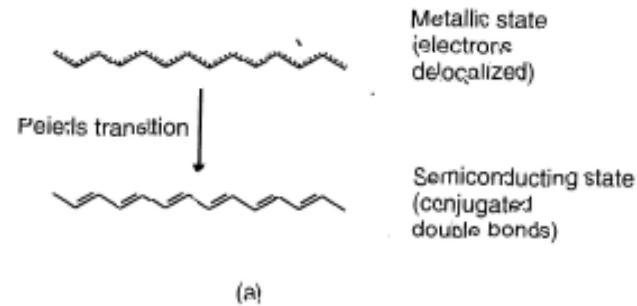
$$E_g = E_{LUMO} - E_{HOMO} = (N+1) \left[ \frac{\hbar^2 \pi^2}{2m(Na)^2} \right] \approx \left( \frac{\hbar^2 \pi^2}{2ma^2} \right) \left( \frac{1}{N} \right)$$

# Peierls Transition in Polyacetylene: Bond Length Alternation (BLA)

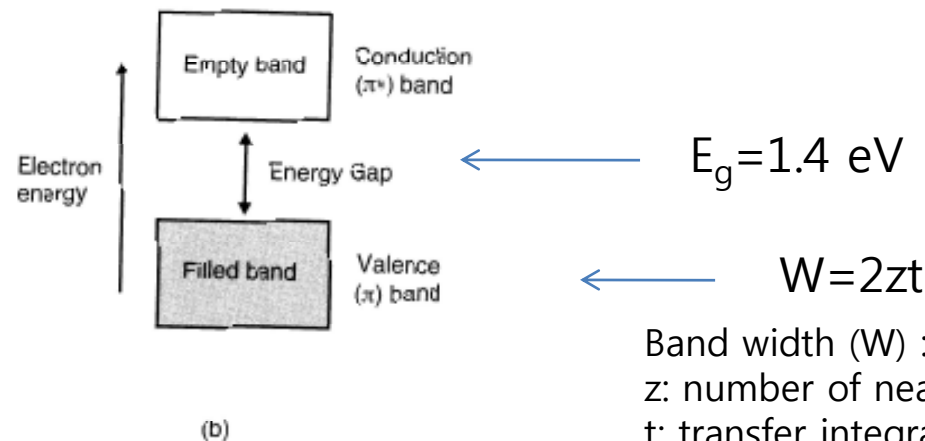
- 1955 Peierls showed that monoatomic metallic chain is unstable and will undergo a metal-to-insulator transition at low temperature
- Transition from a metal with no gap at the Fermi level into a semiconductor with a gap at  $\pi/a$
- Compromise between elastic energy (displacing the atom) and electronic energy: 'electron-lattice coupling'



# Band Structure of Polyacetylene



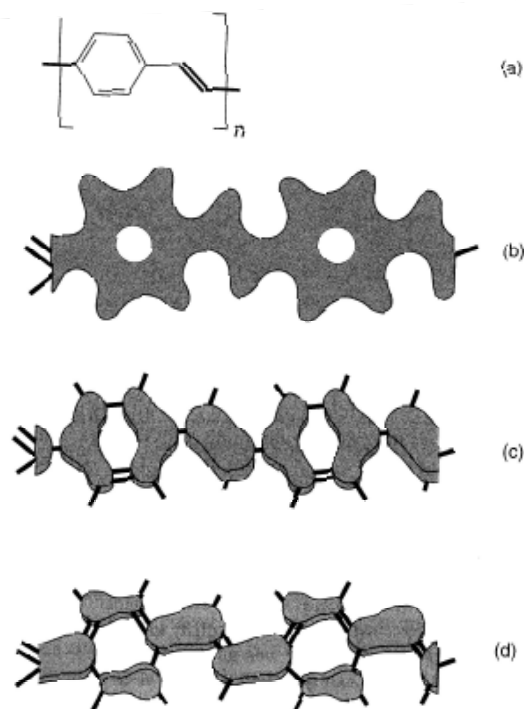
*The greater degree of conjugation  
The larger the value of  $W$   
The higher the drift mobility*



Band width ( $W$ ) : ca 10 eV  
 $z$ : number of nearest neighbors (2 for PA)  
 $t$ : transfer integral (2.5 eV for PA)

**Figure 3.29** (a) The electrons associated with the  $\text{CH}^\bullet$  radicals in *trans*-polyacetylene will delocalize over the chain. The Peierls distortion leads to single/double bond alternation. (b) Resulting energy bands.

# Conjugated Polymers and Other Semiconducting Materials



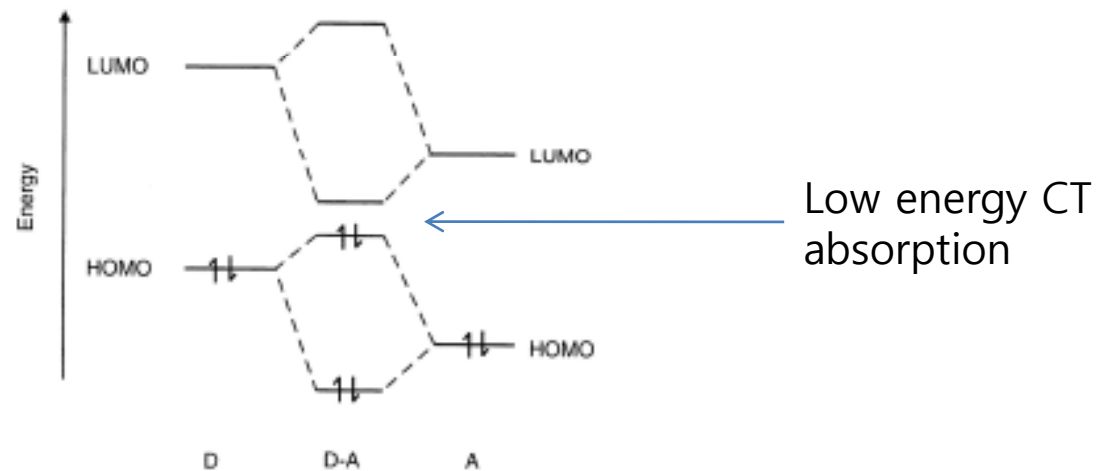
**Figure 3.30** (a) Repeat unit of poly(*p*-phenylenevinylene), PPV. (b) Total charge density. (c) HOMO charge density. (d) LUMO charge density. Reprinted from *J. Phys.: Condens. Matter*, **16**, Clarke SJ, Brand S, Abram RA, 'First-principles studies of the structural and electronic properties of poly-*para*-phenylene vinylene', pp. 8609–8620, Copyright (2004), with permission from IOP Publishing Limited.

