Fundamentals of Solid State Physics

Thermal Properties

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Thermal Properties

- Heat Capacity (Thermal Capacity) 热容
- Thermal Conductivity 热导
- Thermal Expansion 热膨胀
- ...

Thermal Properties

- Thermal properties are the combinations of properties of lattice vibration (phonons) and free electrons

- For insulators, there are no free electron. Thermal properties of lattice vibration (phonons) dominate.

- For metals,
  thermal properties = phonon part + free electron part

  Thermal capacity $$C_V = C_{V,p} + C_{V,e}$$

  Thermal conductivity $$\kappa = \kappa_p + \kappa_e$$

Fundamentals of Solid State Physics

Thermal Properties - Phonons

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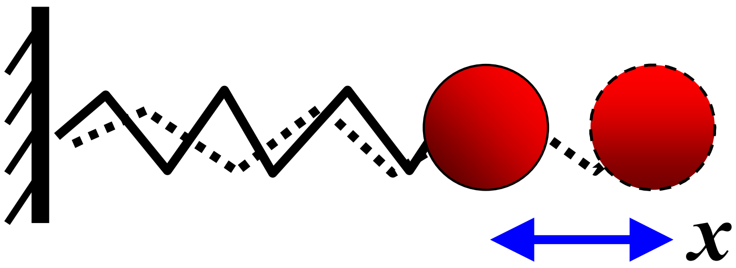
Harmonic Oscillator: Classical Theory

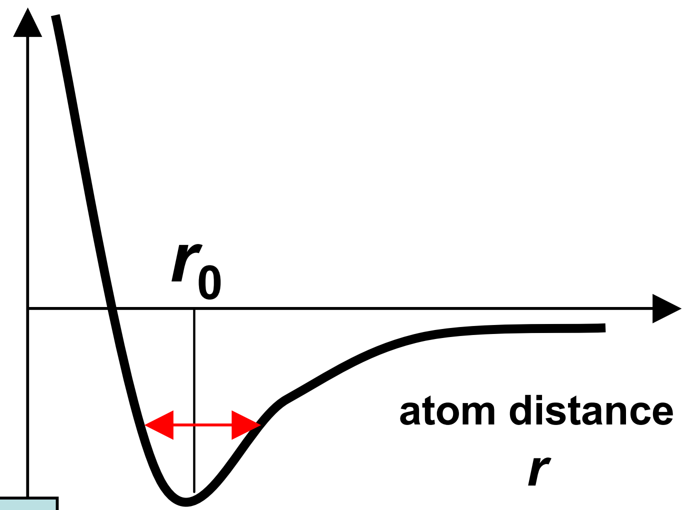
- **Vibration amplitude is continuous**
- **Energy is continuous, and temperature dependent**



energy of one spring + one atom
= potential energy + kinetic energy

$$E = \frac{1}{2}Kx^2 + \frac{1}{2}mv^2 = \frac{1}{2}k_BT + \frac{1}{2}k_BT = k_BT$$

Equipartition Theorem (能量均分定理)



Thermal vibration around r_0

Internal Energy 内能

- **Total vibration energy of a crystal**
  - all the springs + all the atoms (3*NL*)

