

The QM model of Solids

- Thermocouples
- Thermionic emission
- Phonons

Fig 4.29

Seebeck Effect/Thermocouples

- An effect that is best understood using the Fermi energy and electron distribution is the Seebeck effect which is exploited in thermocouples
- Heat one end of rod the “hot electrons” will diffuse to the cold side producing a charge distribution as the “solid” at the hot end is now not charge neutral.
- Two few electrons.
- A metal with have Seebeck coefficient that quantifies this effect.
- Not simple because the electron MFP is fct of temperature.
- In the hot end of the rod the electrons can get “trapped” by the higher phonon concentration (more scattering! Smaller MFP)
- The Coefficient can be negative!
- Use for thermocouples by making a ring of two different materials.

Fig 4.29

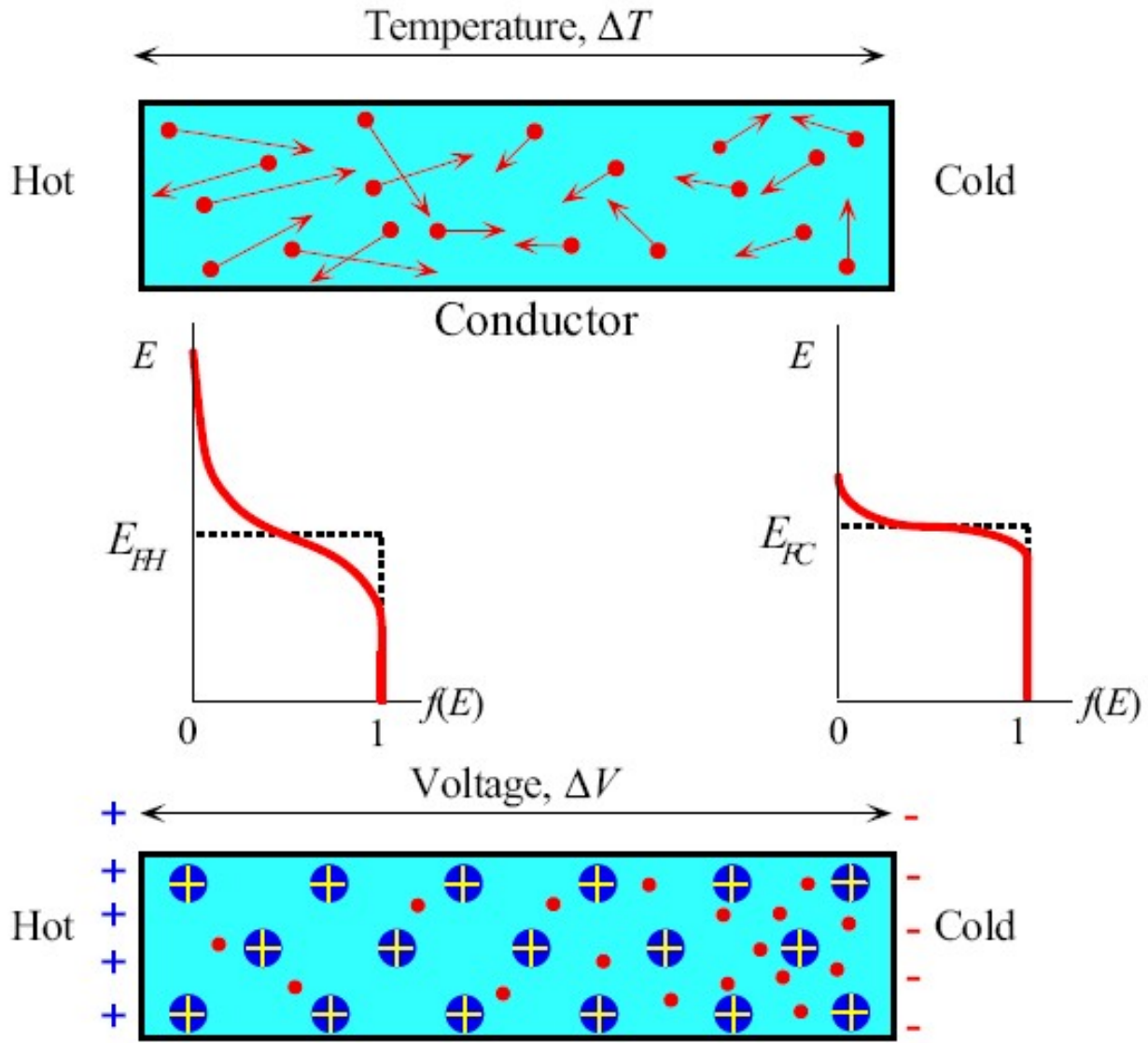


Fig 4.30

Seebeck Effect

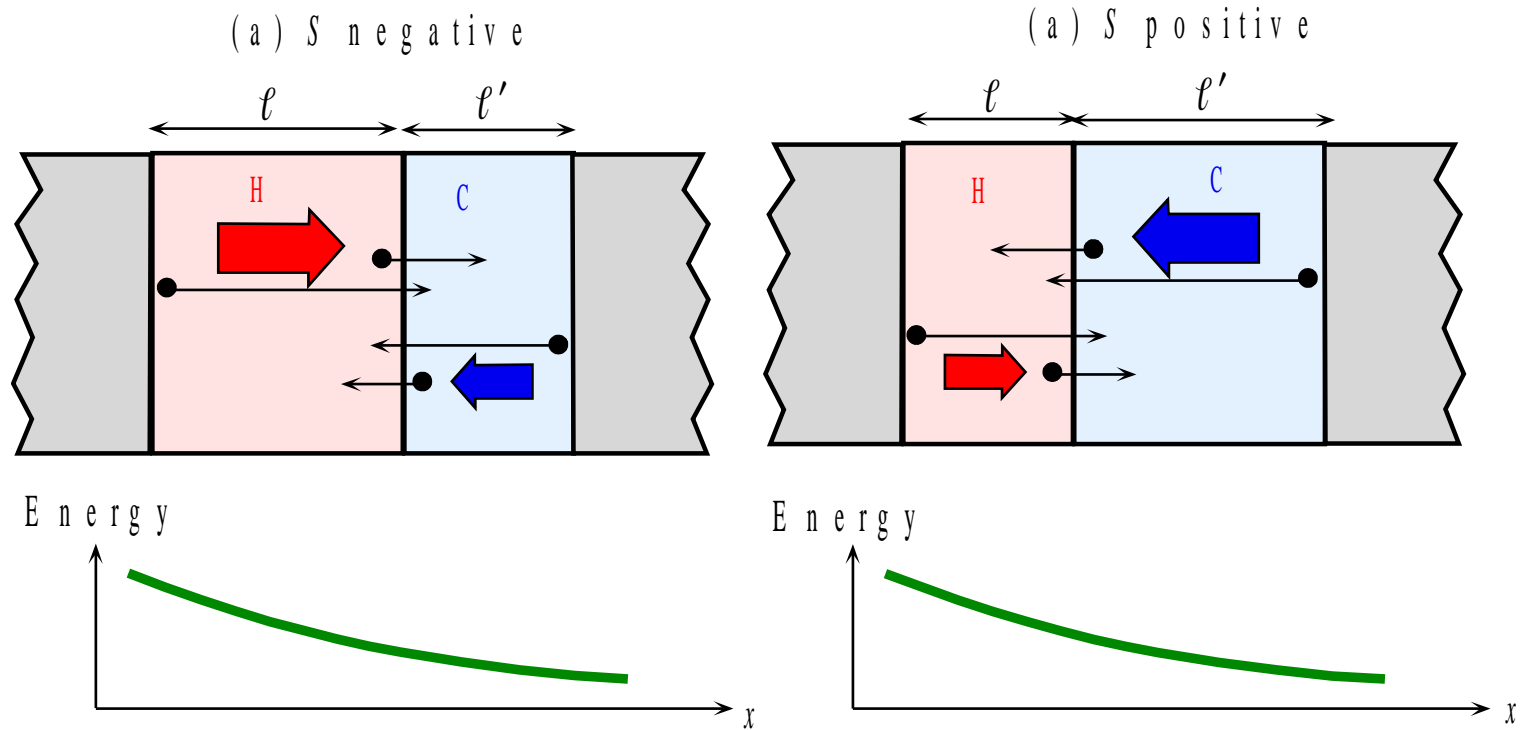
Seebeck effect (thermoelectric power)

is the built-in potential difference ΔV across a material due to a temperature difference ΔT across it.

$$S = \frac{\Delta V}{\Delta T}$$

Sign of S

is the potential of the cold side with respect to the hot side; negative if electrons have accumulated in the cold side.



Consider two neighboring regions H (hot) and C (cold) with widths corresponding to the mean free paths ℓ and ℓ' in H and C. Half the electrons in H would be moving in $+x$ direction and the other half in $-x$ direction. Half of the electrons in H therefore cross into C, and half in C cross into H.

Fig 4.31

Seebeck coefficient for metals

$$S \approx -\frac{\pi^2 k^2 T}{3eE_{FO}} x$$

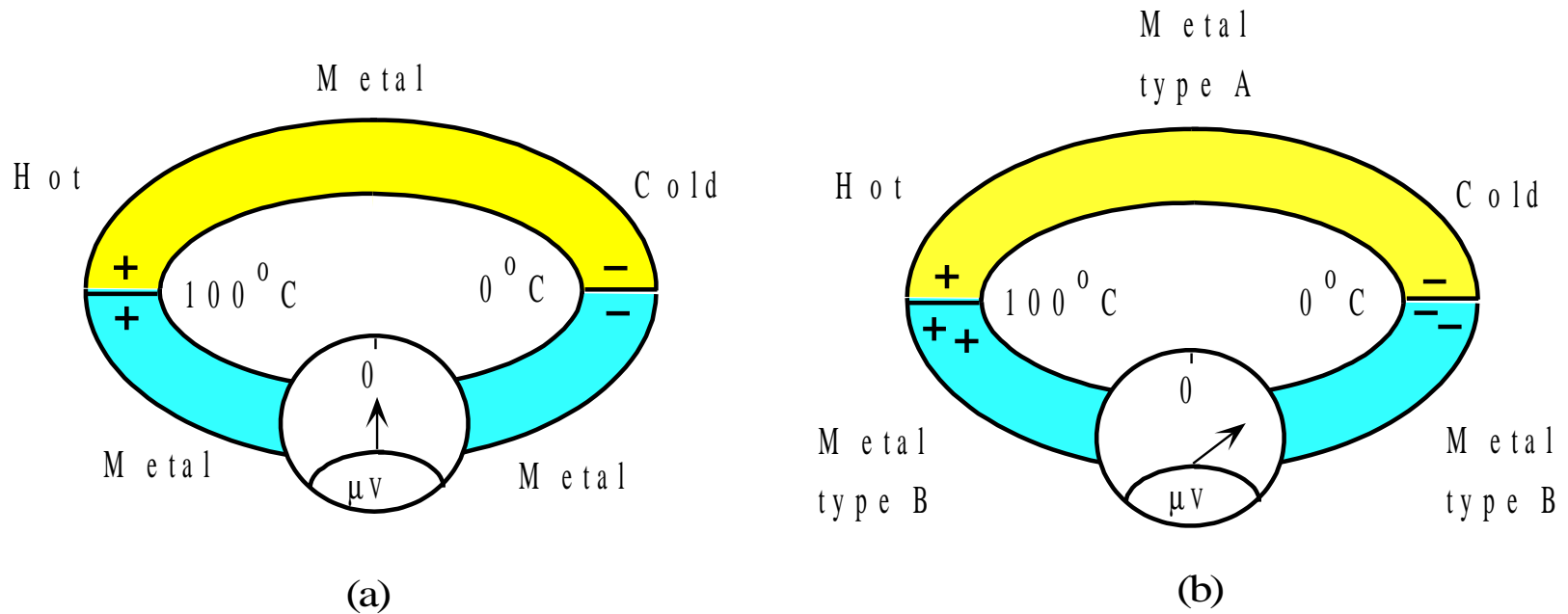
Mott and Jones thermoelectric power equation