**Table 3.1** Room temperature carrier mobilities for field effect transistors based on organic semiconductors. After Dimitrakopoulos and Mascaro [6] and Pearson *et al.* [7]. The electron mobilities in single crystal silicon and gallium arsenide are also given.

Material	Carrier mobility ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )
Si single crystal (electrons)	1500
GaAs single crystal (electrons)	8500
Pentacene	$10^{-3} - 1$
Polyacetylene	$10^{-4}$
Polythiophene	$10^{-5}$
Phthalocyanine	$10^{-4} - 10^{-2}$
Thiophene oligomers	$10^{-4} - 10^{-1}$
Organometallic dmit complex	0.2
$\text{C}_{60}$	0.3



# Charge Transfer (CT) Complex

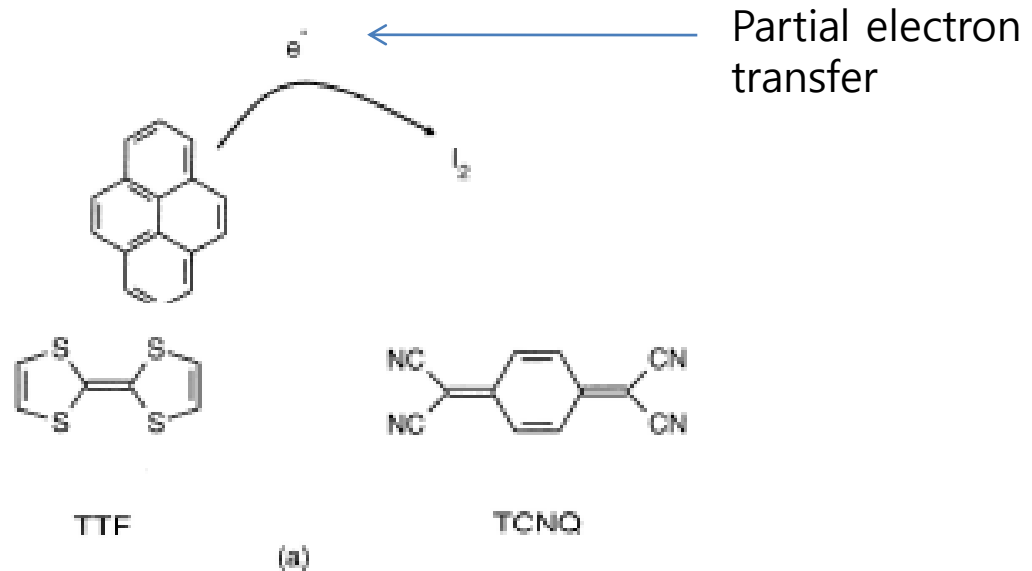


## Conductivities:

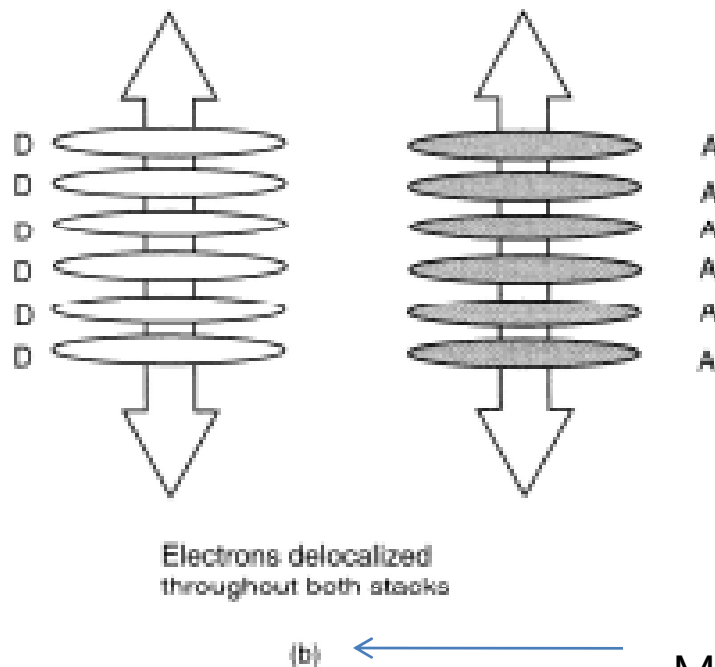
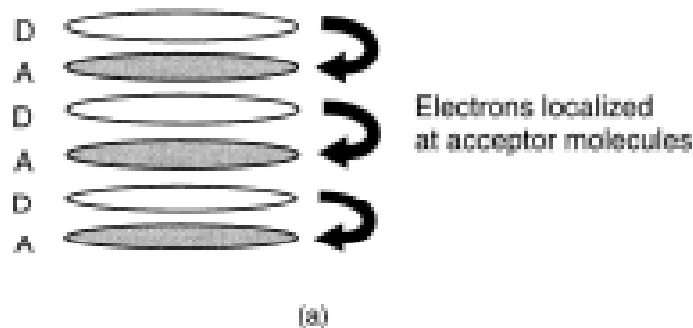
pyrene:  $10^{-12} \text{ Sm}^{-1}$