$$\boxed{U = 3NLk_BT}$$

N - # of primitive cells
L - # of atoms in a primitive cell

- **Heat capacity (Specific heat) 比热容**
  - energy per unit of temperature

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3NLk_B}$$

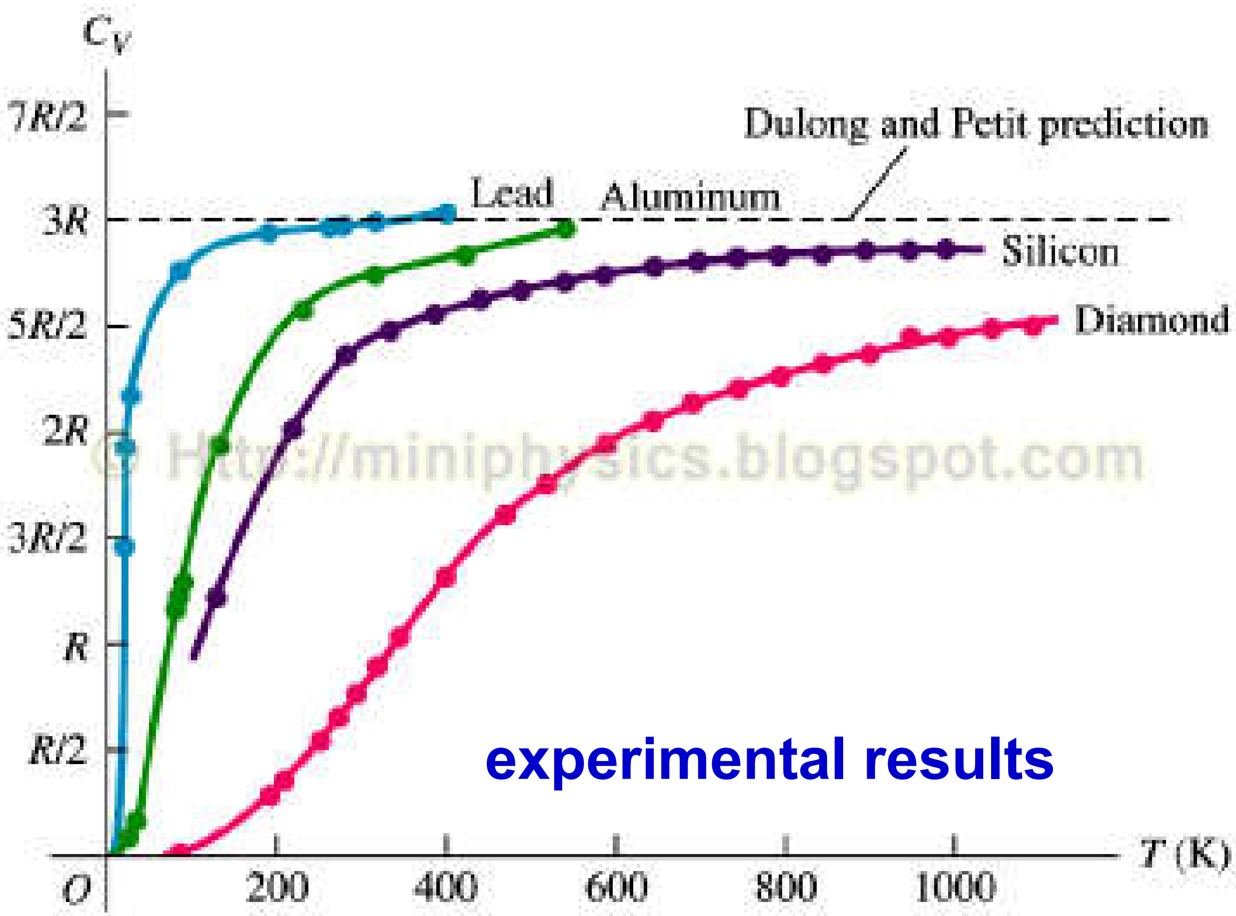
Dulong–Petit Law

In the system, every atom contributes an energy of $3k_BT$

Heat Capacity C_V

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3NLk_B$$

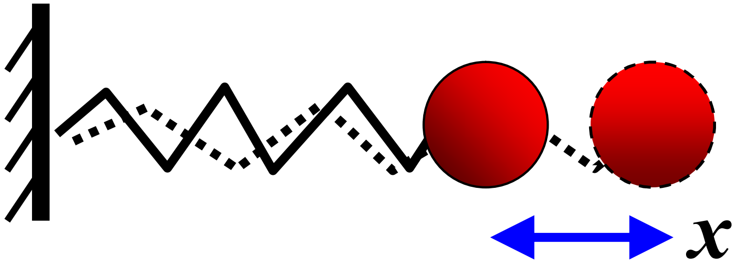
Dulong–Petit Law



→ ***only valid at high temperature***

Harmonic Oscillator: Quantum Theory

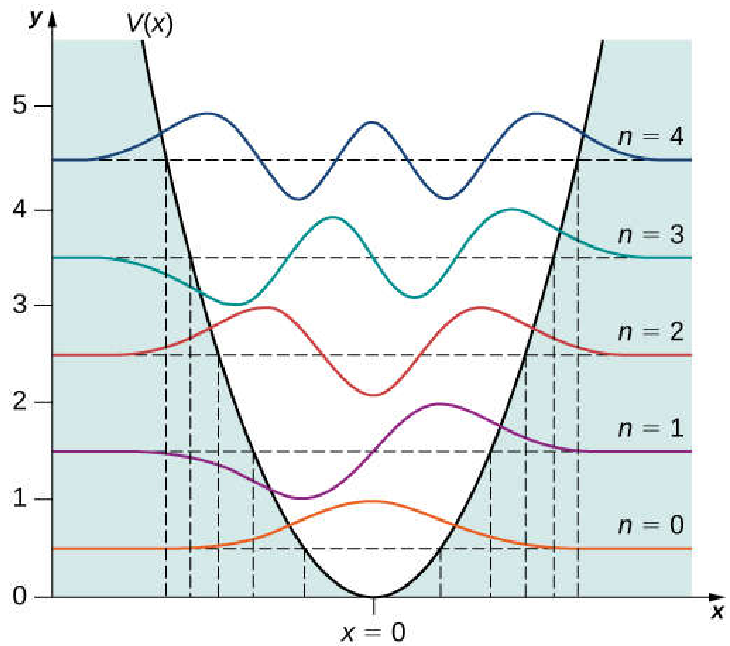
$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)+V(x)\cdot\psi(x)=E\psi(x)$$



$$V(x)=\frac{1}{2}Kx^2=\frac{1}{2}m\omega^2x^2$$

$$\omega=\sqrt{\frac{K}{m}}$$

$$\rightarrow \quad E_n=\left(\frac{1}{2}+n\right)\hbar\omega \qquad n=0,1,2,\ldots$$