x = a numerical constant that takes into account how various charge transport parameters, such as the mean free path ℓ , depend on the electron energy.

- x values are tabulated in Table 4.3
- Parameter x is very material dependent

Table 4.3 Seebeck coefficients of selected metals (from various sources)

Metal	S at 0 °C ($\mu\text{V K}^{-1}$)	S at 27 °C ($\mu\text{V K}^{-1}$)	E_F (eV)	x
Al	-1.6	-1.8	11.6	2.78
Au	+1.79	+1.94	5.5	-1.48
Cu	+1.70	+1.84	7.0	-1.79
K		-12.5	2.0	3.8
Li	+14		4.7	-9.7
Mg	-1.3		7.1	1.38
Na		-5	3.1	2.2
Pd	-9.00	-9.99		
Pt	-4.45	-5.28		



(a) If same metal wires are used to measure the Seebeck voltage across the metal rod, then the net emf is zero. (b) The thermocouple from two different metals, type A and B. The cold end is maintained at 0°C which is the reference temperature. The other junction is used to sense the temperature. In this example it is heated to 100°C .

Fig 4.32

Thermocouple

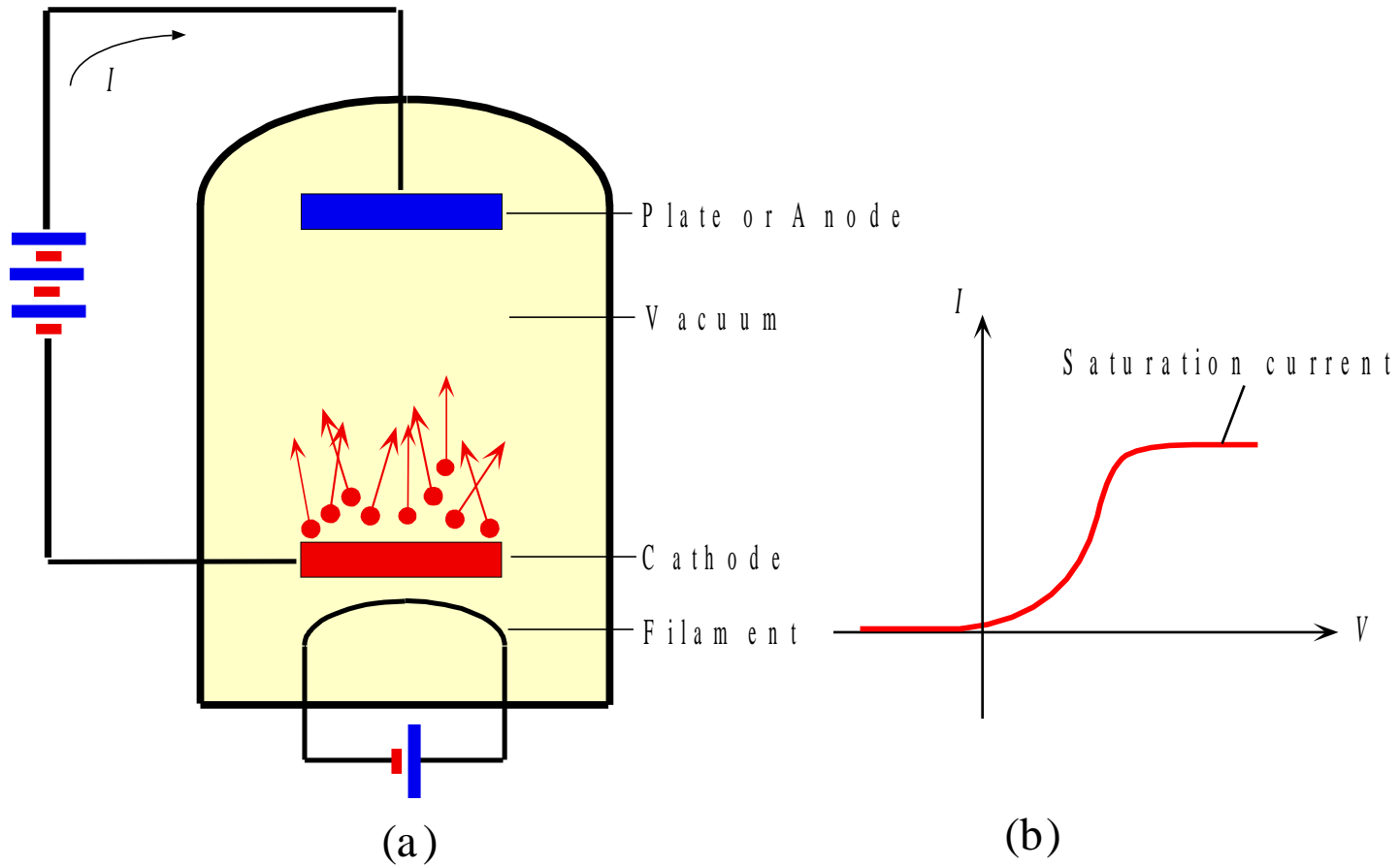
We can only measure differences between thermoelectric powers of materials.

When two different metals A and B are connected to make a **thermocouple**, then the net EMF is the voltage difference between the two elements.

$$V_{AB} = \int_{T_0}^T (S_A - S_B) dT = \int_{T_0}^T S_{AB} dT$$

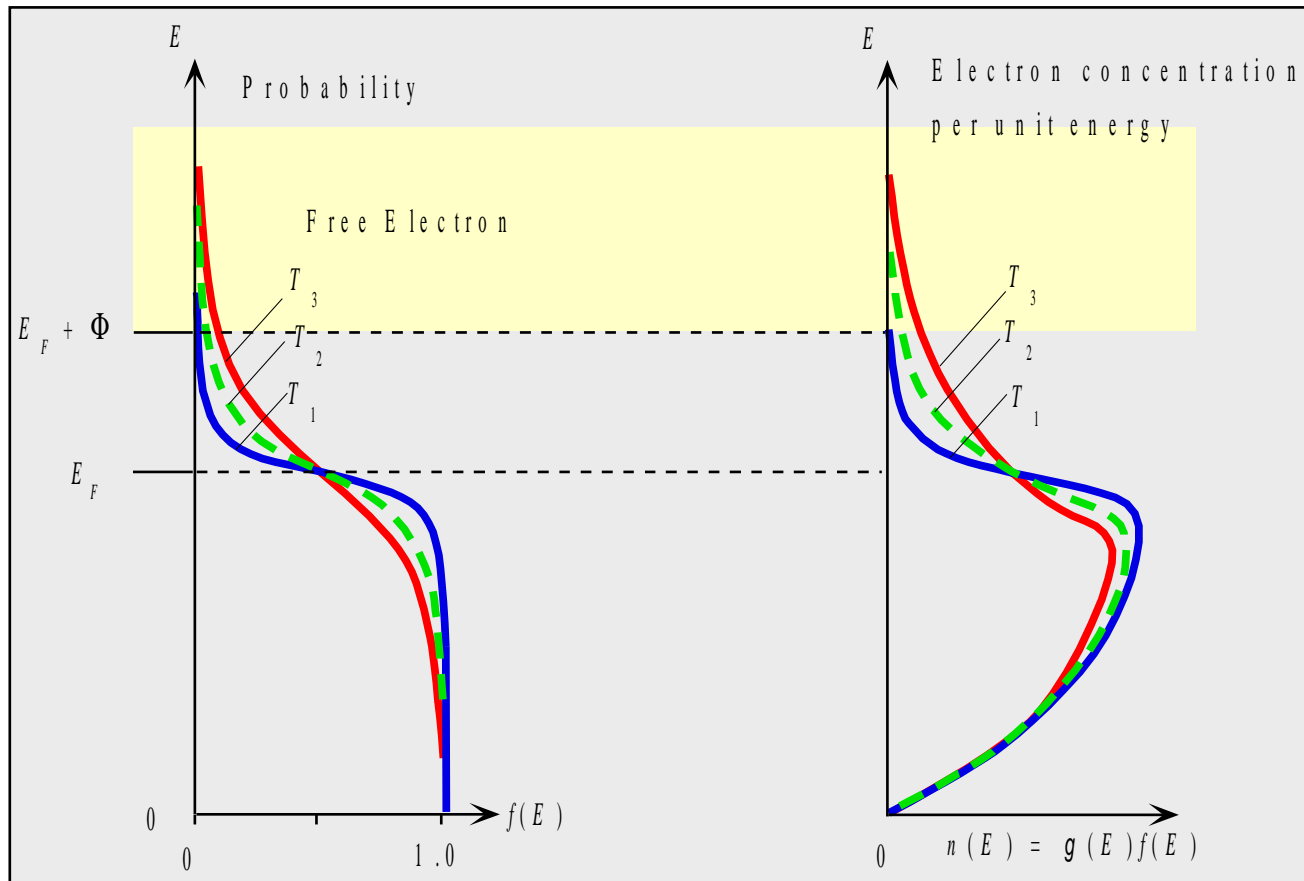
Thermionic emission

- Vacuum tubes were based on thermionic emission (ie temperature activated electron emission) from a surface.
- Now used in modern integrated MEMs structures
- If for electron at the surface $E > E_F + \phi$ it will leave the surface.
- So hot electrons can be emitted
- As Maxwellian tail is appropriate we get an $e^{-E/kt}$ type relationship for current
- Can modulate the current by changing the barrier height with an applied voltage
- Non-linear device I-V curve exponential.



