

Structure of Matter

The Solid State

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Lectures (Tuesday & Friday)

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Last time:

Phonons cont'd

Thermal properties

Today:

Thermal properties cont'd

Metals (free electron model)

Debye specific heat

Total energy :

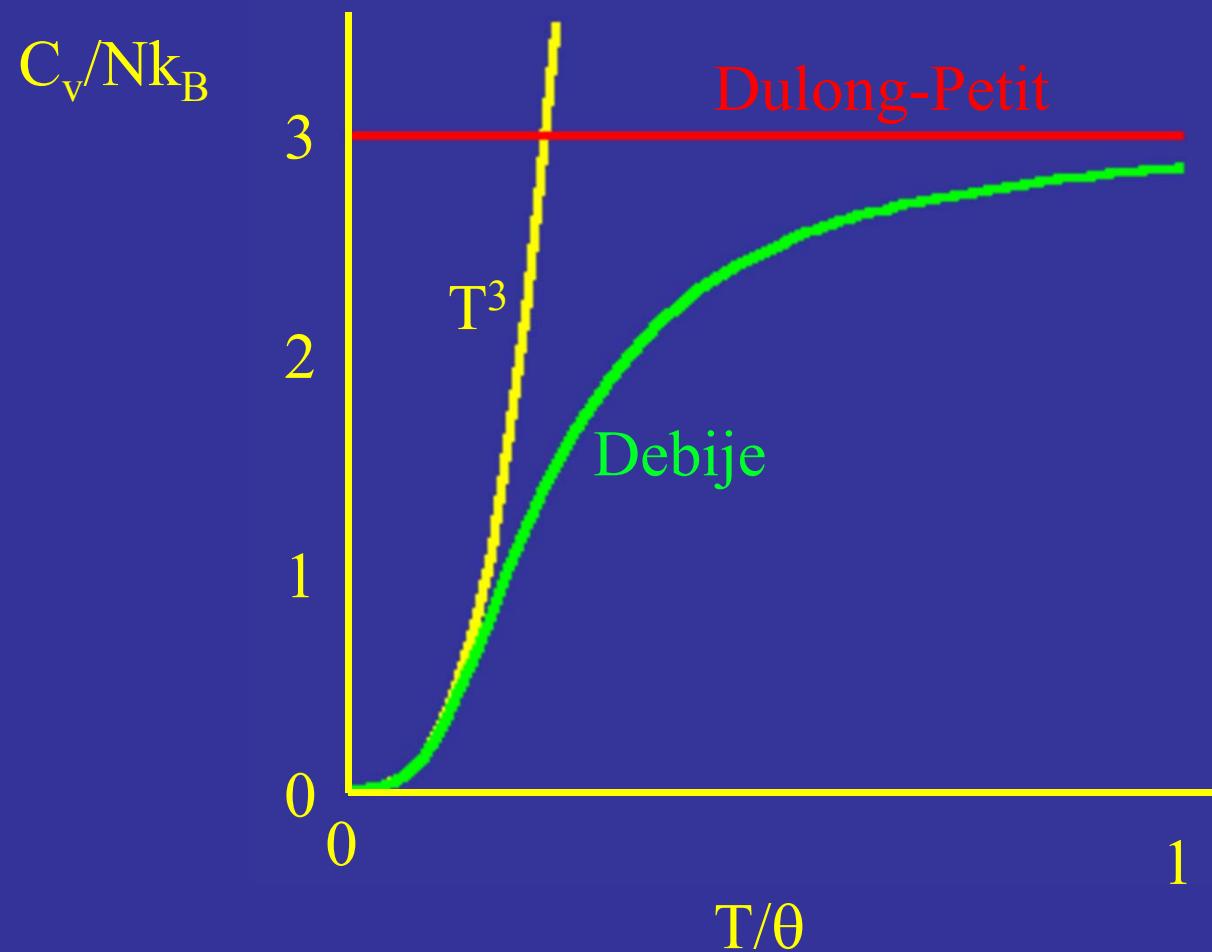
$$U = \frac{3V_{cell}\hbar}{2\pi^2 v^3} \int_0^{\omega_D} \frac{\omega^3}{\exp(\hbar\omega/k_B T) - 1} d\omega$$

Specific heat:

$$C_{lat} = \frac{dU}{dT} = \frac{3V_{cell}\hbar}{2\pi^2 v^3} \int_0^{\omega_D} \frac{\omega^3 \exp(\hbar\omega/k_B T)}{\left(\exp(\hbar\omega/k_B T) - 1\right)^2} \frac{\hbar\omega}{k_B T^2} d\omega$$

$$C_{lat} = \frac{dU}{dT} = 9N_{atom} \left(\frac{T}{\theta} \right)^3 \cdot \int_0^{\theta/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$
$$x = \frac{\hbar\omega}{k_B T}$$