Vibration energy is quantized

https://phys.libretexts.org/Bookshelves/University_Physics/Book%3A_University_Physics_(OpenStax)/Book%3A_University_Physics_III_-_Optics_and_Modern_Physics_(OpenStax)/07%3A_Quantum_Mechanics/7.06%3A_The_Quantum_Harmonic_Oscillator

Harmonic Oscillator: Quantum Theory

- **Quantum theory**
  - **Vibration energy is quantized**
  - **At each ω state, the energy is the ground state energy ($\hbar\omega/2$) plus energy of *n* phonons ($\hbar\omega$)**

$$\boxed{E(\omega) = \left(\frac{1}{2} + n\right)\hbar\omega} \qquad n = 0, 1, 2, \ldots$$

  - **average *n* in each state follows Bose-Einstein distribution**

$$\boxed{\overline{n} = \frac{1}{e^{\hbar\omega/k_B T} - 1}}$$

  - **If there are *N* primitive cells, and *L* atoms in each cell, the total number of states is 3*NL***

Internal Energy 内能

- Internal energy is the ground state energy plus the energy of all the phonons

$$U = U_0 + \sum_{i=1}^{3NL} \frac{\hbar\omega_i}{e^{\hbar\omega_i/k_BT} - 1}$$

$$= U_0 + \int_0^{\omega_{\max}} g(\omega)\frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1} d\omega$$

phonon energy

ground state

DOS

average phonon number in each state

heat capacity $$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Heat Capacity C_V

- **At high temperature, *T* >> 0 K**

$$
\begin{aligned}
U &= U_0 + \sum_{i=1}^{3NL} \frac{\hbar\omega_i}{e^{\hbar\omega_i / k_B T} - 1} \\
&\approx U_0 + \sum_{i=1}^{3NL} \frac{\hbar\omega_i}{\hbar\omega_i / k_B T} \\
&= U_0 + 3NLk_B T
\end{aligned}
$$

heat capacity $$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3NLk_B$$ **constant**

Dulong–Petit Law

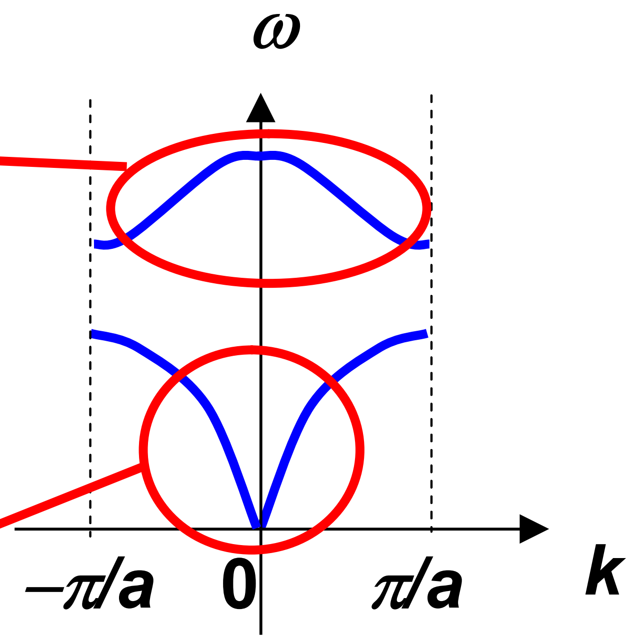
Heat Capacity C_V

- At low and medium temperatures

For optical phonons:

assume all the phonons have the same ω_0

The Einstein Model (爱因斯坦模型)



For acoustic phonons:

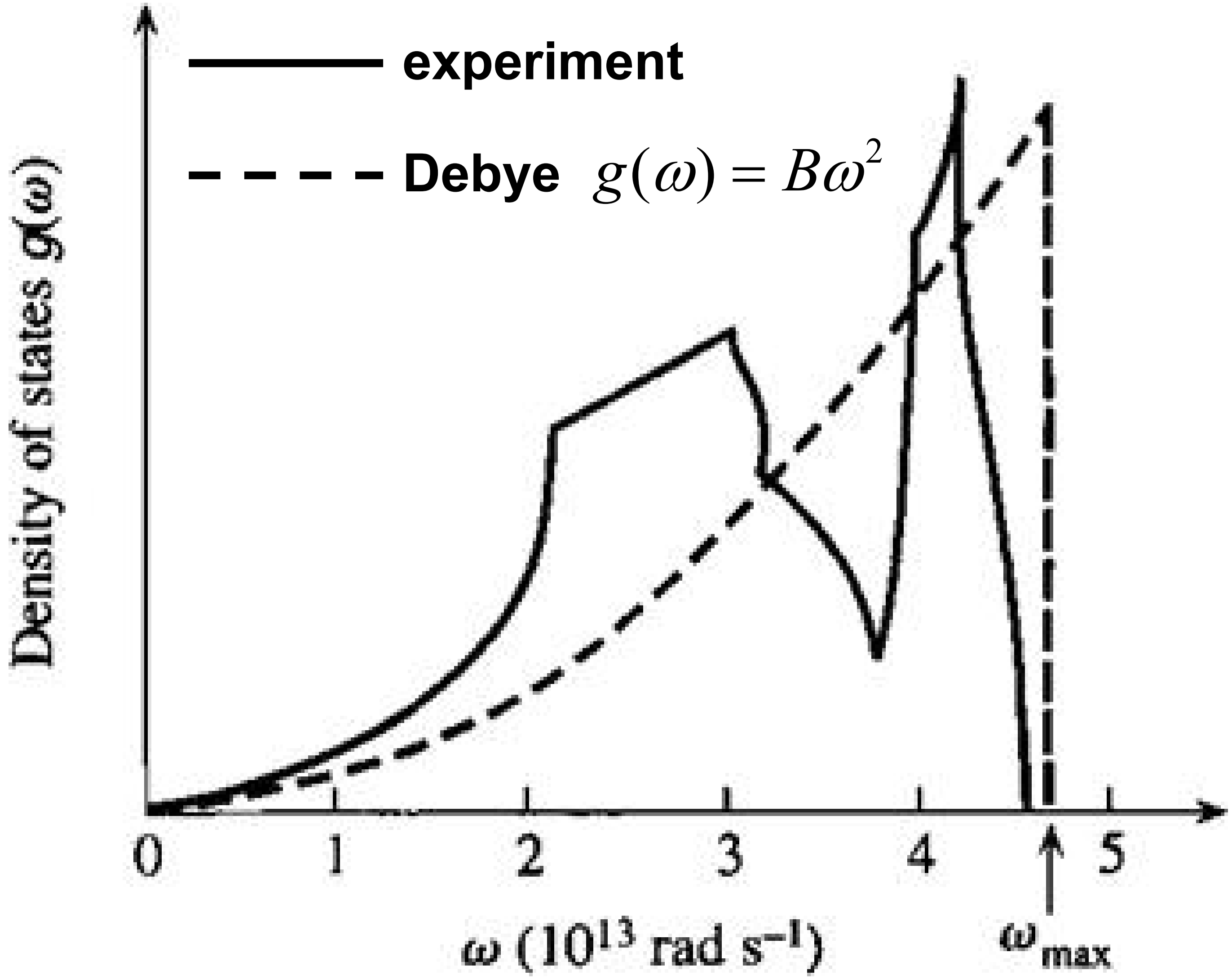
assume linear ω-k relation

The Debye Model (德拜模型)

$$\boxed{g(\omega) = B\omega^2}$$

Phonon Density of States $g(\omega)$

DOS for copper



Heat Capacity C_V

- At very low temperature, T --> 0 K
- Most phonons have ω --> 0, just focus on the acoustic branch

The Debye Model

$$U = U_0 + \int_0^{\omega_{\max}} g(\omega) \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} d\omega$$

$$\approx U_0 + \int_0^{\omega_{\max}} B\omega^2 \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} d\omega$$

heat capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \approx \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta_D}\right)^3 \propto T^3$$

Debye T^3 Law

$$\theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar v_g}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

Debye Temperature

Heat Capacity C_V

- At very low temperature, *T* --> 0 K
- Most phonons have ω --> 0, just focus on the acoustic branch

$$\theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar v_g}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

Debye Temperature is around room temperature for most materials

	θ_D (K)
C (diamond)	2230
Si	645
Al	428
Cu	343

http://hyperphysics.phy-astr.gsu.edu/hbase/Tables/thrcn2.html

Heat Capacity C_V

- **At median temperature, assume all the phonons in an optical branch have frequency ω_0**

The Einstein Model

$$U = U_0 + N \frac{\hbar\omega_0}{e^{\hbar\omega_0/k_BT} - 1}$$

heat capacity (of one branch)