(a) Thermionic electron emission in a vacuum tube.
 (b) Current-voltage characteristics of a vacuum diode.

Fig 4.34



Fermi Dirac function, $f(E)$ and the energy density of electrons, $n(E)$, (electrons per unit energy and per unit volume) at three different temperatures. The electron concentration extends more and more to higher energies as the temperature increases. Electrons with energies in excess of $E_F + \Phi$ can leave the metal (thermionic emission).

Fig 4.35

Thermionic Emission

Richardson-Dushman thermionic emission equation

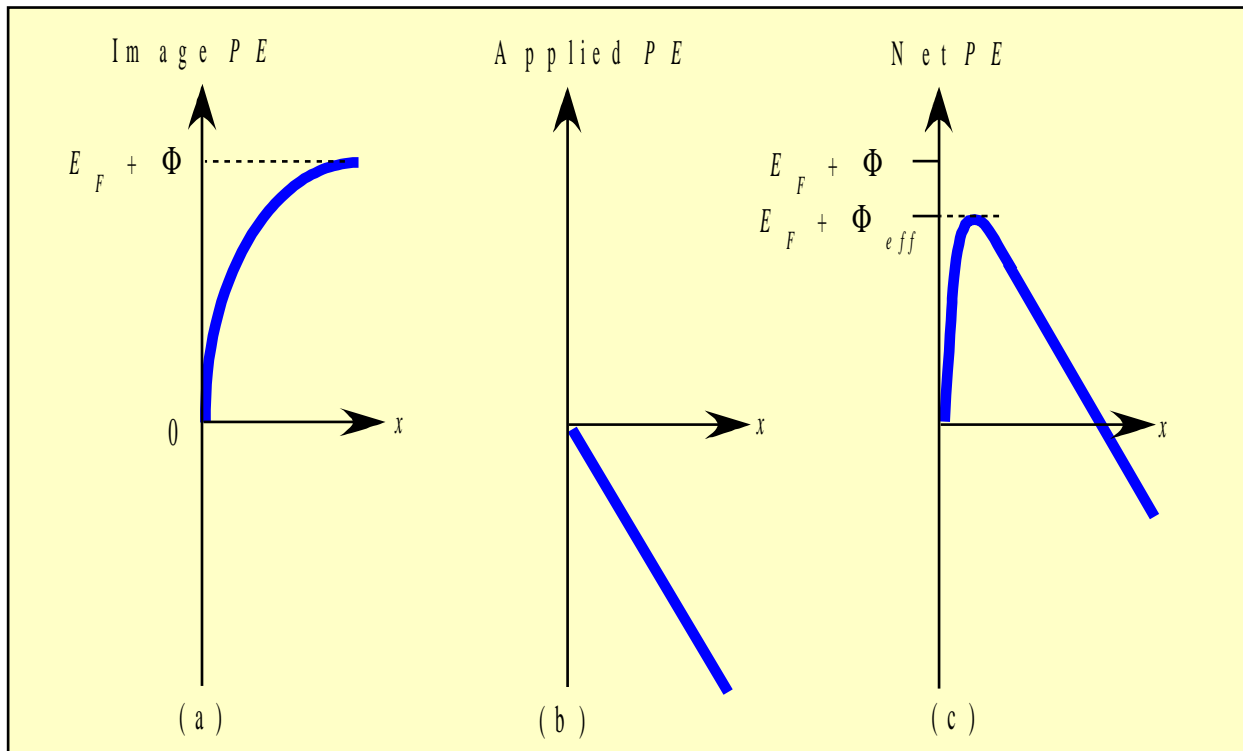
$$J = B_o T^2 \exp\left(-\frac{\Phi}{kT}\right)$$

$$B_o = 4\pi e m_e k^2 / h^3 = 120 \times 10^6 \text{ A m}^{-2} \text{ K}^{-2}$$

Richardson-Dushman constant

$$J = B_e T^2 \exp\left(-\frac{\Phi}{kT}\right)$$

where B_e = effective emission constant due to electron reflection at the surface (impedance mismatch)



- (a) *PE* of the electron near the surface of a conductor,
 (b) Electron *PE* due to an applied field e.g. between cathode and anode
 (c) The overall *PE* is the sum.

Fig 4.36

Schottky effect

When a positive voltage is applied to the anode with respect to the cathode, the electric field at the cathode helps the thermionic emission process by lowering the PE barrier Φ by an amount $\beta_s \mathcal{E}^{1/2}$. The current density in field assisted thermionic emission is

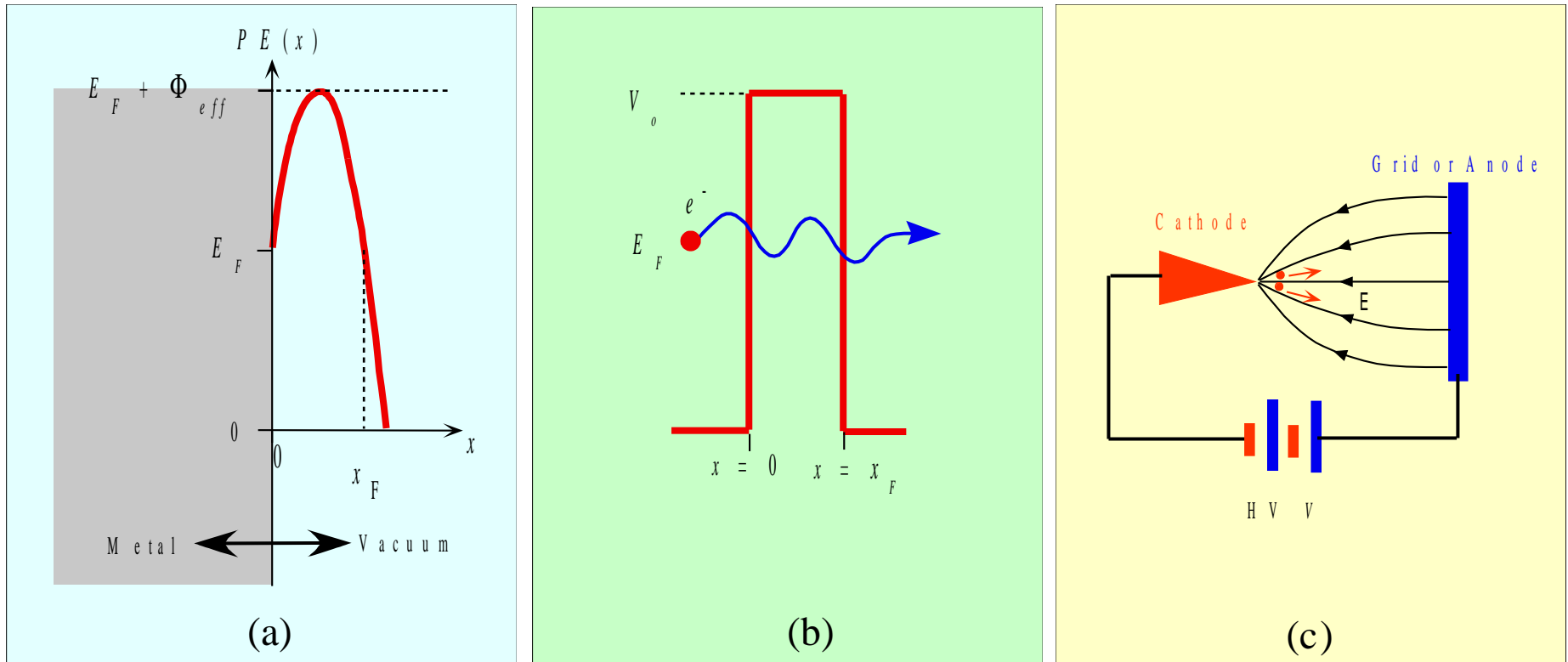
$$J = B_e T^2 \exp\left(-\frac{\Phi - \beta_s \mathcal{E}^{1/2}}{kT}\right)$$

Metal's work function Schottky coefficient

Field Assisted (tunneling)

- If the field is very large (sharp points)
- The barrier becomes very thin and QM tunneling can occur
- Not temperature dependent
- Get Exp. Relationship with applied field $\sim \exp(-E_c/E)$
- Used in MEMS structures for display technology (many many very small CRT's)

Field assisted emission is field assisted tunneling from the cathode



(a) Field emission is the tunneling of an electron at an energy E_F through the narrow PE barrier induced by a large applied field. (b) For simplicity we take the barrier to be rectangular. (c) A sharp point cathode has the maximum field at the tip where the field-emission of electrons occurs.

Fig 4.37

Field-assisted Tunneling

Field-assisted tunneling probability

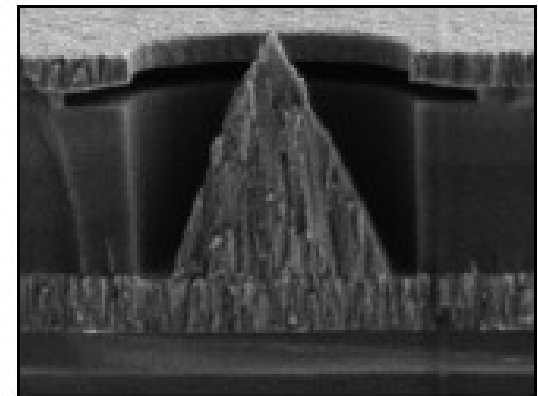
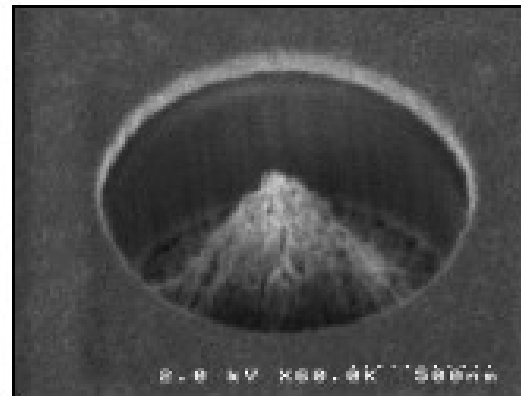
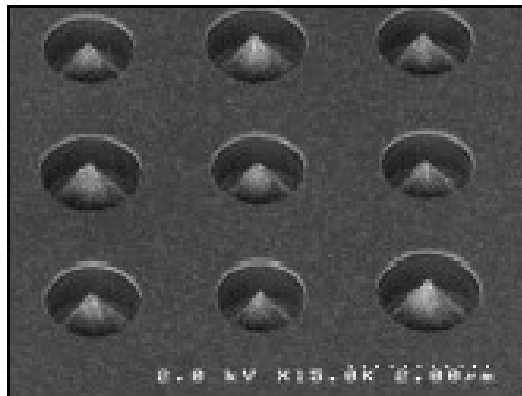
Effective work function due to the Schottky effect

$$p \approx \exp \left[- \frac{2(2m_e \Phi_{\text{eff}})^{1/2} \Phi}{e \mathcal{E}} \right]$$