Specific heat



Einstein model

Simpler model, approximation for optical phonons

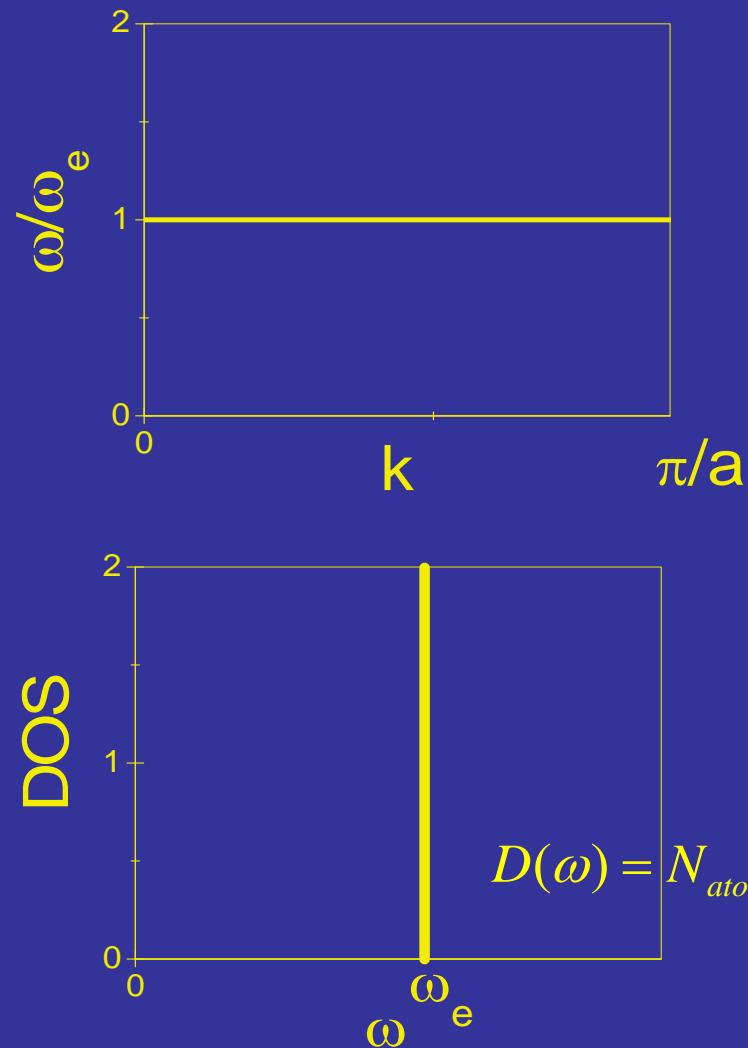
$$D(\omega) = N_{atoms} \delta(\omega - \omega_e)$$

$$U = 3N_{atoms} \langle n(\omega_e) \rangle \hbar \omega_e = \frac{3N_{atoms} \hbar \omega_e}{e^{\hbar \omega_e / k_B T} - 1}$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3N_{atoms} k_B \left(\frac{\hbar \omega_e}{k_B T} \right)^2 \frac{e^{\hbar \omega_e / k_B T}}{\left(e^{\hbar \omega_e / k_B T} - 1 \right)^2}$$

Limits $T \rightarrow 0 : C_V \propto x^2 e^{-x} = 0$
 $T \rightarrow \infty : C_V = 3N_{atoms} k_B$

Einstein model, C_V



$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3N_{atoms}k_B \left(\frac{\hbar\omega_e}{k_B T} \right)^2 \frac{e^{\hbar\omega_e/k_B T}}{(e^{\hbar\omega_e/k_B T} - 1)^2}$$

The plot shows the normalized specific heat $C_V / (3Nk_B)$ as a function of the normalized temperature $k_B T / \hbar\omega$. The curve starts at 0 for $k_B T / \hbar\omega = 0$ and increases monotonically, asymptotically approaching 1 as the temperature increases.

Thermal conductivity



Thermal energy flux:

$$J_u = \frac{dw}{dt}$$

Thermal gradient:

$$\frac{dT}{dx} = \frac{T_r - T_l}{L}$$

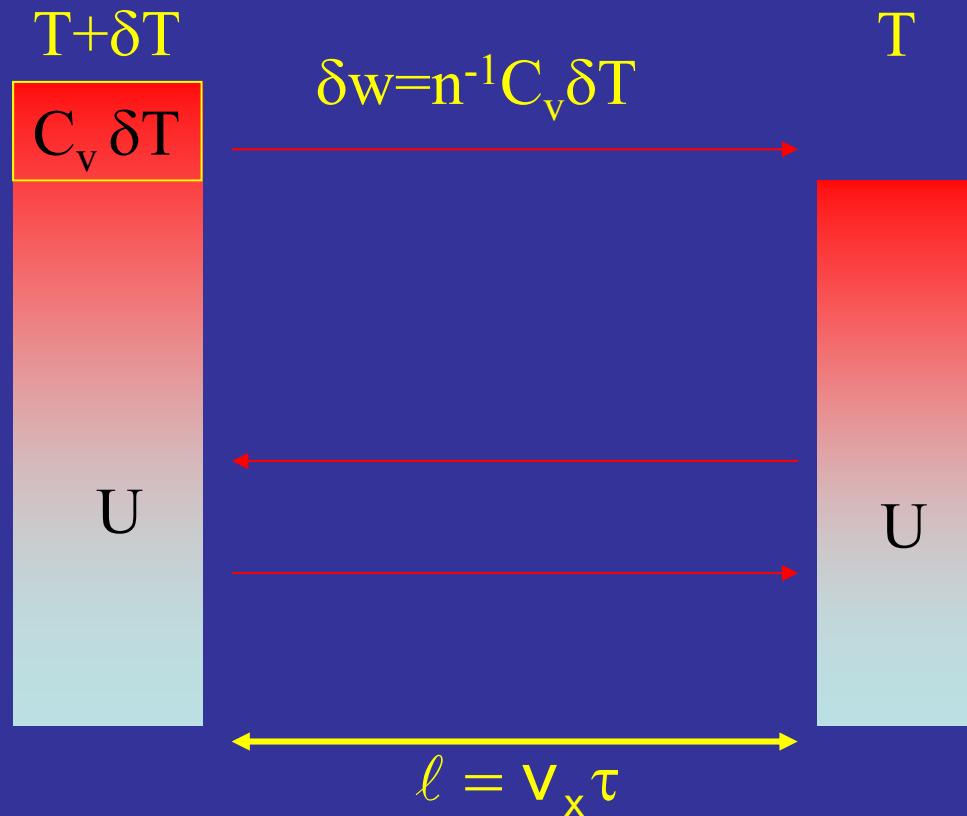
$$J_u = -\kappa \frac{dT}{dx}$$

κ : Thermal conductivity

Is due to diffusion of particles (here phonons)