Iodine:  $10^{-7} \text{ Sm}^{-1}$

CT complex:  $1 \text{ Sm}^{-1}$



# Stacking in CT Complexes

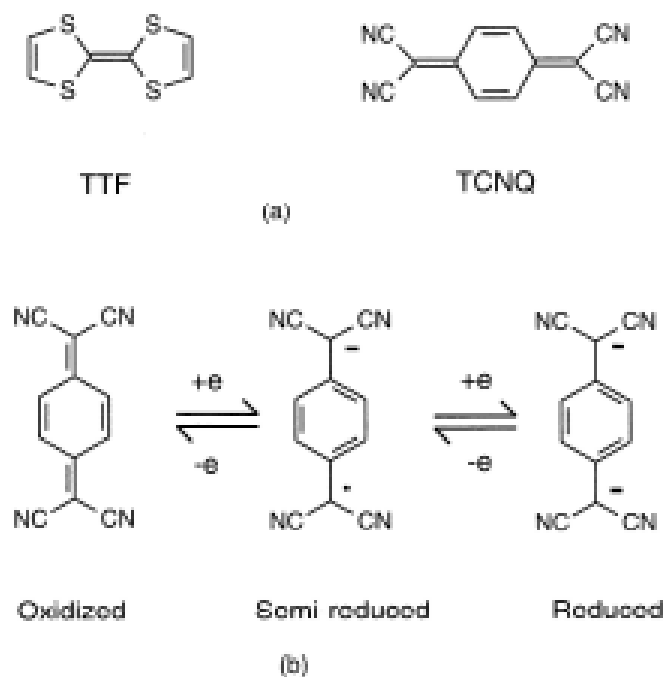


- Band width is much less ( $\sim 1$  eV) compared to the conjugated polymer..

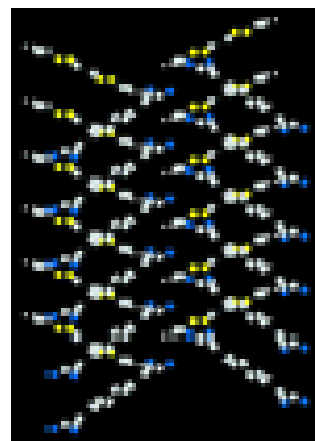
- CT complex is **intermolecular** 1-D conductor, while conjugated polymer is a 1-D **intramolecular** conductor.

More chances for higher conductivity

# TTF-TCNQ: Organic Metal



A 1:1 TTF:TCNQ salt exhibits a high room temp conductivity ( $5 \times 10^2 \text{ Sm}^{-1}$ ) and metallic behavior is observed as temperature is reduced to 54K.



Segregated parallel stacking (*Chem. Rev.*, **104** (11), 5565 -5592, 2004)

# Doping Polyacetylene

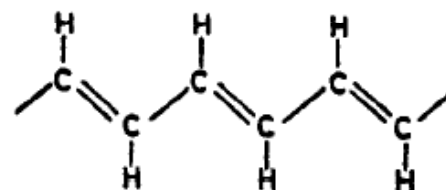
1014

*Journal of the American Chemical Society* / 100:3 / February 1, 1978

**Table I.** Conductivity of Polycrystalline Polyacetylene and Derivatives (As-Grown Films)

Material	Conductivity, $\sigma$ ( $\Omega^{-1}$ $\text{cm}^{-1}$ ) (25 °C)
<i>cis</i> -(CH) <sub>x</sub> <sup>a,b</sup>	$1.7 \times 10^{-9}$
<i>trans</i> -(CH) <sub>x</sub> <sup>a,b</sup>	$4.4 \times 10^{-5}$
<i>trans</i> -[(CH)(HBr) <sub>0.04</sub> ] <sub>x</sub>	$7 \times 10^{-4}$
<i>trans</i> -(CHCl <sub>0.02</sub> ) <sub>x</sub>	$1 \times 10^{-4}$
<i>trans</i> -(CHBr <sub>0.05</sub> ) <sub>x</sub> <sup>c</sup>	$5 \times 10^{-1}$
<i>trans</i> -(CHBr <sub>0.23</sub> ) <sub>x</sub> <sup>b,c</sup>	$4 \times 10^{-1}$
<i>cis</i> -[CH(ICI) <sub>0.14</sub> ] <sub>x</sub>	$5.0 \times 10^1$
<i>cis</i> -(CHI <sub>0.25</sub> ) <sub>x</sub>	$3.6 \times 10^2$
<i>trans</i> -(CHI <sub>0.22</sub> ) <sub>x</sub> <sup>b,c</sup>	$3.0 \times 10^1$
<i>trans</i> -(CHI <sub>0.20</sub> ) <sub>x</sub> <sup>b</sup>	$1.6 \times 10^2$
<i>cis</i> -[CH(IBr) <sub>0.15</sub> ] <sub>x</sub>	$4.0 \times 10^2$
<i>trans</i> -[CH(IBr) <sub>0.12</sub> ] <sub>x</sub>	$1.2 \times 10^2$
<i>trans</i> -[CH(AsF <sub>5</sub> ) <sub>0.03</sub> ] <sub>x</sub>	$7 \times 10^1$
<i>trans</i> -[CH(AsF <sub>5</sub> ) <sub>0.10</sub> ] <sub>x</sub> <sup>b</sup>	$4.0 \times 10^2$
<i>cis</i> -[CH(AsF <sub>5</sub> ) <sub>0.14</sub> ] <sub>x</sub>	$5.6 \times 10^2$
<i>trans</i> -[Na <sub>0.28</sub> (CH)] <sub>x</sub>	$8 \times 10^1$

<sup>a</sup> H. Shirakawa, T. Ito, and S. Ikeda, unpublished results; see ref 1-3. <sup>b</sup> Composition obtained by chemical analysis from Galbraith Laboratories, Inc. (sum of all elements is ~99.8-100.1%). <sup>c</sup> See ref 1-3.