Field-assisted tunneling: the Fowler-Nordheim equation

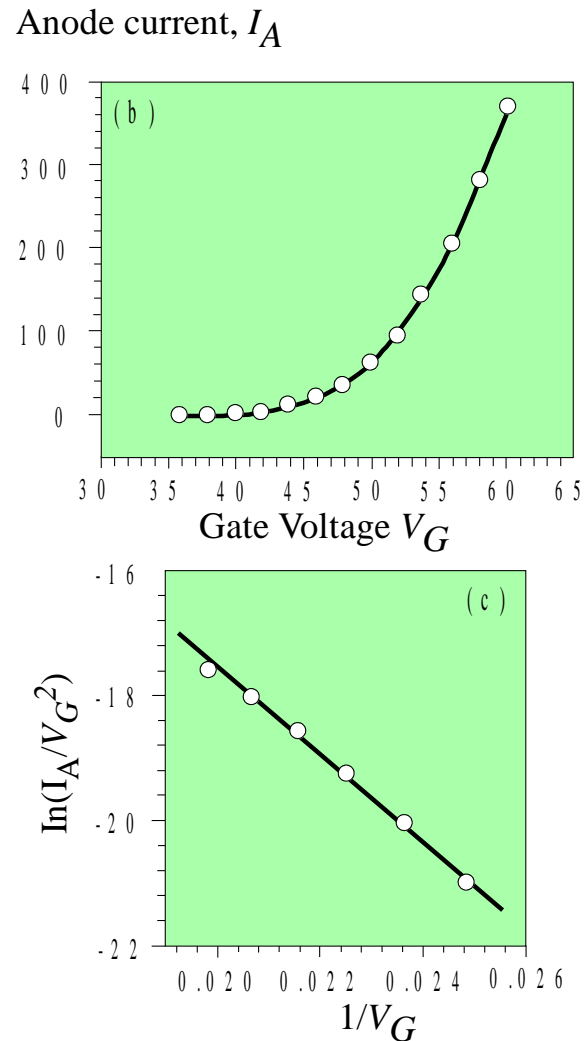
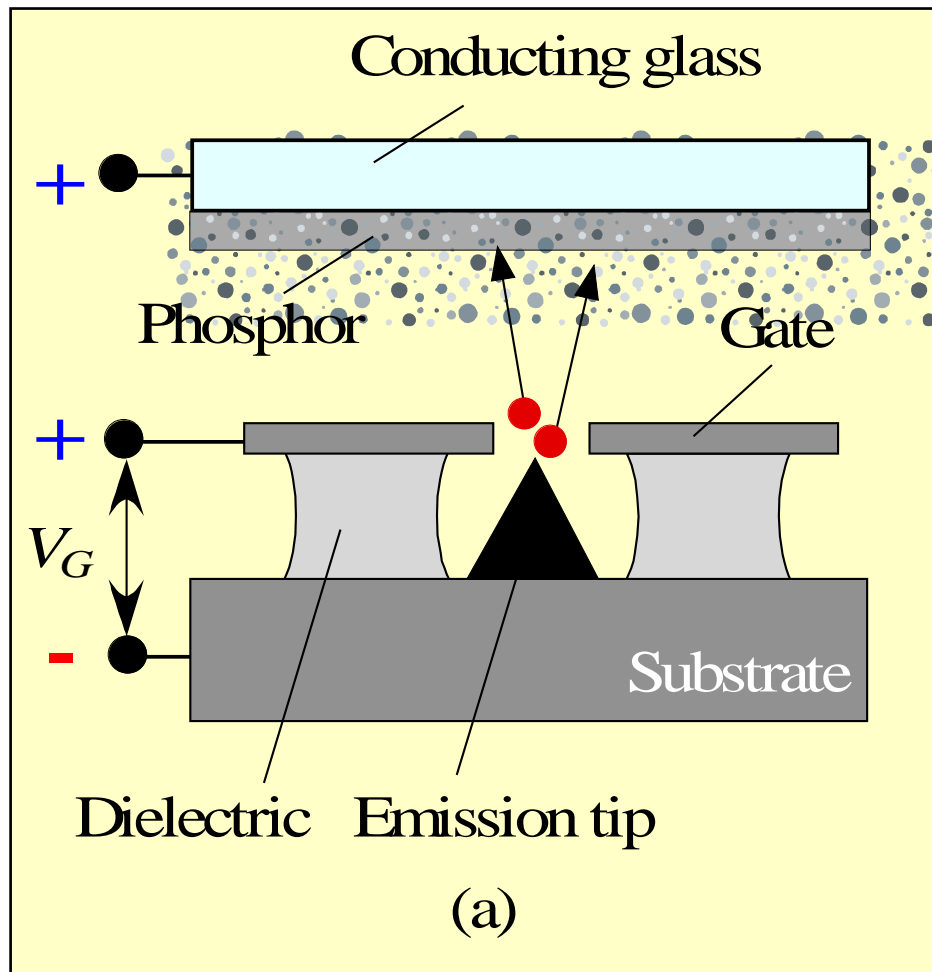
$$J_{\text{field-emission}} \approx C \mathcal{E}^2 \exp \left(- \frac{\mathcal{E}_c}{\mathcal{E}} \right)$$

Applied field at the cathode



Left: A scanning electron microscope image of an array of electron field emitters (icebergs). Center: One iceberg. Right: A cross section of a field emitter. Each iceberg is a source of electron emission arising from Fowler–Nordheim field emission; for further information see B. Chalamala, et al., *IEEE Spectrum*, April 1998, pp. 42–51.

| SOURCE: Courtesy of Dr. Babu Chalamala, Flat Panel Display Division, Motorola.

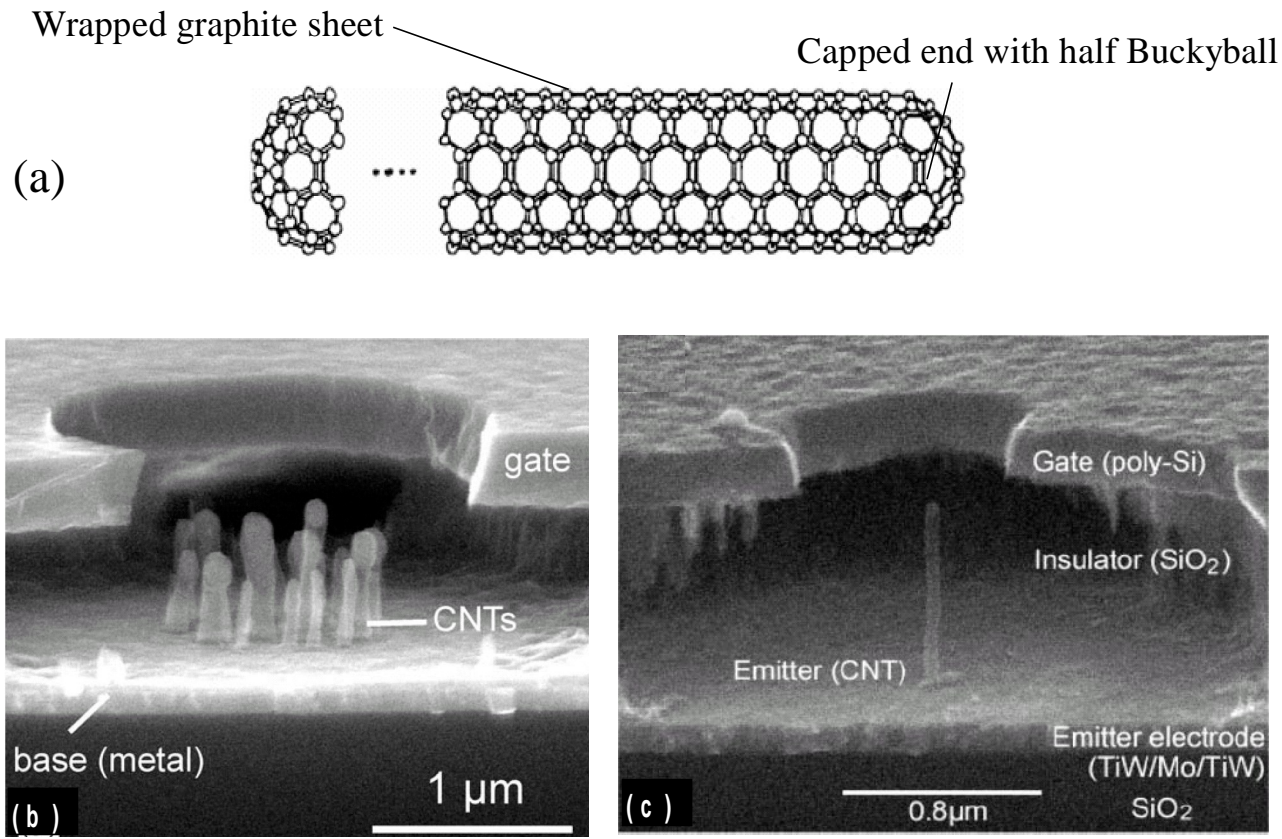


(a) Spindt type cathode and the basic structure of one of the pixels in the FED. (b) Emission (anode) current vs, gate voltage (c) Fowler-Nordheim plot that confirms field emission.

Fig 4.38

CNT (Carbon NanoTube)

A carbon nanotube (CNT) is a very thin filament-like carbon molecule whose diameter is in the nanometer range but whose length can be quite long, e.g., 10-100 microns, depending on how it is grown or prepared.



(a) A carbon nanotube (CNT) is a whisker-like very thin and long carbon molecule with rounded ends; almost a perfect shape as an electron field-emitter. **(b)** Multiple CNTs as electron emitters. **(c)** A single CNT as an emitter.

[SOURCE: Courtesy of Professor W.I. Milne, University of Cambridge; G. Pirio *et al*, *Nanotechnology*, **13**, 1, 2002.]