Thermal conductivity

$$J_u = -\kappa \frac{dT}{dx}$$



$$J_u = \frac{dw}{dt} = n \langle \mathbf{v}_x \cdot \delta \mathbf{w} \rangle = C_v \langle v_x \delta T \rangle$$

$$\delta T = -v_x \tau \cdot \frac{dT}{dx}$$

$$J_u = -C_v \tau \frac{dT}{dx} \langle v_x^2 \rangle$$

$$\left. \begin{aligned} \langle v_x^2 \rangle &= \frac{1}{3} v^2 \\ \tau &= \ell / v \end{aligned} \right\} \Rightarrow J_u = -\frac{1}{3} C_v v \ell \frac{dT}{dx}$$

$$\rightarrow \kappa = \frac{1}{3} C_v v \ell$$

Scattering of phonons

Phonon mean free path ℓ limited by

- Imperfections, crystal boundaries, isotopes
- Phonon-phonon scattering (normal processes)
- Phonon-phonon scattering (Umklapp processes)

Harmonic approximation: NO phonon-phonon scattering

Scattering of phonons

Imperfections etc.: $\ell = T$ independent: $\kappa \propto v\ell C_v(T) \propto T^3$

Normal processes:

$$\hbar\omega_{k_1} + \hbar\omega_{k_2} = \hbar\omega_{k_3}$$

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3$$

No net change of phonon momentum

Umklapp processes:

$$\hbar\omega_{k_1} + \hbar\omega_{k_2} = \hbar\omega_{k_3}$$

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{G}$$

Momentum transferred to crystal: $\hbar\vec{G}$



Thermal conductivity

$$\kappa = \frac{1}{3} C_v v \ell$$

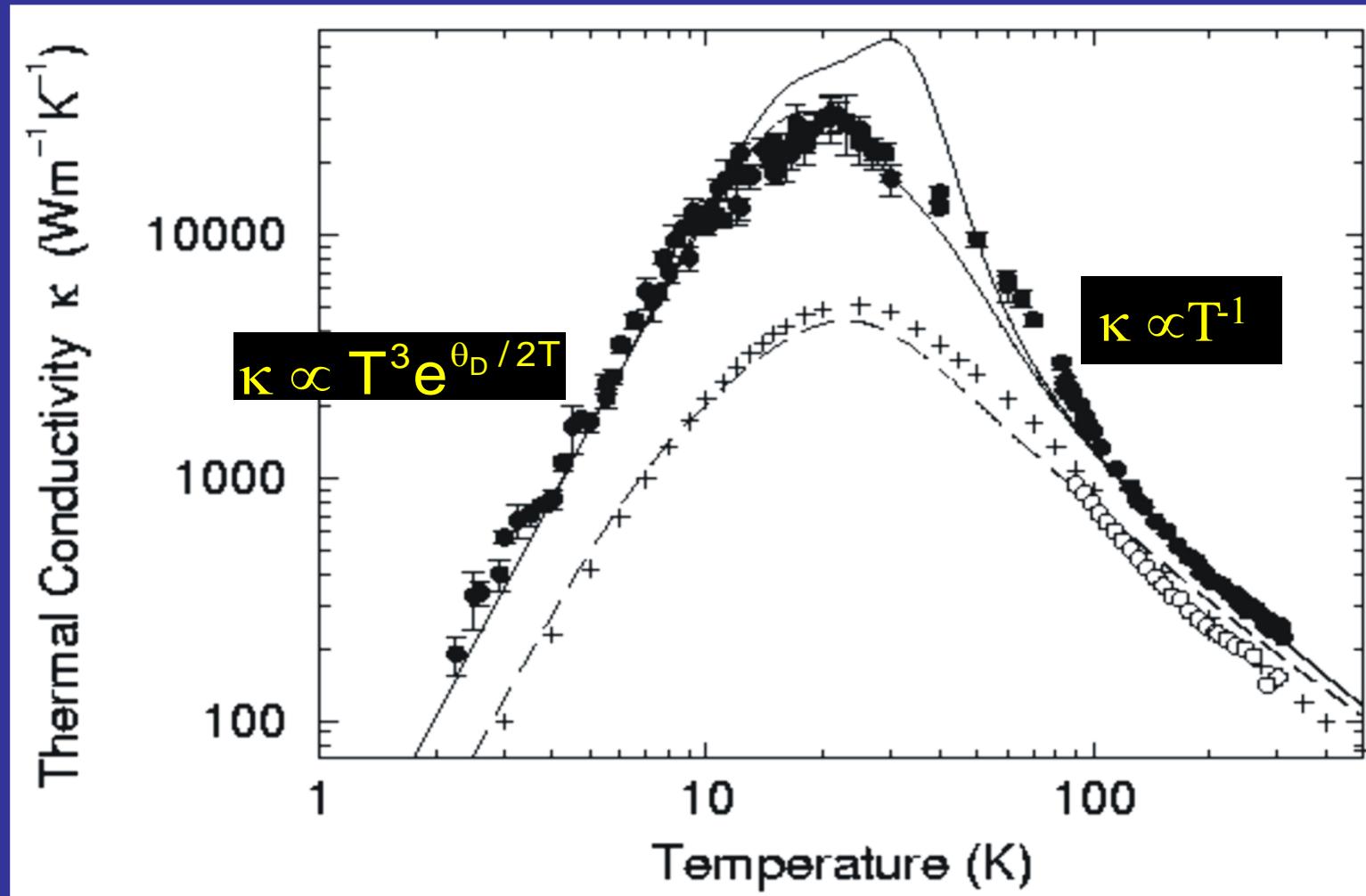
High T: C_v constant, $\ell \propto n(\omega) \propto T^{-1}$ $\rightarrow \kappa \propto T^{-1}$