(2)

(CH)<sub>x</sub> (2) polymer were doped with controlled amounts of electron-attracting species such as chlorine, bromine, iodine, or AsF<sub>5</sub>, their electrical conductivity could be systematically and controllably varied over a wide range, with up to 10<sup>11</sup> overall increase in conductivity. The most highly conducting films exhibited a conductivity at room temperature of several hundred  $\Omega^{-1} \text{ cm}^{-1}$ —by far the highest conductivity observed for any covalent organic polymer. The (CH)<sub>x</sub> polymer films used in the studies were prepared using the techniques developed previously by Shirakawa et al.<sup>4</sup>

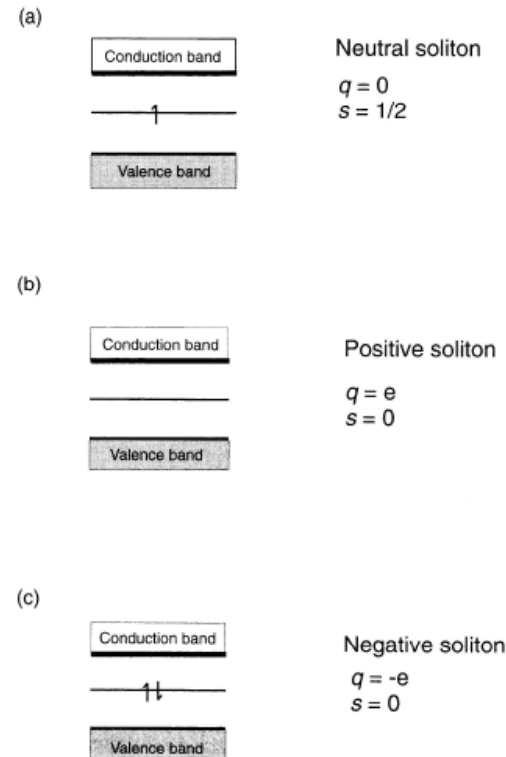
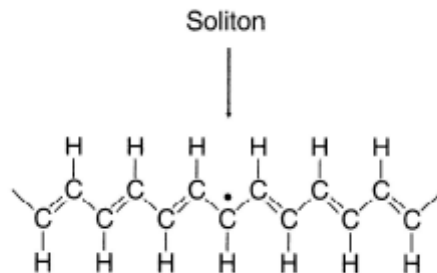
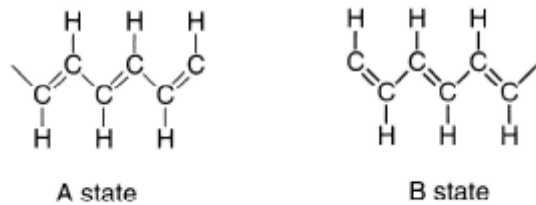
C. K. Chiang,<sup>14</sup> M. A. Drury,<sup>15</sup> S. C. Gau<sup>15</sup>  
A. J. Heeger,<sup>14</sup> E. J. Louis,<sup>15</sup> A. G. MacDiarmid<sup>15</sup>  
Y. W. Park,<sup>14</sup> H. Shirakawa<sup>15,16</sup>

*Department of Chemistry, Department of Physics and  
Laboratory for Research on the Structure of Matter  
University of Pennsylvania  
Philadelphia, Pennsylvania 19104*

*Received September 6, 1977*

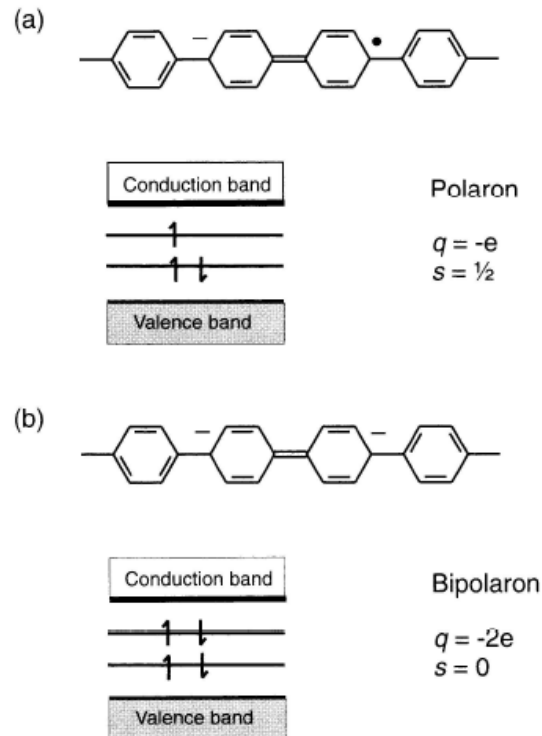
# Solitons in Polyacetylene(PA)

- Solitary wave (phase kink) at the boundary of two degenerate BLA states of PA
- Soliton is an extended wave over about 7 C atoms; mobile, esr active
- Charged soliton (+, -) is a charge carrier in PA; hopping by the capture of a mobile electron from a neutral soliton in an adjacent chain.
- Doping generates charged solitons which progresses to the formation of soliton band



# Polarons and Bipolarons

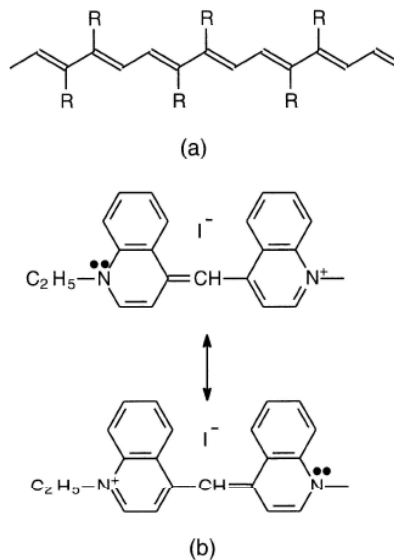
- Defects in conjugated polymers with non-degenerate GS
- Positive (negative) polaron is a radical cation (anion); Bipolaron is a bound state of two charged polarons of like charge. Polaron refers to the distortion of the lattice.
- Polaron/bipolaron are charge carriers in conjugated polymers with non-degenerate GS



**Figure 3.40** Schematic diagram of (a) a polaron and (b) a bipolaron in poly(*p*-phenylene). The charge  $q$  and spin  $s$  of the defects are indicated.