Fig 4.39

Phonons

- A number of times I have mentioned phonons. A phonon is the QM way of describing heat energy in the lattice.
- Modeling the crystal a “balls on springs” is essentially using a simple harmonic oscillator model of the solid.
- The simplest way of understanding phonons is to use QM simple harmonic oscillator rather than a classical one.
- Parabolic PE in the SCE.
 - Quantization of the E and p arises
 - E separated by $\hbar\omega$
 - Zero point energy

Fig 4.39

Quantum Harmonic Oscillator

Harmonic potential energy

$$V(x) = \frac{1}{2} \overset{\text{Constant}}{\beta} x^2$$

Schrodinger equation for the harmonic oscillator

$$\frac{d^2\psi}{dx^2} + \frac{2M}{\hbar^2} \left(E - \frac{1}{2} \beta x^2 \right) \psi = 0$$

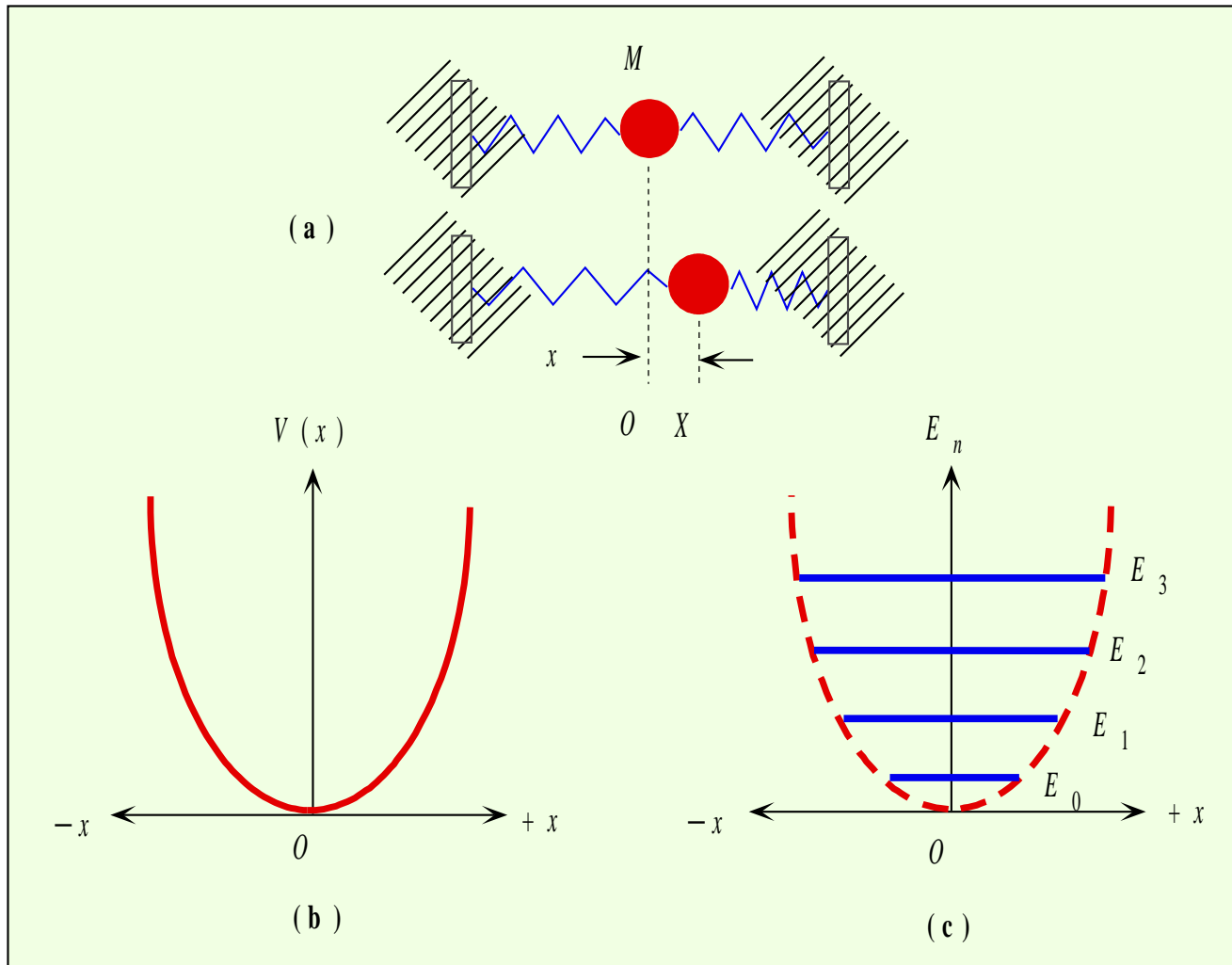
Energy of the harmonic oscillator

$$E_n = \left(n + \frac{1}{2} \right) \omega$$

Angular vibrational frequency of the oscillator.

$$\omega = (\beta/M)^{1/2}$$

Quantum number = 0, 1, 2, ...



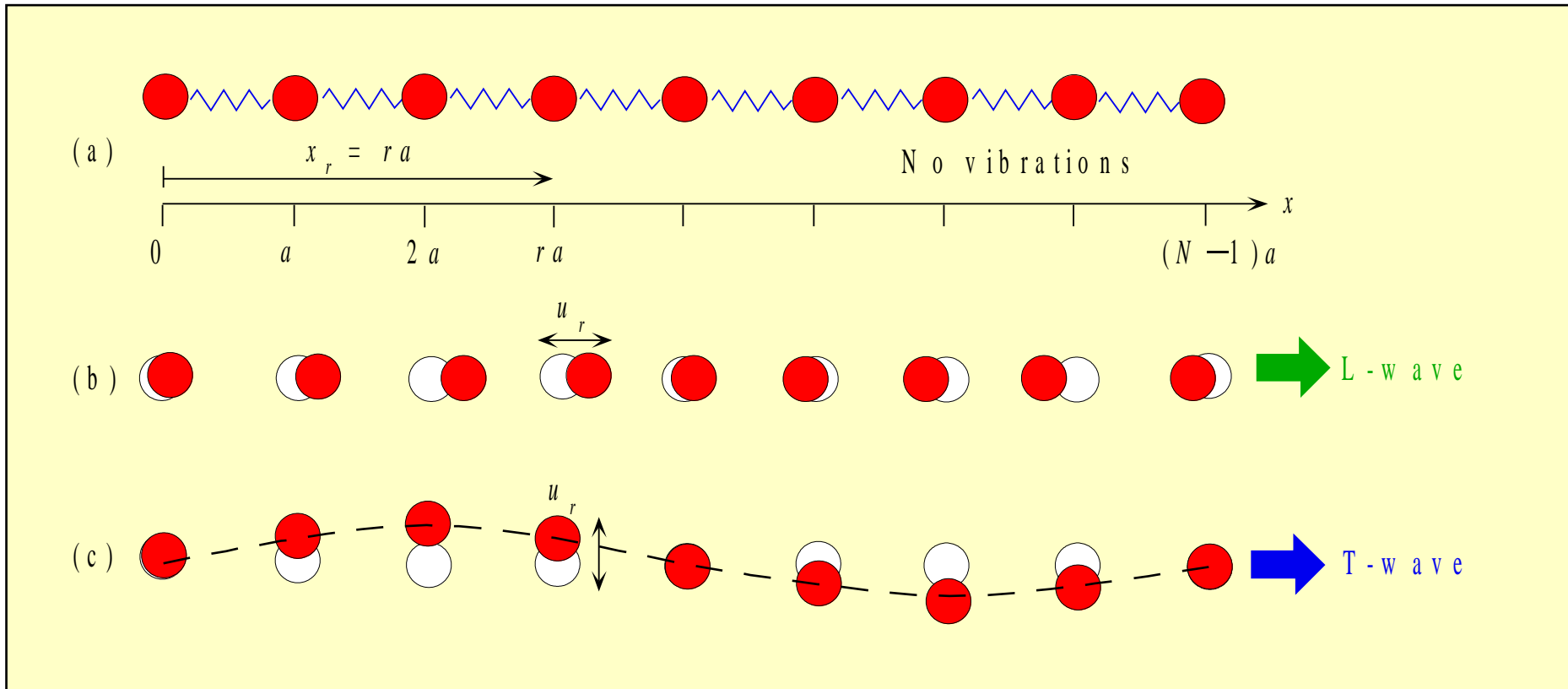
(a) Harmonic vibrations of an atom about its equilibrium position assuming its neighbors are fixed. (b) The PE curve $V(x)$ vs. displacement from equilibrium, x . (c) The energy is quantized.

Fig 4.40

Types of phonons

- Two types of Phonons: quantized vibrational state of energy
 - Acoustic – vibrations of acoustic frequencies (heat)
 - Longitudinal
 - Transverse
 - Optical – vibrations at optical frequencies (not in book)
 - Only in materials with two atoms/unit cell
 - Very high frequency – excited by optical signals
 - Physics very similar to electrons in lattice (periodic structure)
 - Bosons (each state can have many phonons)
 - Cut off frequency no phonons with $\omega > 2(\beta/M)^{1/2}$

Fig 4.40



(a) A chain of N atoms through a crystal in the absence of vibrations. (b) Coupled atomic vibrations generate a traveling longitudinal (L) wave along x . Atomic displacements (u_r) are parallel to x . (c) A transverse (T) wave traveling along x . Atomic displacements (u_r) are perpendicular to the x -axis. b and c are snapshots at one instant.