Low T: imperfections give $\kappa \propto T^3$

Umklapp: $\ell^{-1} \propto n(\hbar\omega_D / 2) = \frac{1}{e^{\theta_D / 2T} - 1} \approx e^{-\theta_D / 2T}$

$$\kappa \propto T^3 e^{\theta_D / 2T}$$

Thermal conductivity



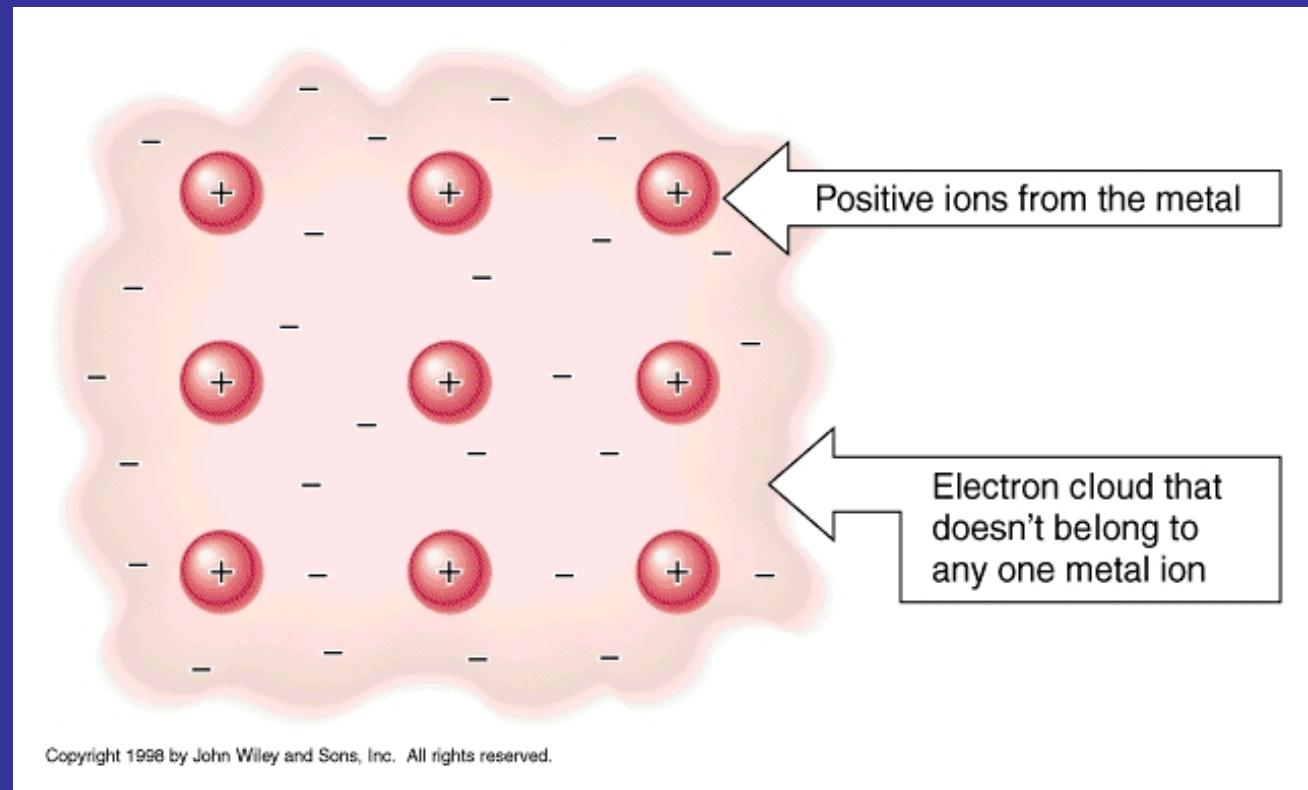
Isotope pure Silicon (T. Ruf et al. Sol. St. Comm. 2000)

METALS

Free electron model

Metals

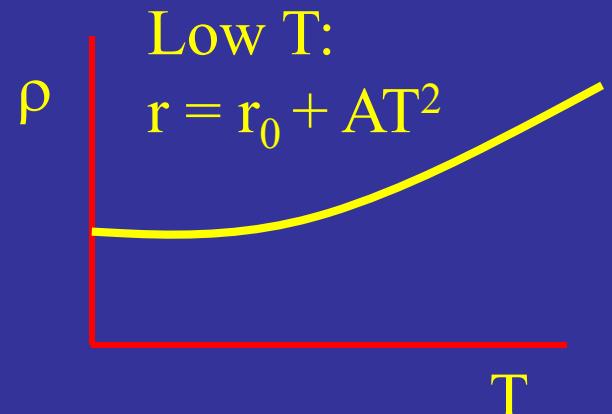
- Shiny, mirror
- High conductivity
- Non-directional bonding, deformable
- Non-specific bonding, alloying
- Close packing



What is a metal ?