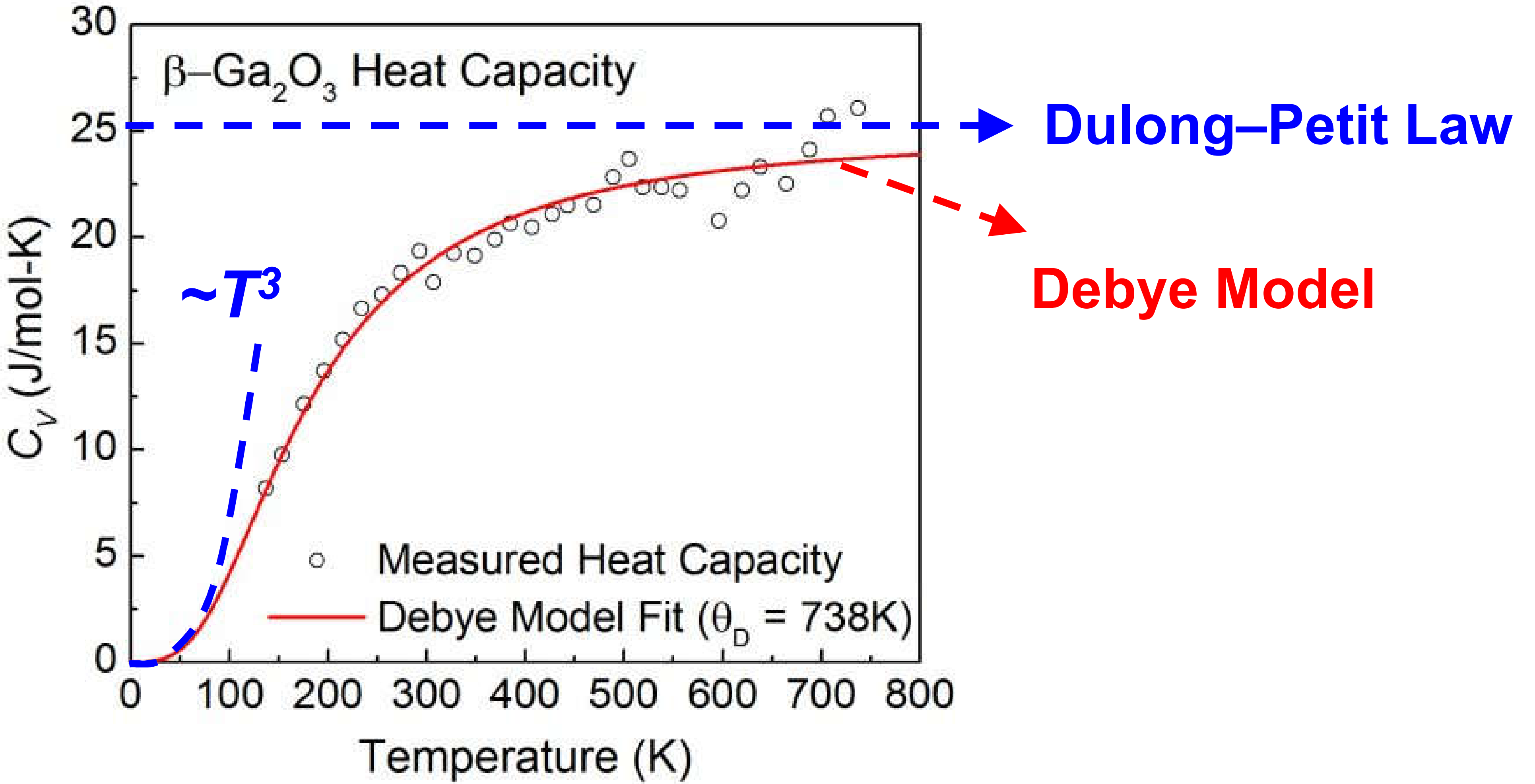
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = Nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2 \frac{e^{\hbar\omega_0/k_BT}}{(e^{\hbar\omega_0/k_BT} - 1)^2}$$