Fig 4.41

Lattice Waves: Phonons

Traveling-wave-type lattice vibrations along x

$$u_r = A \exp\left[j \left(\underset{\uparrow}{Kx_r} - \underset{\uparrow}{\omega t} \right) \right]$$

Phonon Energy

Phonon wavevector

Phonon frequency

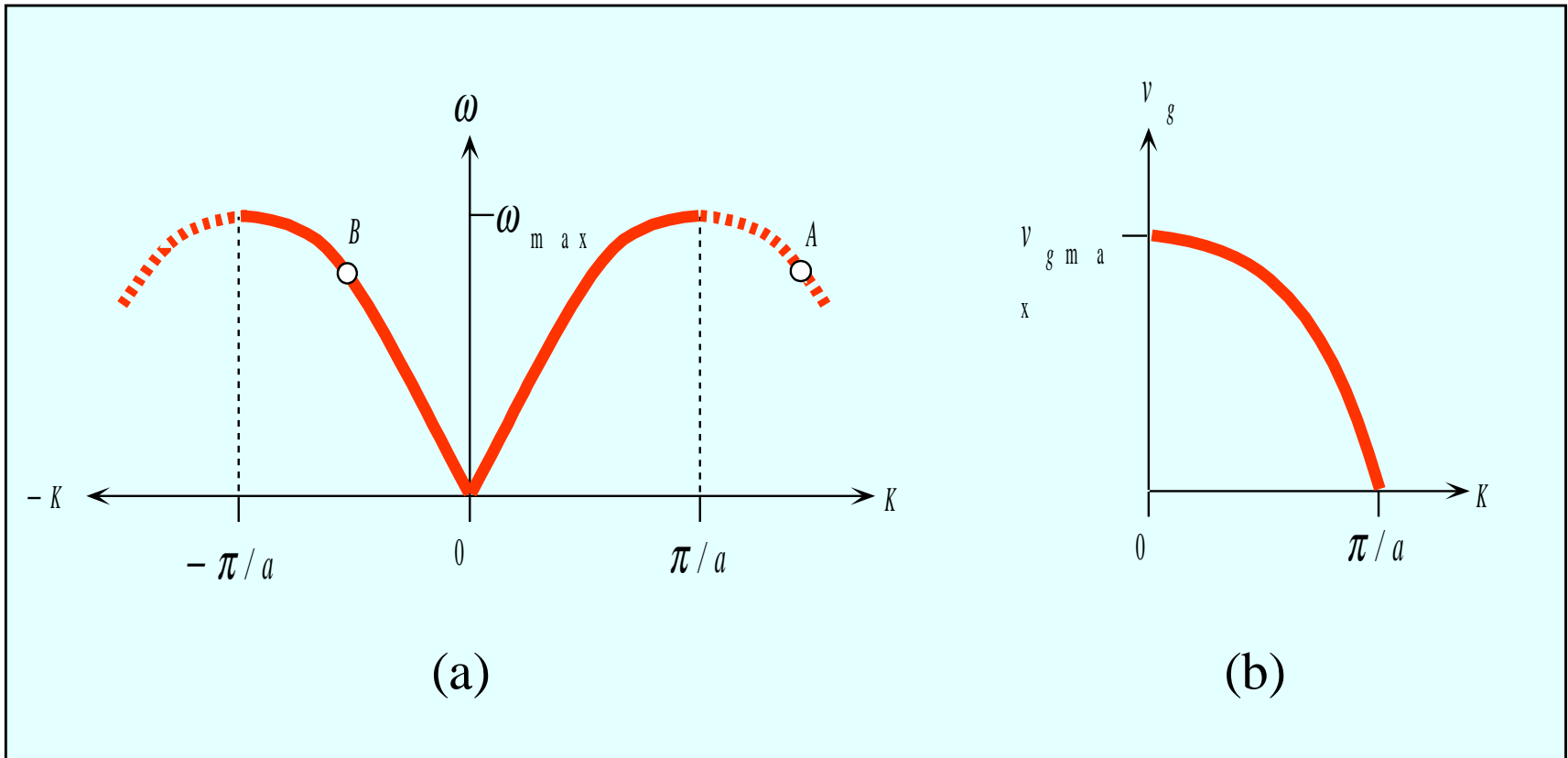
$$E_{\text{phonon}} = \hbar \omega = h \nu$$

Phonon Momentum

$$P_{\text{phonon}} = \hbar K$$

Dispersion Relation

$$\omega = 2 \left(\frac{\beta}{M} \right)^{1/2} \left| \sin \left(\frac{1}{2} Ka \right) \right|$$



(a) Frequency ω vs. wavevector K relationship for lattice

(b) Group velocity v_g vs. wavevector K .

- **Omega max is largest freq. In system**

Fig 4.42

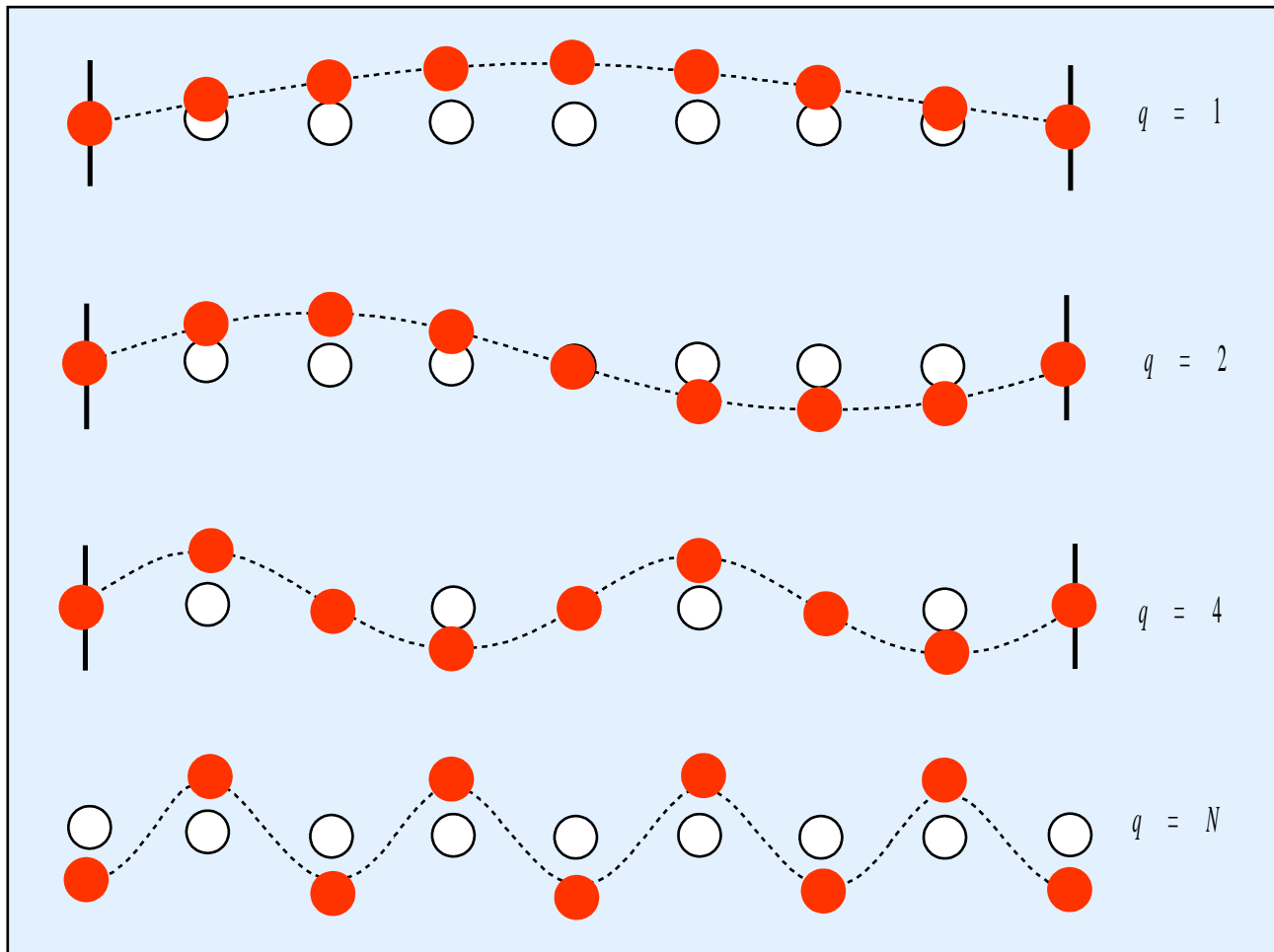
Group Velocity

The velocity at which traveling waves carry energy

$$v_g = \frac{d\omega}{dk} = \left(\frac{\beta}{M} \right)^{1/2} a \cos\left(\frac{1}{2} Ka \right)$$

$$v_g \approx \left(\frac{Y}{\rho} \right)^{1/2}$$

Y = elastic modulus (Example 1.5), ρ = density



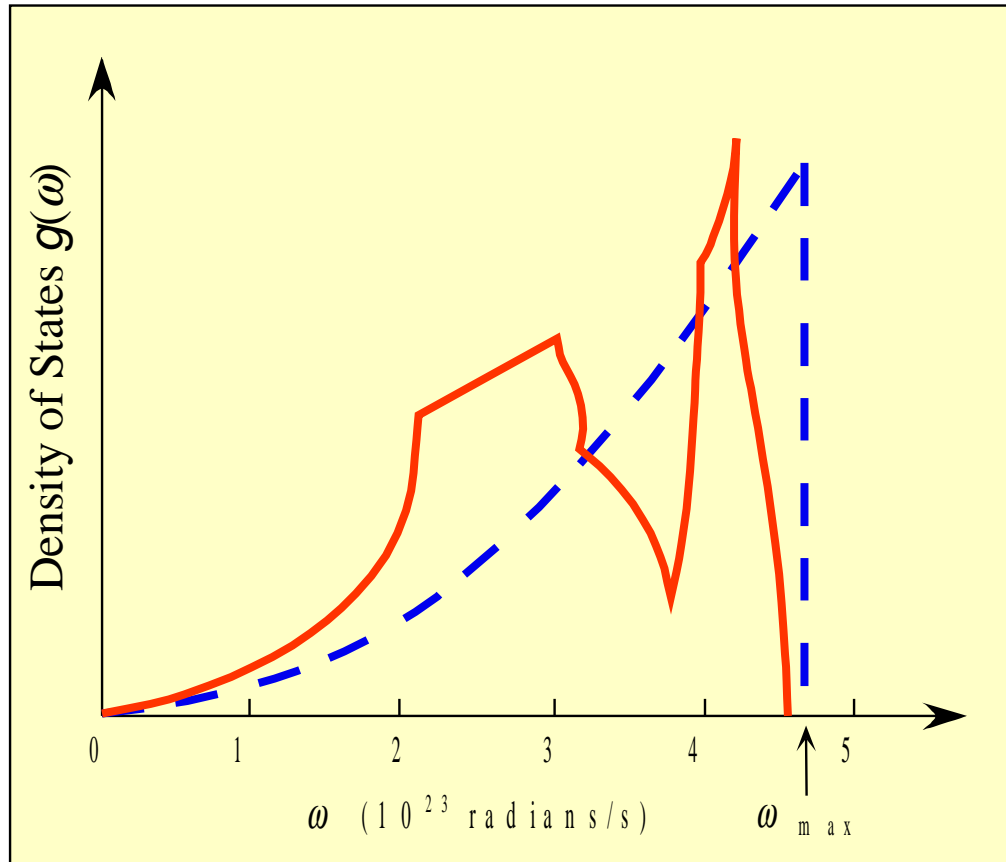
Four examples of standing waves in a linear crystal corresponding to $q = 1, 2$ and 4 . q is maximum when alternating atoms are vibrating in opposite directions. A portion from a very long is crystal shown.