Electrical conductivity:

$$\rho_{300\text{ K}} \sim 1.7 \text{ (Cu)} - 153 \text{ } \mu\Omega \cdot \text{cm (Pu)}$$



Thermal conductivity:

$$\text{Cu: } K_{300\text{ K}} \sim 3.9 \text{ W/Kcm} \quad \text{Pu: } K_{300\text{ K}} \sim 0.049 \text{ W/Kcm}$$

$$\text{Wiedemann-Franz: } K/\sigma = \alpha T$$

$$\text{Quartz: } K \sim 0.13 \text{ W/Kcm} \quad \text{NaCl: } K \sim 0.27 \text{ W/Kcm}$$

Reflectivity:

Highly reflecting upto plasma-frequency

$$\omega < \omega_p \quad \omega_p^2 = 4 \pi n e^2 / m$$

- Free electron model (Drude, sommerfeld theory)
- Statistics and density of states
- Heat capacity
- Electrical conductivity (Ohm's law)
- Influence of a magnetic field (Hall effect)
- Thermal conductivity and Wiedemann-Franz law

Electrons in metals

P. Drude: 1900 kinetic gas theory of electrons, classical
Maxwell-Boltzmann distribution
independent electrons
free electrons
scattering from ion cores (relaxation time approx.)

A. Sommerfeld: 1928
Fermi-Dirac statistics

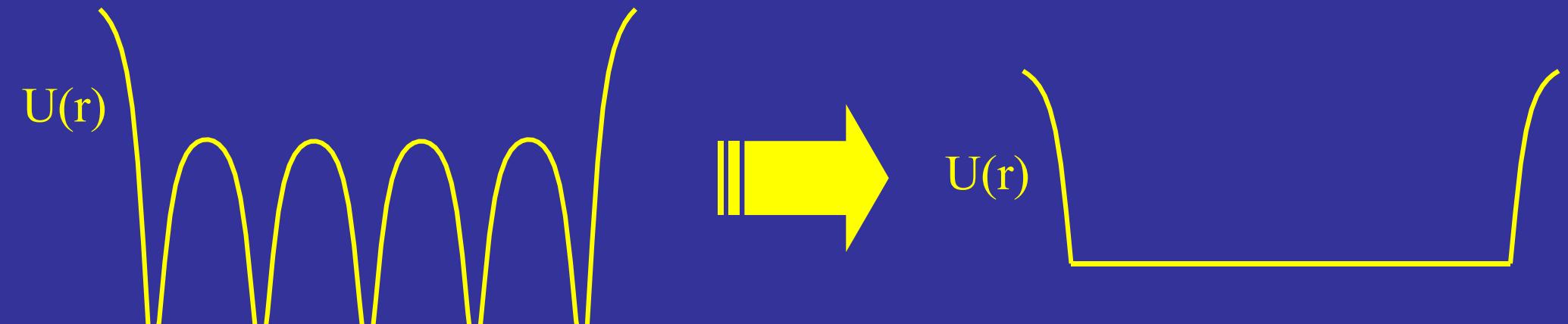
F. Bloch's theorem: 1928
Periodic potential, Bloch electrons

L.D. Landau: 1957
Interacting electrons (Fermi liquid theory)

Free electron approximation

Electrons in a lattice
Krönig-Penning model
Tight binding model

Forget lattice, consider
only the electrons in a box
Free electron model



Neglect periodic potential & scattering (Pauli)

Reasonable for “simple metals” (Alkali Li,Na,K,Cs,Rb)

Eigenstates & energies

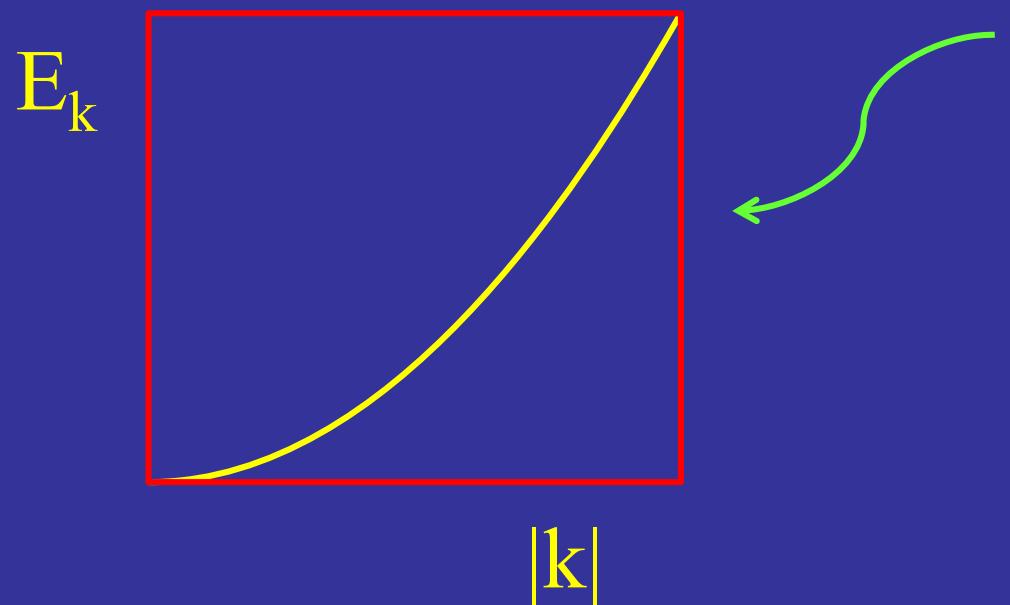
$$\left(\frac{-\hbar^2}{2m} \nabla^2 + V \right) \psi = i\hbar \frac{d\psi}{dt}$$