$$= Nk_B\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$

$$\theta_E = \frac{\hbar\omega_0}{k_B}$$

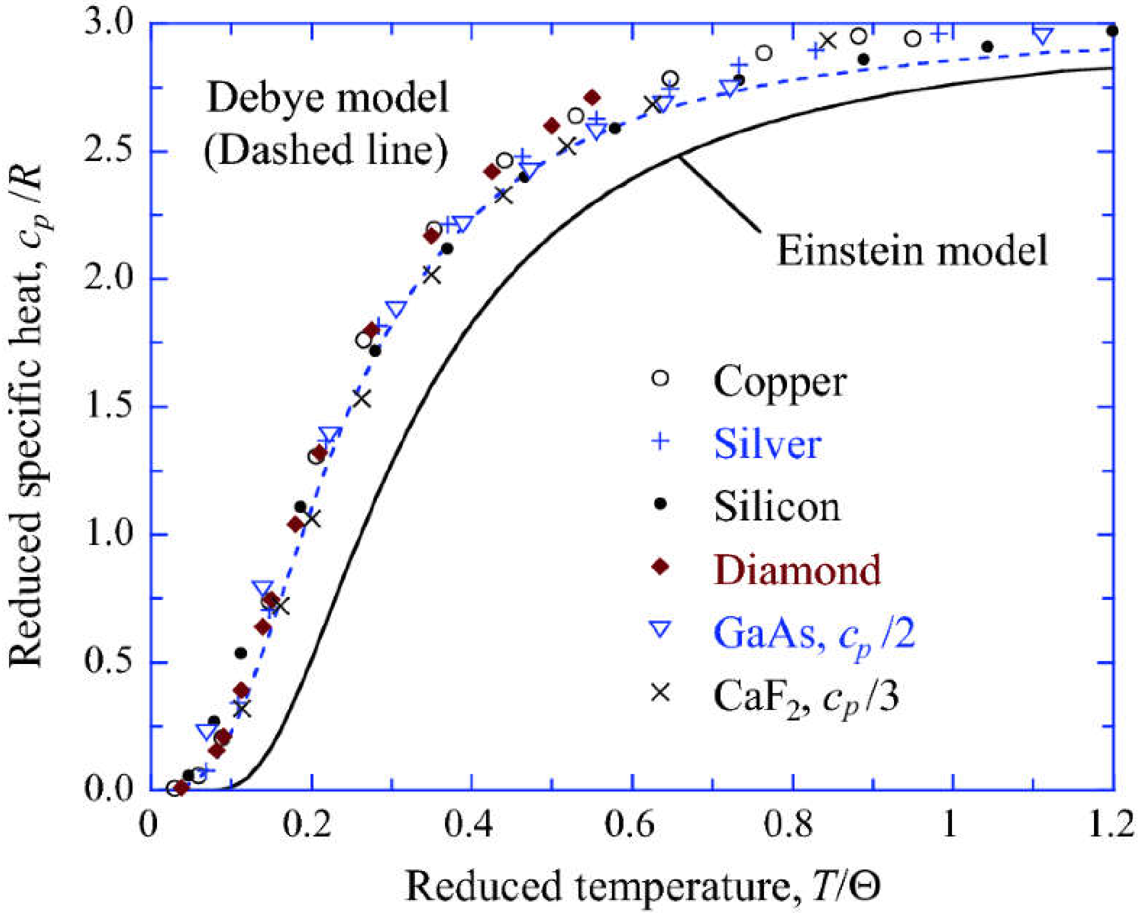
Einstein Temperature

Heat Capacity C_V - Example



Z. Guo, *et al.*, *Appl. Phys. Lett.* **106,** 111909 (2015)

Heat Capacity C_V - Example

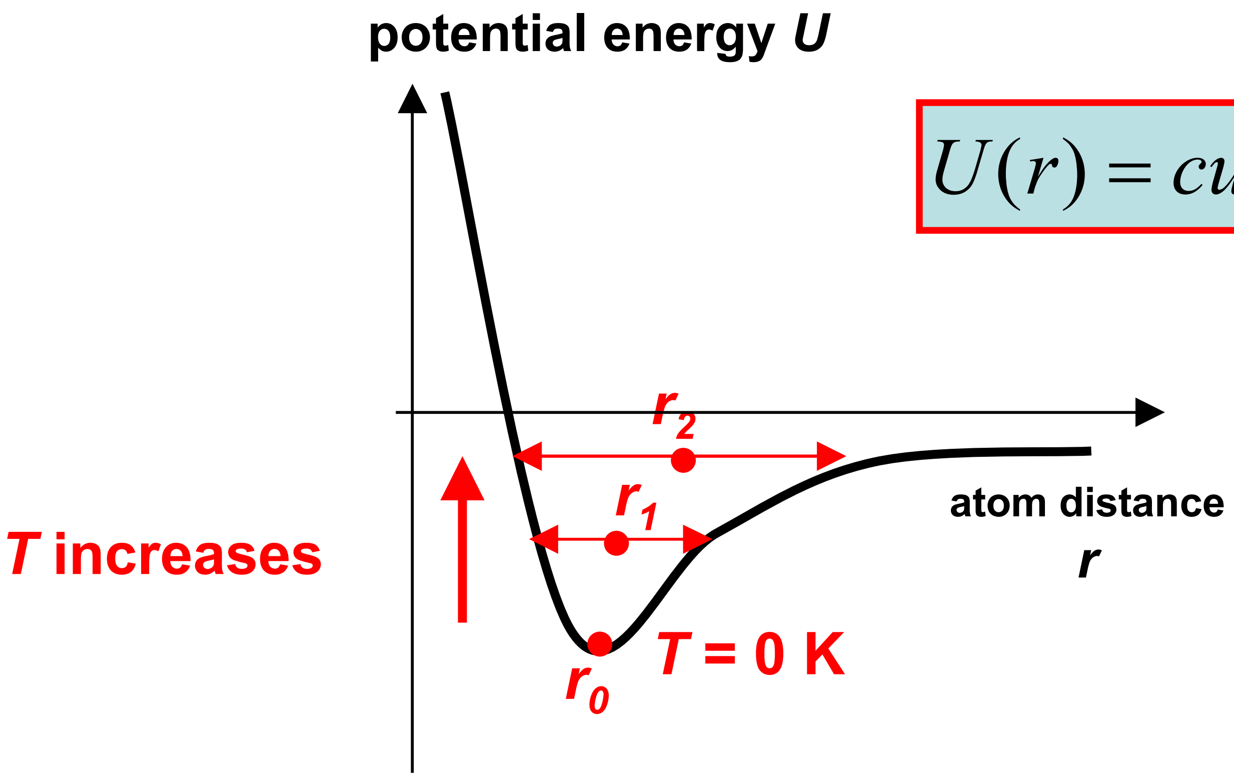


The Debye Model matches better with experimental results

Zhang Z.M. (2020) Thermal Properties of Solids and the Size Effect.
In: Nano/Microscale Heat Transfer. Mechanical Engineering Series. Springer, Cham.
https://doi.org/10.1007/978-3-030-45039-7_5

Thermal Expansion 热膨胀

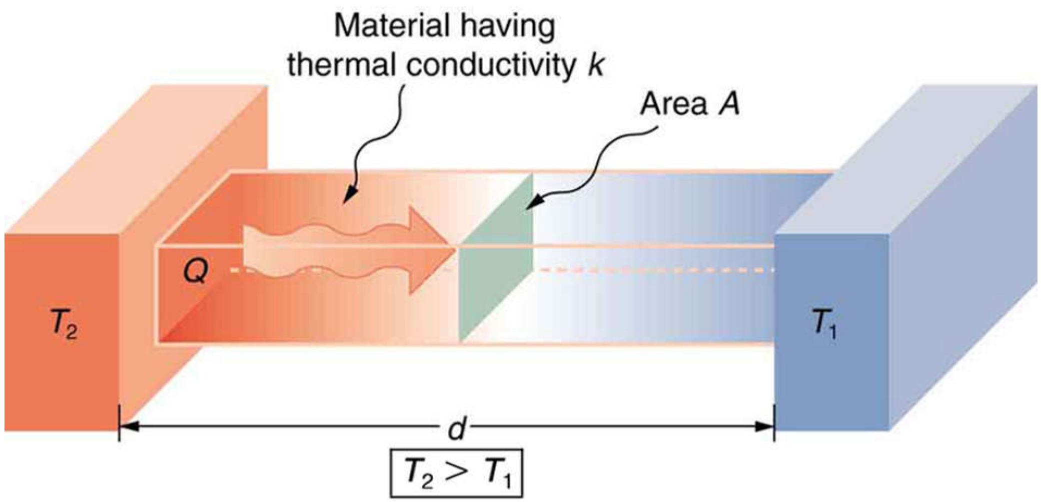
- Thermal expansion originates from the *anharmonic* nature of the potential
- Vibration increases with temperature



Thermal Conduction 热导

- **Fourier's Law**
  - **heat flux is proportional to the temperature gradient**

$$Q = -\kappa \cdot \frac{dT}{dx}$$



https://www.khanacademy.org

Q - heat flux (W/m^2)
κ - thermal conductivity (W/m/K)
T - temperature (K)

Thermal Conductivity 热导率

- **Thermal conductivity κ**

$$\kappa = \frac{1}{3} C_V v_g l = \frac{1}{3} C_V v_g^2 \tau_p$$

Ashcroft & Mermin, p20

C_V **- thermal capacity**
v_g **- sound speed**
l **- phonon mean free path**
τ_p **- phonon relaxation time**

l and τ_p **is dependent on crystal structure, defects, impurities, ...**

Q: Which material has the highest thermal conductivity?