# Superconductivity

- Superconductivity  $\equiv$  vanished resistivity
- 1957 BCS (Bardeen, Cooper, Schrieffer) theory: Attractive interaction btw electrons provided by the exchange of phonons to form 'Cooper Pair'
- Cooper pair have opposite spin (no net spin) and the quasi-particle which does not obey Fermi-Dirac statistics. Cooper pairs are able to move through the lattice without any energy exchange in collision, which means no resistivity.
- Currently 135K is the highest record superconductor (oxide material); [YBCO](#), critical temperature 92 K; organic CT salt 13K, fullerenes 33K. From about 1993 the highest temperature superconductor was a ceramic material consisting of thallium, mercury, copper, barium, calcium, and oxygen, with  $T_c=138$  K.
- 1964 Little predicted rt superconducting polymer: not achieved yet!



**Figure 3.41** (a) Proposed structure of a room temperature polymeric superconductor by Little [12]. Side groups, designated R, are attached to a polyacetylene backbone. (b) Suggestion for R substituent. These side groups are resonating hybrids of the two extreme structures depicted.

# Ionic Conductivity vs. Electronic Conductivity

- Ionic conductivity give rise to the **time-dependent current**. Ions travelling through a sample under the influence of an applied E field will accumulates at the defects or at one of the solid electrode **reducing the ionic current to zero over a period**.

1. Presence of ionic conductivity is indicated when the **conductivity and permittivity** show the strong correlation as below. This is due to the rdxn of Coulomb forces btw ions in a high-permittivity medium

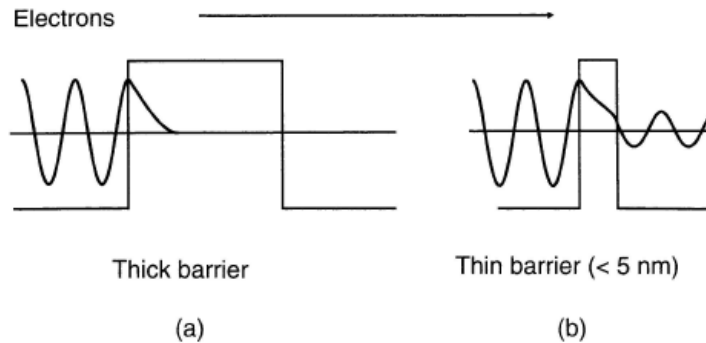
$$\log \sigma = -\frac{A}{\epsilon_s} + B \quad \text{where A and B are constants and } \epsilon_s \text{ is the static real part permittivity}$$

2. Mott and Gurney model applies when ionic conductivity exists.

$$J \propto \sinh \frac{eaE}{2k_B T} \quad \text{where a is the distance btw potential wells associated}$$

with the ionic movement

# Quantum Mechanical Tunneling



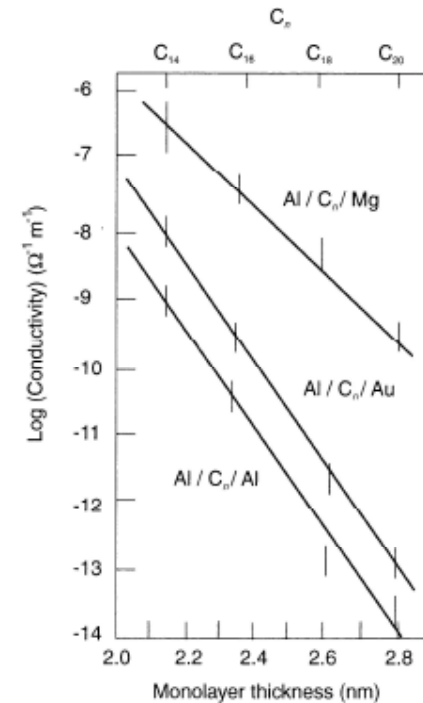
Tunneling current  $\sigma_t$  at low applied voltage

$$\sigma_t = A \exp(-Bd)$$

where  $d$  is thickness and  $A$  &  $B$  are constants

Tunneling current  $\sigma_t$  at higher applied voltage  
for symmetrical rectangular barrier

$$I = 2I_0 \left[ \frac{\pi C k T}{\sin(\pi C k T)} \right] \exp(-B V^2) \sinh\left(\frac{C V}{2}\right)$$



**Figure 3.43** Logarithm of conductivity versus monolayer thickness for different metal/monolayer/metal structures.  $C_n$  is the number of carbon atoms in the monolayer compound. Reprinted with permission from Polymeropoulos EE, *J. Appl. Phys.*, **48**, 'Electron tunnelling through fatty-acid monolayers', pp. 2404–2407, Copyright 1977, American Institute of Physics.