Fig 4.43

Debye Temperature

- As the materials temperature is increase more phonon frequencies are excited.
- At the Debye temperature we have all frequencies present in the material.
- Increasing beyond this creates more phonons, not higher frequencies.
- By using a density of states fct $g(E)$ and average energy of the phonons we can obtain the Debye temperature and the heat capacity.
- Classical heat capacity is for materials above the Debye temperature when all modes are excited.

Fig 4.43



Density of states for phonons in copper. The solid curve is deduced from experiments on neutron scattering . The broken curve is the three-dimensional Debye approximation, scaled so that the areas under the two curves are the same. This requires that $\omega_{\max} = 4.5 \times 10^{13}$ radians s^{-1} , or a Debye characteristic temperature $T_D = 344$ K.

Fig 4.44

Debye frequency and temperature

Debye frequency: maximum vibration (angular) frequency in the crystal

$$\omega_{\max} \approx v \left(6\pi^2 N_A / V \right)^{1/3}$$

Avogadro's number

Mean velocity of lattice waves

Crystal volume

Debye temperature: all vibrations are fully excited up to ω_{\max}

$$T_D = \frac{\omega_{\max}}{k}$$

Debye heat capacity

Heat capacity per
mole ↓

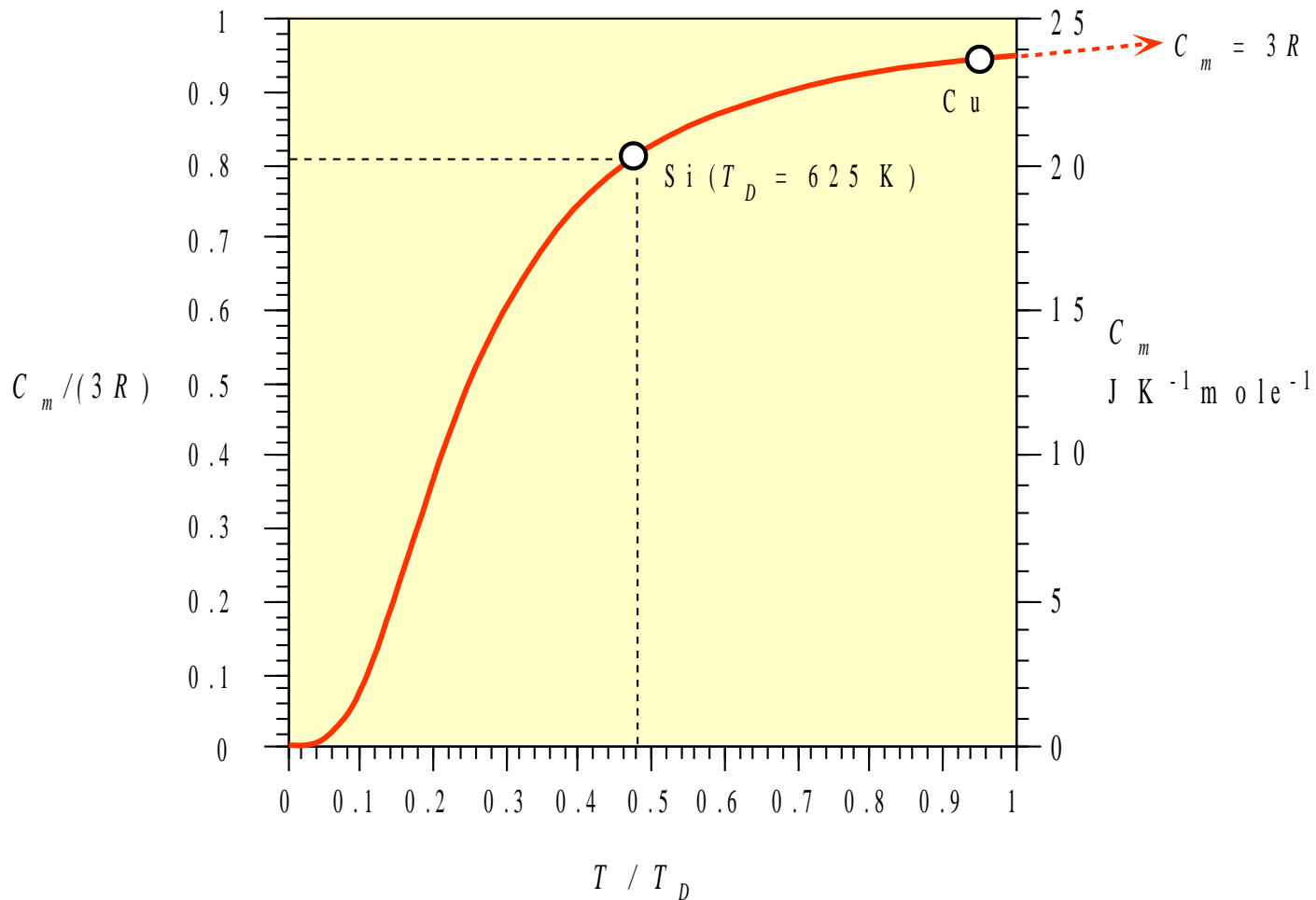
$$C_m \approx 9R \left(\frac{T}{T_D} \right)^3 \int_0^{T=T_D} \frac{x^4 e^x dx}{(e^x - 1)^2}$$

High temperatures

$$C_m \approx 3R$$

Low temperatures

$$C_m \propto \left(\frac{T}{T_D} \right)^3$$



Debye constant-volume molar heat capacity curve. The dependence of the molar heat capacity C_m on temperature with respect to the Debye temperature: C_m vs. T/T_D . For Si, $T_D = 625$ K so that at room temperature (300 K), $T/T_D = 0.48$ and C_m is only $0.81(3R)$.

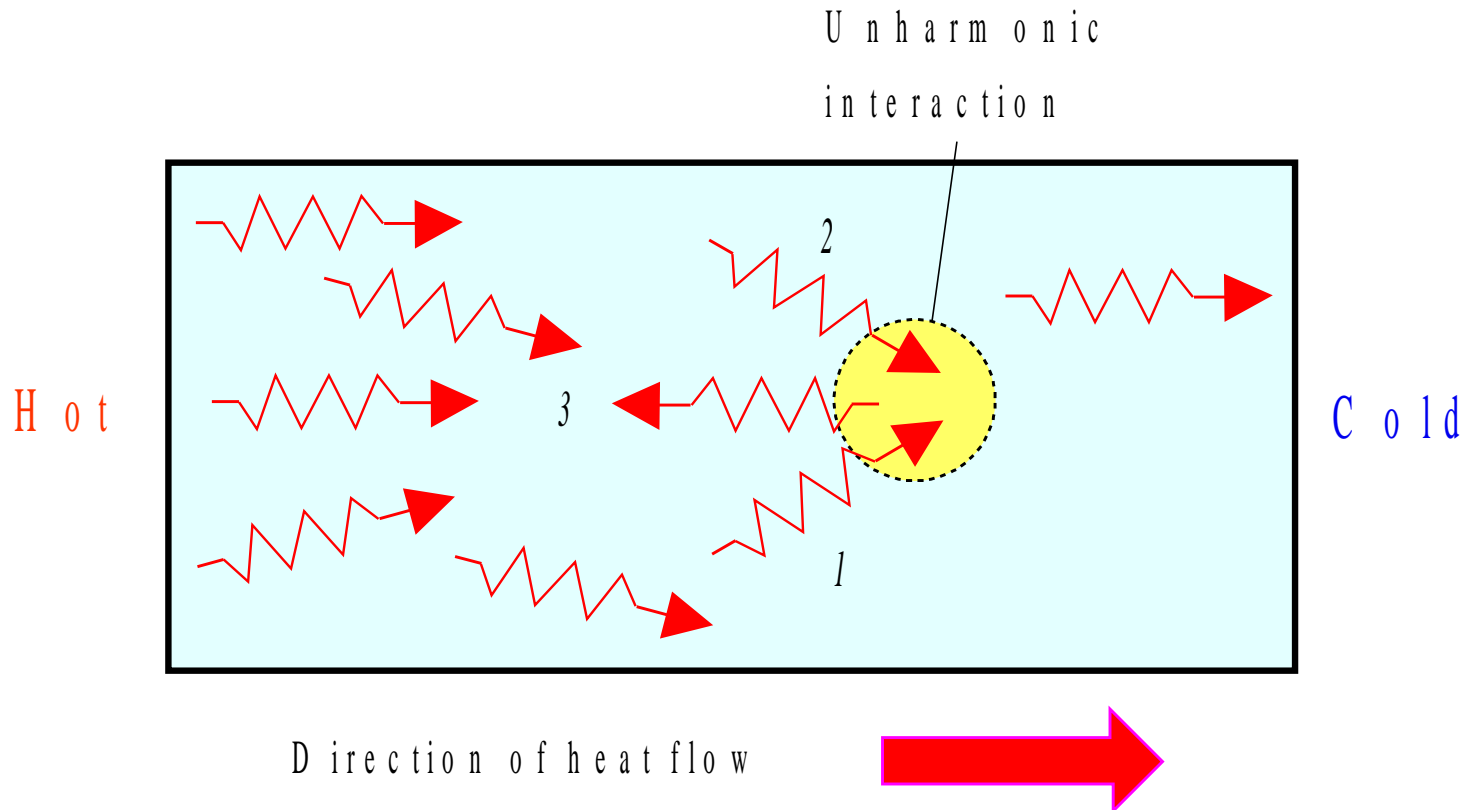
Fig 4.45

Table 4.5 Debye temperatures T_D , heat capacities, and thermal conductivities of selected elements

	Crystal							
	Ag	Be	Cu	Diamond	Ge	Hg	Si	W
T_D (K)*	215	1000	315	1860	360	100	625	310
C_m (J K ⁻¹ mol ⁻¹)†	25.6	16.46	24.5	6.48	23.38	27.68	19.74	24.45
c_s (J K ⁻¹ g ⁻¹)†	0.237	1.825	0.385	0.540	0.322	0.138	0.703	0.133
κ (W m ⁻¹ K ⁻¹)†	429	183	385	1000	60	8.65	148	173

Thermal conductivity (non metals)

- Heat diffuses (phonons diffuse)
- As with any diffusion path thermal diffusivity or conductivity is \sim to the MFP
- Scattering by defects, impurities and other **phonons!**
- Low temperature phonon-phonon collisions negligible.
- High temperatures important.



Phonons generated in the hot region travel towards the cold region and thereby transport heat energy. Phonon-phonon unharmonic interaction generates a new phonon whose momentum is towards the hot region.

Fig 4.47

Thermal Conductivity

Thermal conductivity κ

Measures the rate at which heat can be transported through a medium per unit area per unit temperature gradient.