Plane wave solutions:

$$\psi_{\vec{k}}(r, t) = \psi_0 e^{i(\omega t - \vec{k} \cdot \vec{r})}$$

Energy-momentum relation:

$$E_{\vec{k}} = \frac{\hbar^2}{2m^*} |\vec{k}|^2$$



Particles in a box

Quantization of the k-vector (momentum)

$$n_x \frac{\lambda}{2} = L_x \text{ or } k_x = n_x \frac{\pi}{L_x}$$

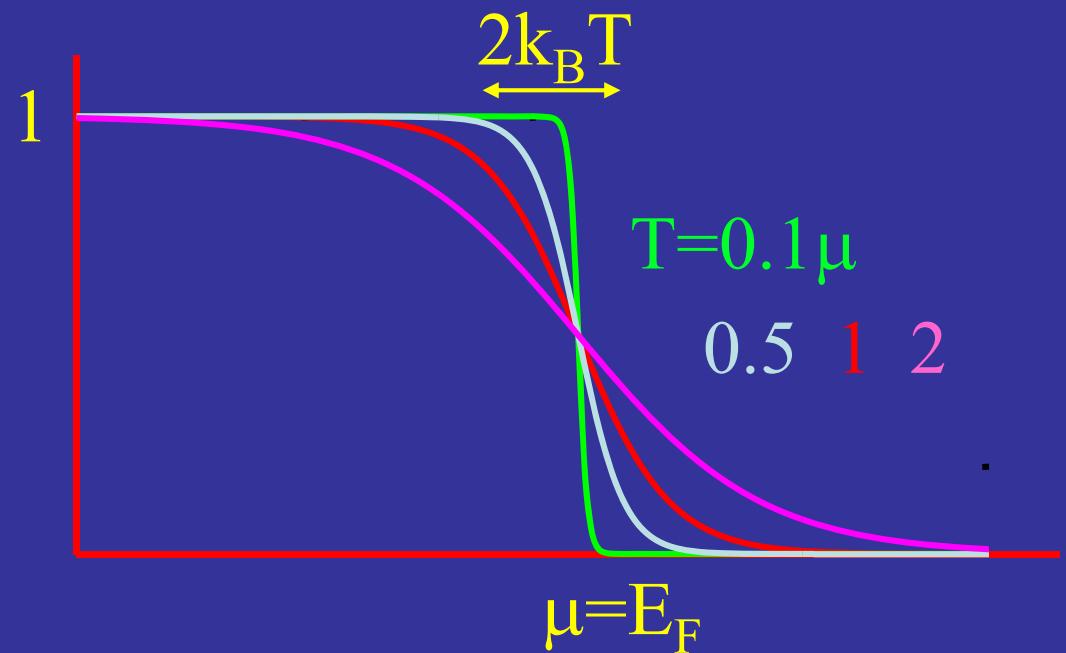
Allowed k values form cubic lattice, length unit 1/L

$$\vec{k} = \pi(n_x / L_x, n_y / L_y, n_z / L_z)$$

Electrons are fermions → Fermi-Dirac distribution

Fermi-Dirac statistics:

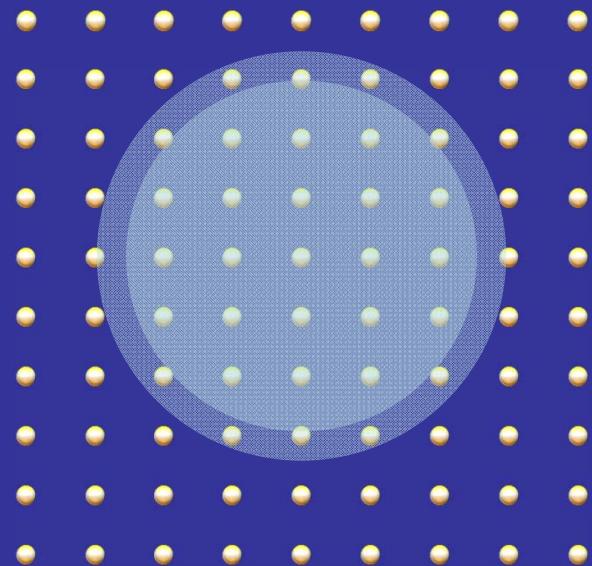
$$f_{FD}(E) = \frac{1}{e^{\frac{E-\mu}{kT}} + 1}$$



Density of states

How many states are there in an interval dE ?

Easy to answer this for an interval dk



Number of states in circle radius k

$$N(k) = \frac{\pi k^2}{(\pi/L)^2}$$

In ring dk

$$dN = \frac{2\pi k}{(\pi/L)^2} dk$$

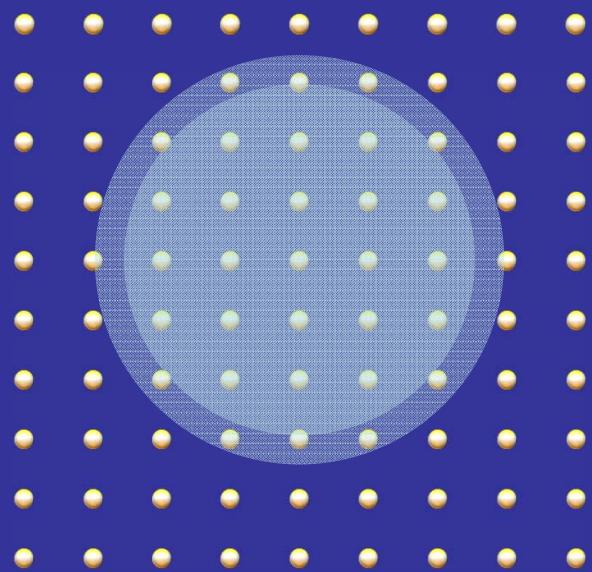
Density of states in k-space

$$D_2(k) = \frac{1}{L^2} \frac{dN}{dk} = \frac{2}{\pi} k$$

In 3D: take sphere & shell: $D_3(k) = \frac{1}{L^3} \frac{dN}{dk} = \frac{4}{\pi^2} k^2$

Density of states

How many states are there in an interval dE ?