# Variable Range Hopping

- Conjugated polymers and molecular materials are more or less disordered thus the band tails are **localized** and there exists a mobility edge
- The electron motion in **localized states** is much smaller than in **extended states**.
- Disordered material- Mean free path is of the order of interatomic distance – diffusive transport ----mobility is expected to be less than  **$6 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$**  (using the Einstein relation btw  $\mu$  and  $D$ )
- Electron transport btw localized states: (1) thermally activated process, (2) tunneling process, (3) **Hopping**=thermally assisted tunneling

Variable range hopping model of Mott

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{\frac{1}{n}}\right]$$

where **n=4** for 3-D, n=3 for 2-D, n=2 for 1-D

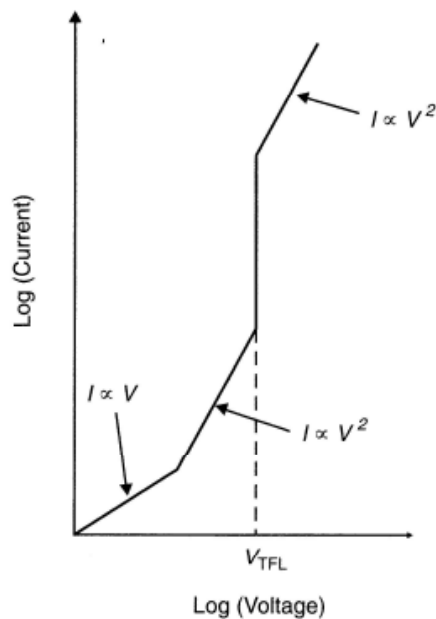
Avg hoping distance varies with  $T \Rightarrow$

Thus it is called 'variable range hopping'

# Space-Charge Injection

- When the electrical contacts are *Ohmic*,  $I$  is linear to  $V$  at low  $V$  region (volume conductivity dominates). However it becomes superlinear due to the injection of excess carriers and thus **space-charge limited** at higher  $V$ .

$$J \propto \frac{V^2}{d^3} \quad \text{SCLC model}$$



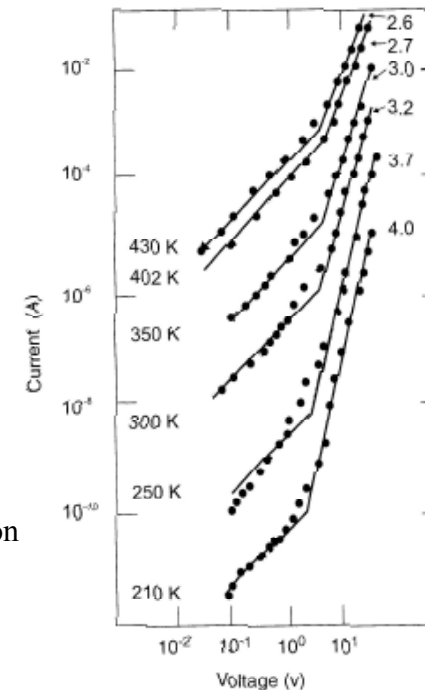
General equation of bulk SCLC

$$J \propto d \left( \frac{V}{d^2} \right)^m$$

where  $m=2$ : trap-free insulator

$m=3$ : double injection (e & h)

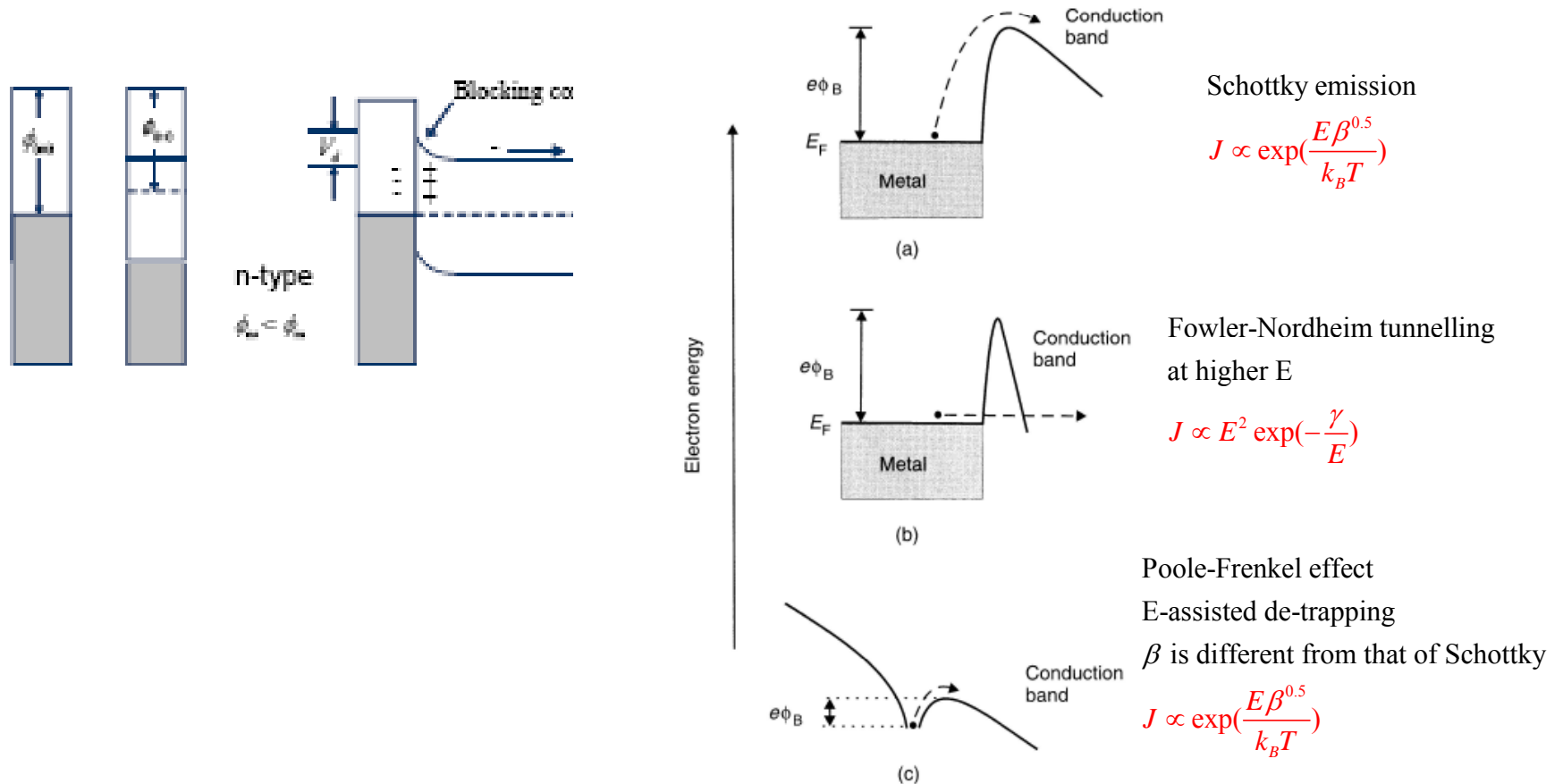
$m=1/2$ : recombinative space charge injection