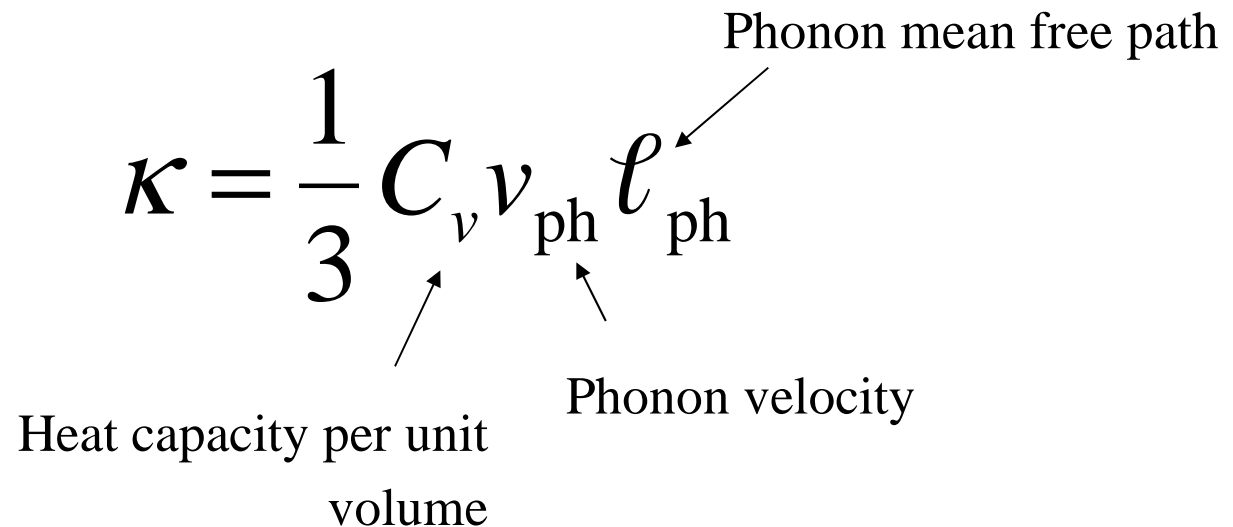
Thermal conductivity due to phonons

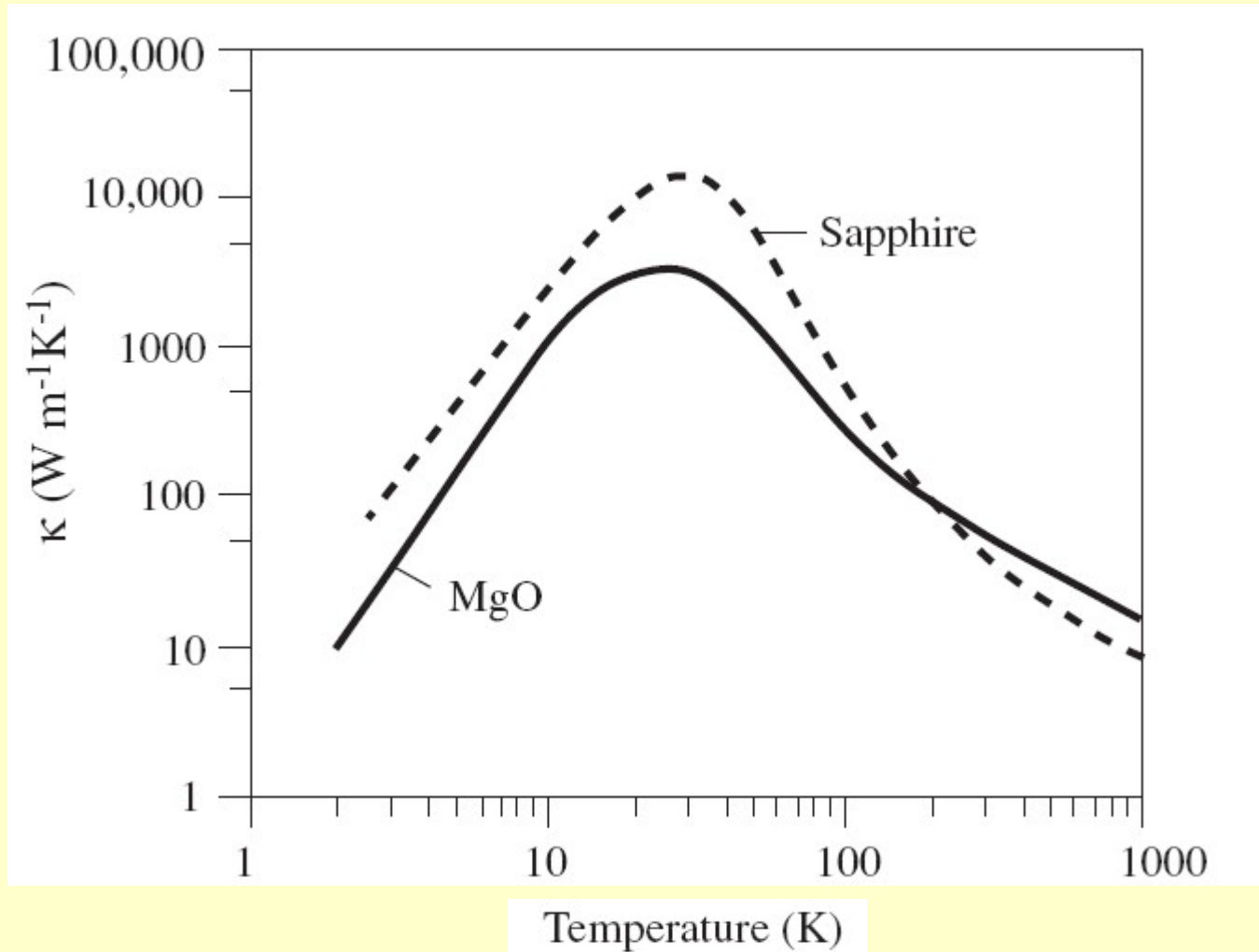
$$\kappa = \frac{1}{3} C_v v_{\text{ph}} \ell_{\text{ph}}$$

Heat capacity per unit volume

Phonon velocity

Phonon mean free path





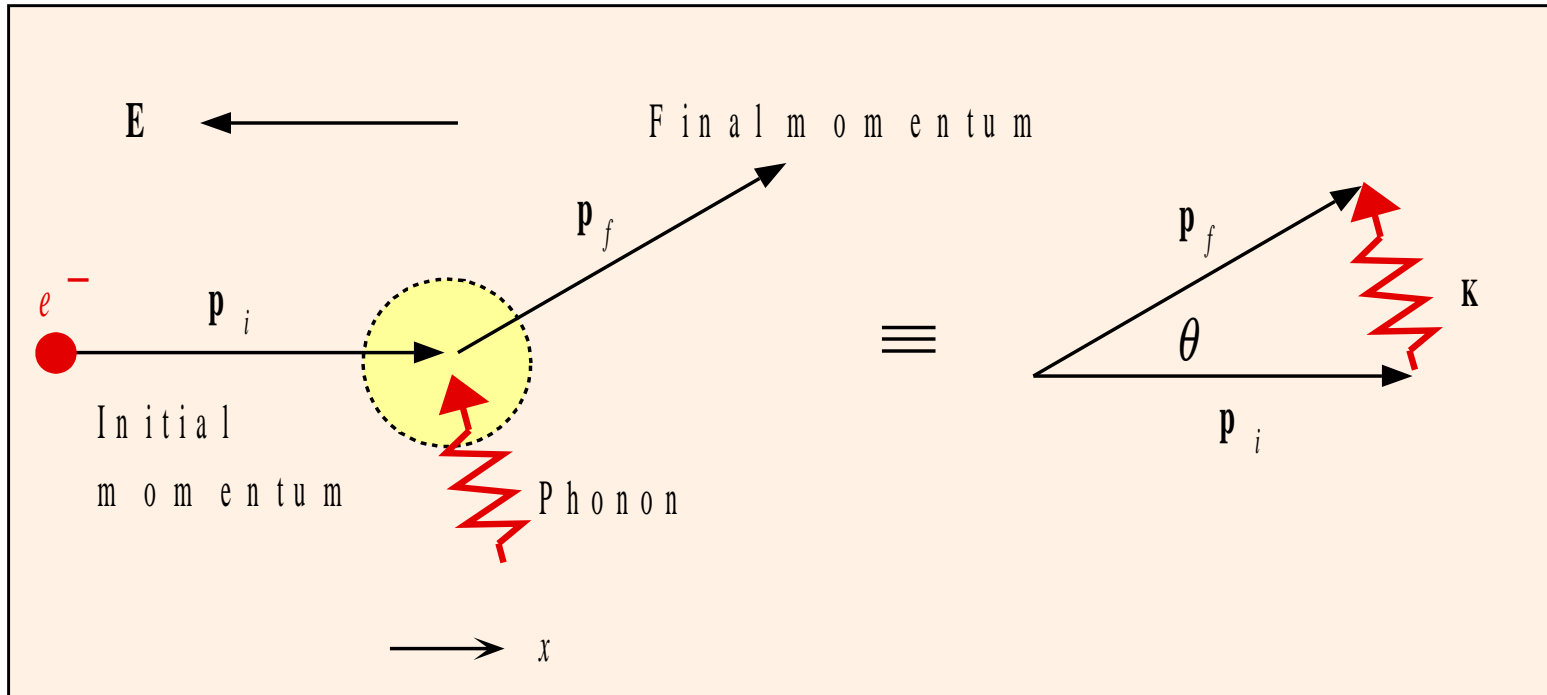
Thermal conductivity of sapphire and MgO as a function of temperature.

Fig 4.48

Phonons and electrical transport

- Our model of electron transport assumed 100% randomization of the electron at every scattering occurrence.
- Now we know more about phonons (the main source of scattering) we can deduce a few things.
 - Most electrons in transport have $E \sim E_f$
 - At high temperatures most phonons are at w_{\max} cause 100% randomization and we have $1/T$ dependence of the conductivity
 - At low temperature ($< T_D$) scattering by phonon only causes a low angle event. We need many events to randomize, less phonons, $1/T_5$ dependence

Fig 4.48



Low angle scattering of a conduction electron by a phonon

Fig 4.49

Electrical Conductivity

Electrical conductivity $T > T_D$

$$\sigma \propto \tau \propto \frac{1}{n_{\text{ph}}} \propto \frac{1}{T}$$

Electrical conductivity $T < T_D$

$$\sigma \propto N\tau \propto \frac{N}{n_{\text{ph}}} \propto \frac{1}{T^5}$$