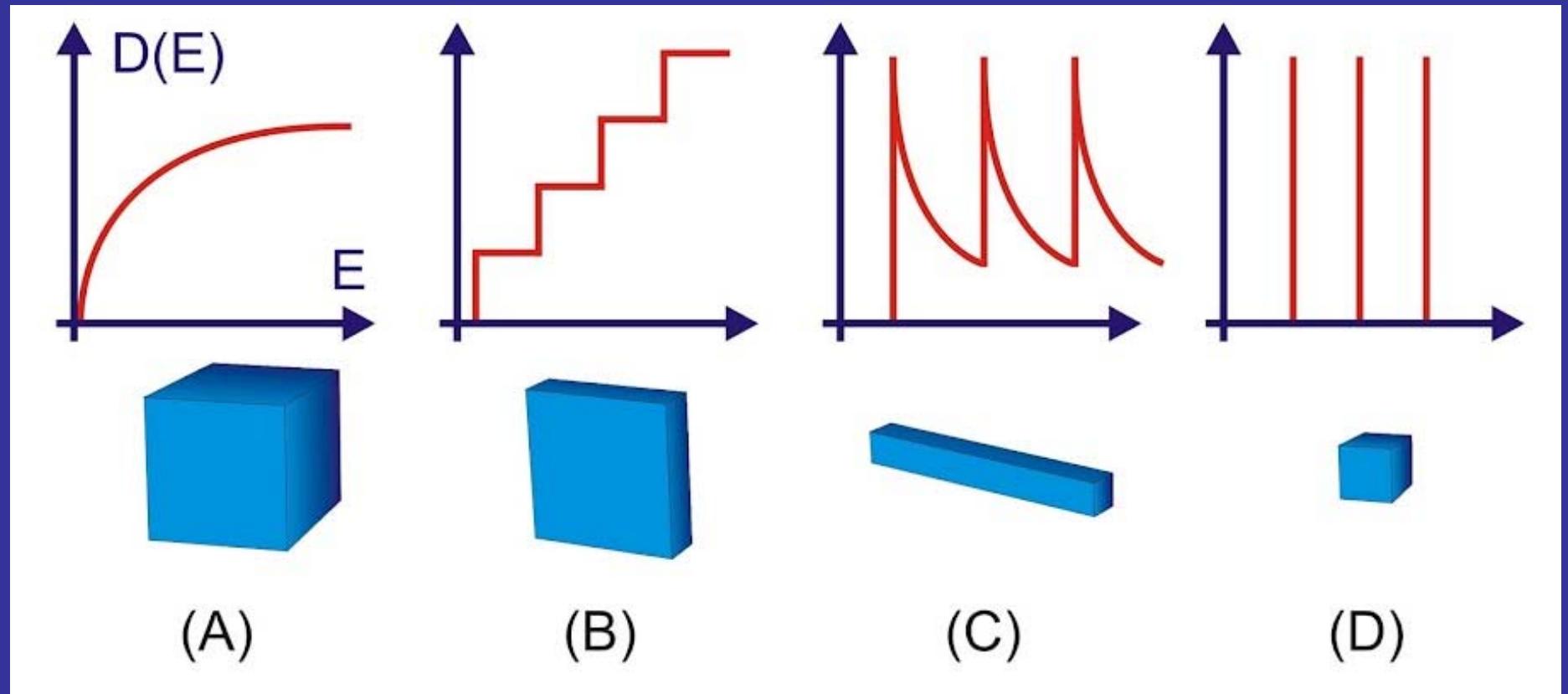


We can use $E(k)$ relation to get $D(E)$:

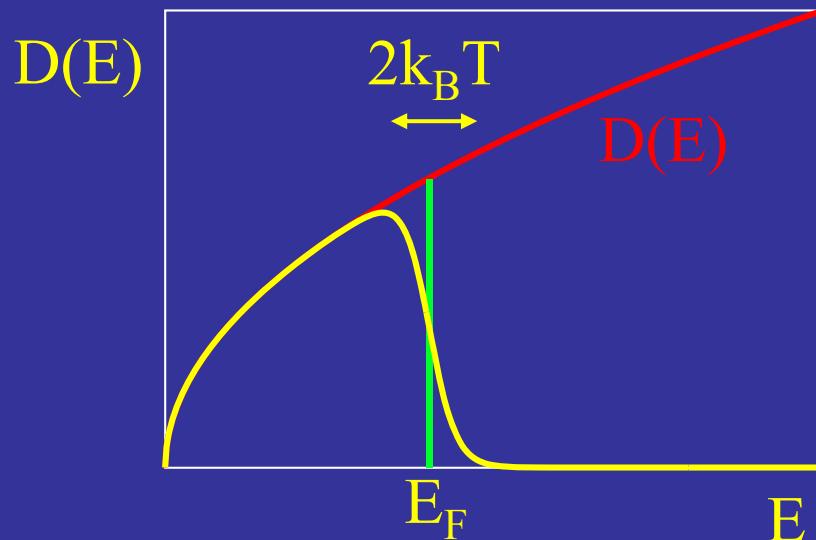
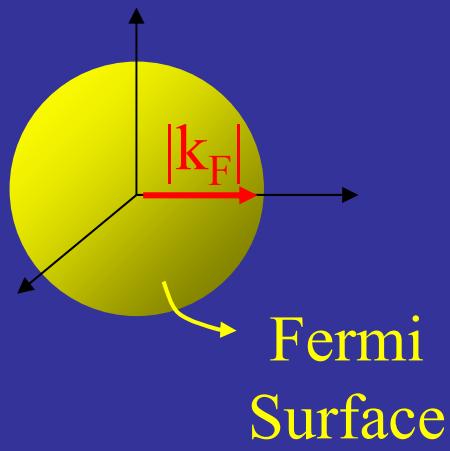
$$D_3(E) = \frac{dN}{dk} \frac{dk}{dE}$$

$$D_3(E) = \frac{4}{\pi^2} k^2 \left(\frac{\hbar^2 k}{m^*} \right)^{-1} = \frac{4\pi}{h^3} (2m^*)^{3/2} \sqrt{E}$$