**Figure 3.45** Current versus voltage characteristics of an Au/copper phthalocyanine/Au sandwich at different temperatures. The linear dependence of current on voltage at low bias is the result of Ohmic conductivity. The super-Ohmic regions at higher bias indicate space-charge limited conductivity. The value of  $m$  from Equation (3.73) is indicated for each curve. Reprinted from *Coordination Chemistry Reviews*, **156**, Gould RD, 'Structure and electrical conduction properties of phthalocyanine thin films', pp. 237–274, Copyright (1996), with permission from Elsevier.

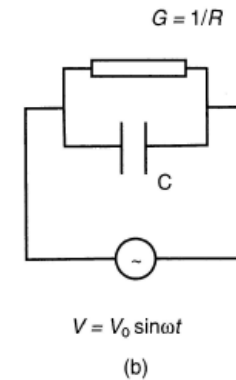
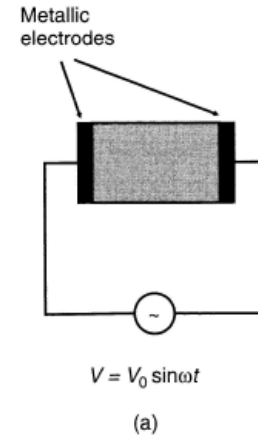
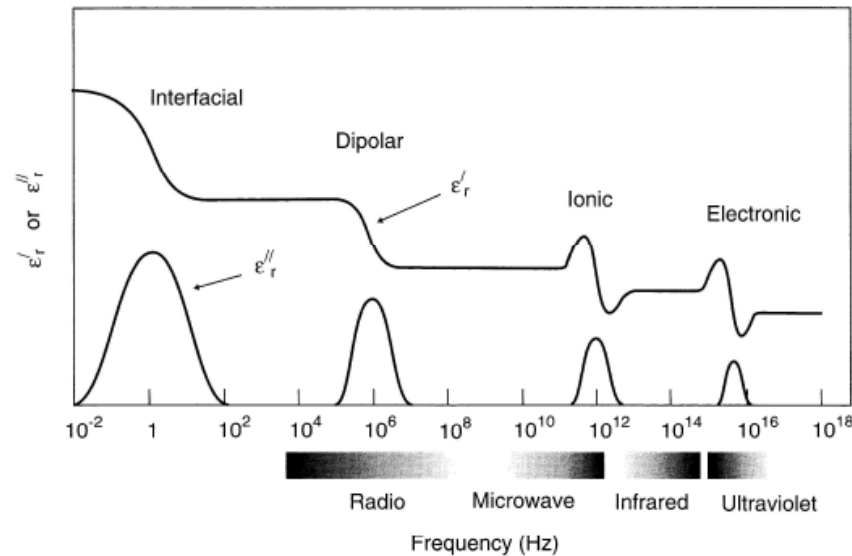
# Schottky and Poole-Frenkel Effects

Redistribution of charge in the interface region → 'band bending' or distortion



**Figure 3.46** (a) Schottky emission of an electron from the Fermi level  $E_F$  in a metal into the conduction band of a semiconductor (or insulator); (b) Fowler–Nordheim tunnelling; (c) Poole–Frenkel effect: the applied electric field lowers the barrier surrounding a trapped carrier and helps it to move into the conduction band.

# AC Conductivity: Complex Permittivity



AC conductivity comprises

both in-phase and  $90^\circ$  out-of-phase components

$$I = V(j\omega C + G) = V(j\omega \frac{A\epsilon_0\epsilon'_r}{d} + \frac{\omega A\epsilon_0\epsilon''_r}{d})$$