DOS in different dimensions



Occupation of states



Using FD and DOS one can now determine the chemical potential

$$n = \int_0^{\infty} D(E) f(E) dE = \frac{4\pi}{h^3} (2m^*)^{3/2} \int_0^{\infty} \frac{\sqrt{E}}{e^{(E-\mu)/kT} + 1} dE$$

$$E_F = \mu(T=0) = \frac{h^2}{2m^*} \left(\frac{3}{8\pi} n \right)^{2/3}$$

Physical properties of simple metals

Bulk modulus at $T=0$: $B = \frac{1}{\kappa} = -V \left(\frac{\delta p}{\delta V} \right) = -V \left(\frac{\delta^2 U}{\delta V^2} \right)$

Total energy N electrons ($n=N/V$)

$$U = V \int_0^\infty D(E) \cdot E \cdot f(E) dE \stackrel{T=0}{=} V \int_0^{E_F} D(E) \cdot E dE = \frac{3}{5} V \cdot n \cdot E_F$$

$$p = -\frac{\partial U}{\partial V} = \frac{2}{3} \frac{U}{V} = \frac{6}{15} n \cdot E_F$$

$$B = -V \frac{\partial p}{\partial V} = \frac{10}{9} \frac{U}{V} = \frac{2}{3} n \cdot E_F$$

$$E_F = \frac{\hbar^2}{2m*} \left(\frac{3}{8\pi} n \right)^{2/3}$$

	$B_{f.e.}$ (Gpa)	B_{obs} (Gpa)
Li	24	12
Na	9	6.5
K	3	3
Rb	2	2
Cs	1.5	1.5
Cu	64	134
Ag	35	100
Al	228	76

White dwarfs & neutron stars

The future of our sun



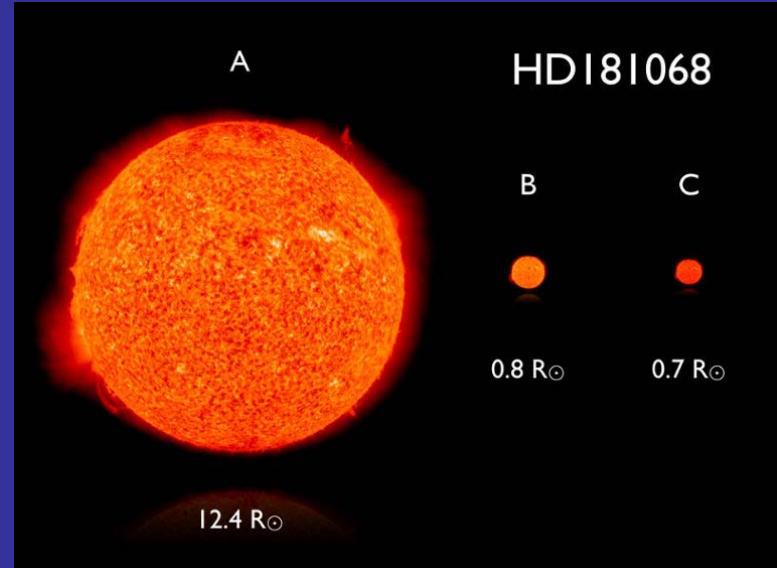
white dwarf G29-38 (NASA)

Star → Red Giant → White dwarf ($M < 1.4 M_{\odot}$)

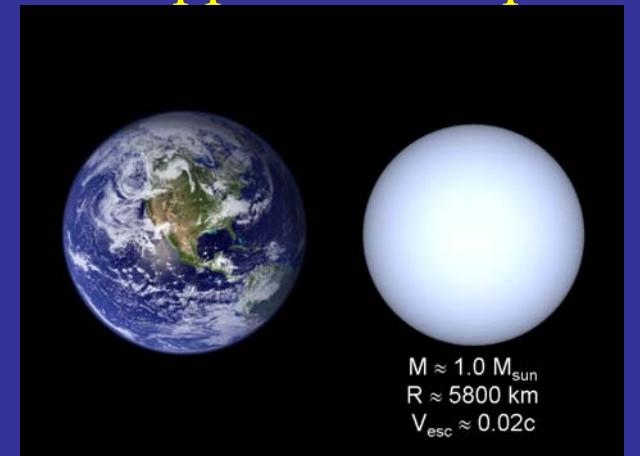
Neutron star ($3 > M/M_{\odot} > 1.4$)

Quark star(?)

Black hole ($M > 3M_{\odot}$)



NASA – Kepler telescope



White dwarfs

Heavy object with mass \sim sun & size \sim earth

$$\text{Total energy } U_{total} = U_{pot} + U_{kin}$$

$$U_{pot} = U_{grav} = -\frac{3}{5}G \frac{M^2}{R}$$

$$\#\text{electrons } N = \frac{M}{2m_p}$$

$$U_{kin} = U_{el} = \frac{2}{5}NE_F = \frac{3}{20} \left(\frac{9\pi}{8} \right)^{2/3} \frac{\hbar^2}{m_e} \left(\frac{M}{m_p} \right)^{5/3} \frac{1}{R^2}$$

$$U_{tot} = \frac{A}{R^2} - \frac{B}{R}$$

$$\text{Minimizing energy yields } \frac{R}{R_\odot} = 0.01 \left(\frac{M_\odot}{M} \right)^{1/3}$$

Pressure electron gas
counteracts gravity. Pressure $\sim 10^{33}$ Pa

Neutron star: Fermi gas of neutrons
(electrons & protons combine)