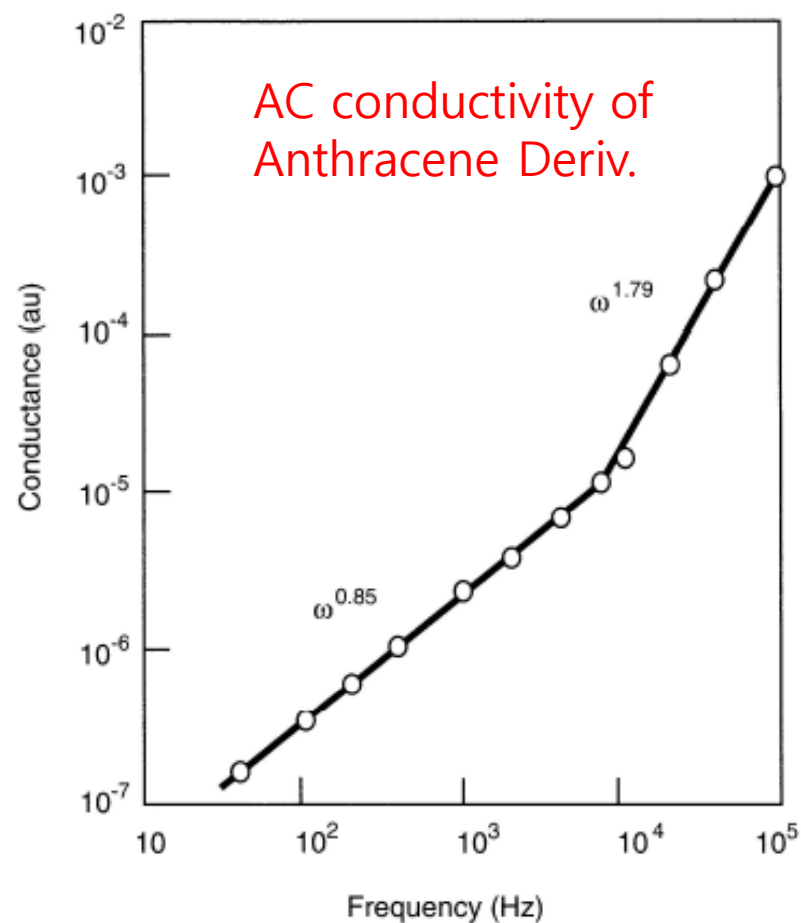
(where  $Y (=j\omega C + G)$  is **admittance**,  $Z (=1/Y)$  is **impedance**)

Thus

$$\sigma_{AC} = \omega \epsilon_0 \epsilon''_r \quad (\text{linear to } \omega \text{ when lossless, } \epsilon''_r = \text{const})$$

In reality, universal law for the dielectrics

$$\sigma_{AC} \propto \omega^n \quad (0.7 < n < 1); \text{ n value doubles at } f > 10^4 \text{ Hz due to the contact resistance effect}$$



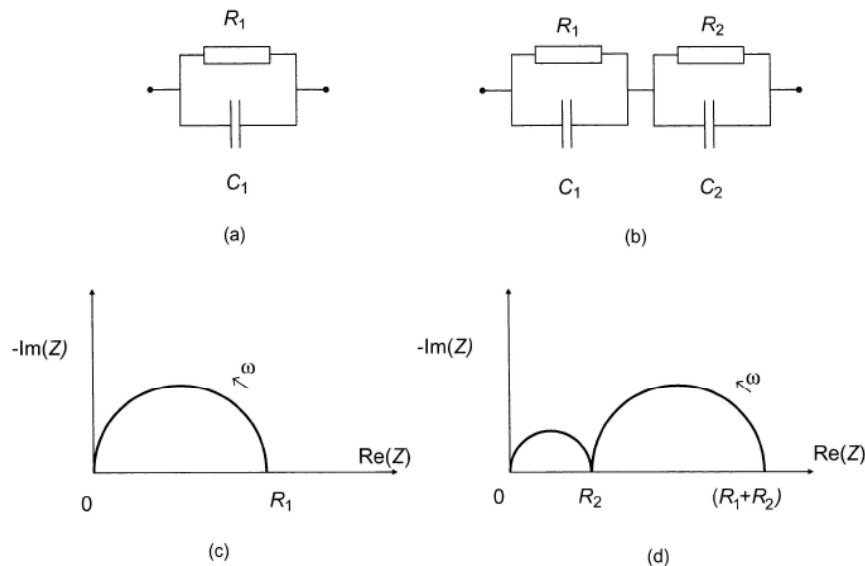
**Figure 3.49** AC conductivity data showing the variation in conductance with frequency for a thin film of an anthracene derivative. Reprinted from *Thin Solid Films*, **68**, Roberts CG, McGinnity JM, Barlow WA, Vincent PS, 'Ac and dc conduction in lightly substituted anthracene Langmuir films', pp. 223–232. Copyright (1980), with permission from Elsevier.

# Impedance Spectroscopy

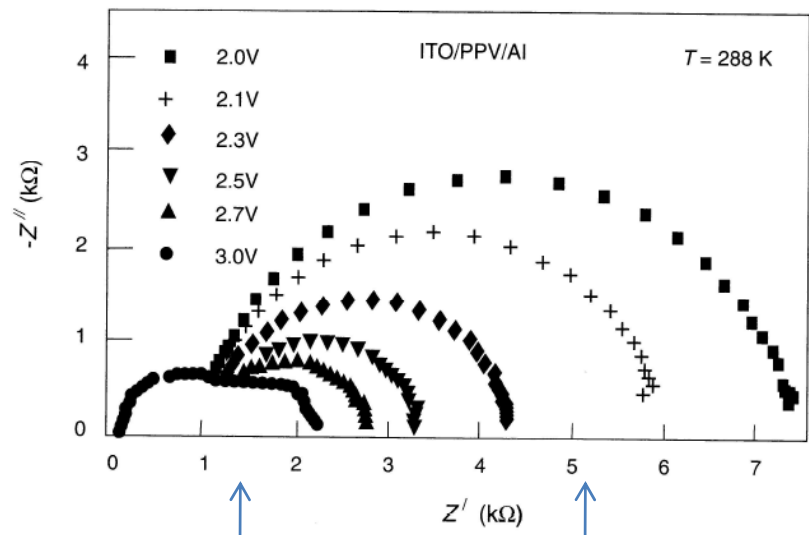
*Debye Equation*

$$\varepsilon'_r = \varepsilon_s + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2} \text{ and } \varepsilon''_r = \frac{(\varepsilon_s - \varepsilon_\infty) \omega \tau}{1 + \omega^2 \tau^2}$$

where  $\varepsilon_s$  and  $\varepsilon_\infty$  are the low- and high-frequency values of the real part of the relative permittivity, respectively, and  $\tau$  is a characteristic time constant of the system



Cole-Cole Diagram for ITO/PPV/Al



bulk

Schottky barrier