Fundamentals of Solid State Physics

Thermal Properties of Free Electrons

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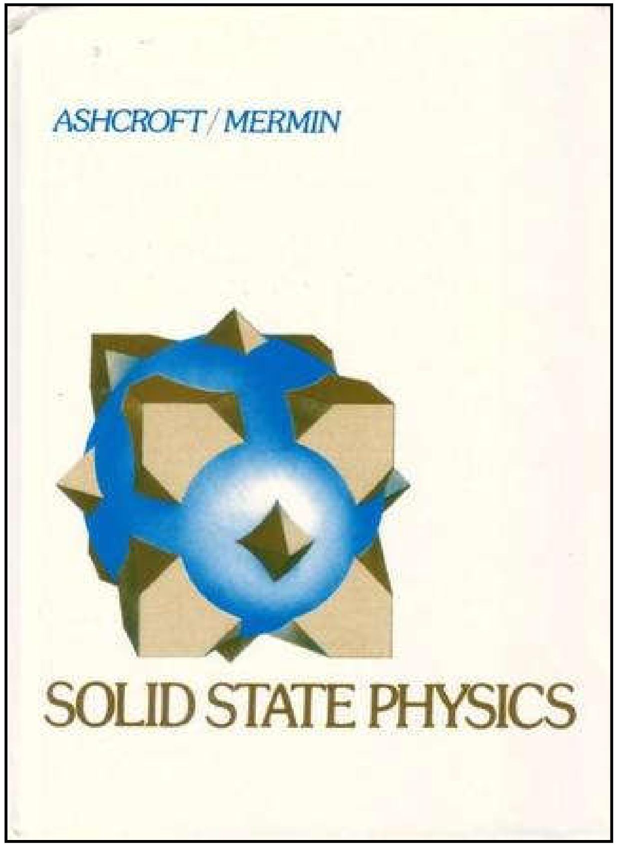
Review

- Lecture 3.1, Sommerfeld Model
- Ashcroft & Mermin, Chapter 2



Density of States (DOS) 态密度

$$g(E) = \frac{dn}{dE}$$

DOS - number of energy states/levels per unit energy in [*E*, *E*+*dE*], per unit volume

$$k = (3\pi^2 n)^{1/3}$$

$$E = \frac{\hbar^2 k^2}{2m_e}$$

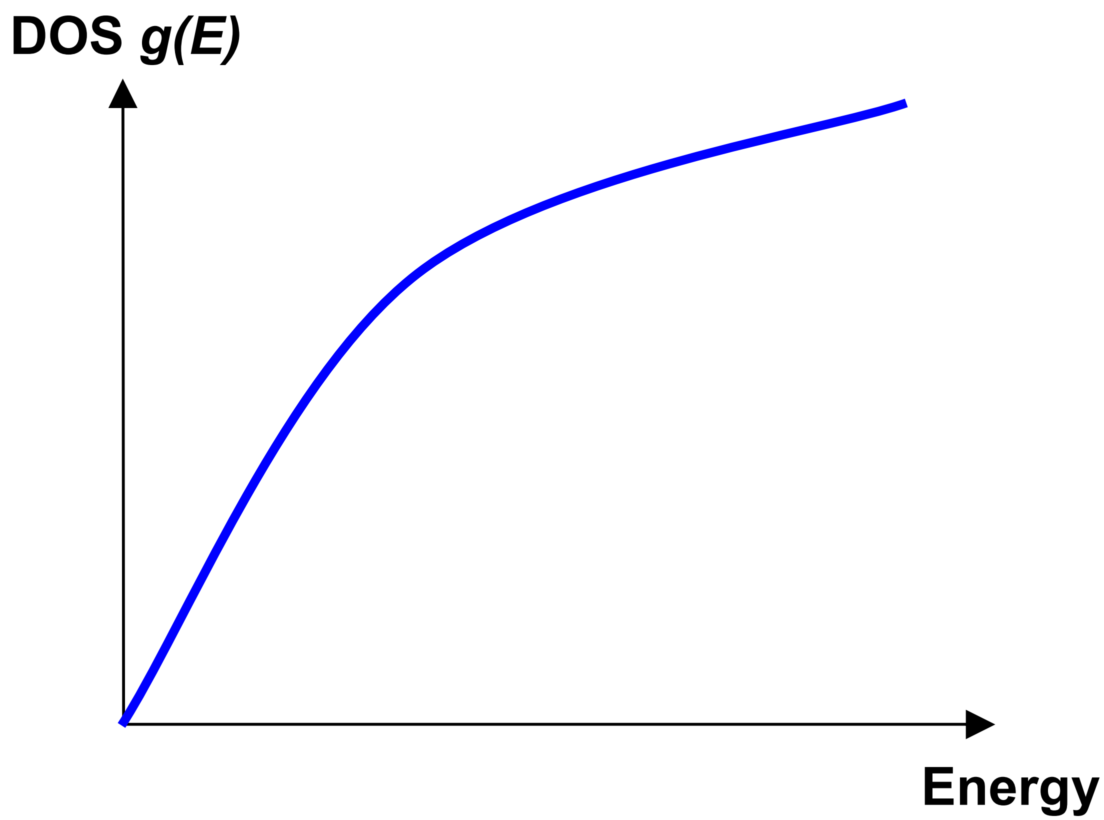
$$\rightarrow \quad n = \frac{1}{3\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} E^{3/2}$$

n **- free electron density**

$$\rightarrow \quad g(E) = \frac{dn}{dE} = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} E^{1/2}$$

Density of States (DOS) 态密度

$$g(E)=\frac{dn}{dE}=\frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}E^{1/2}$$



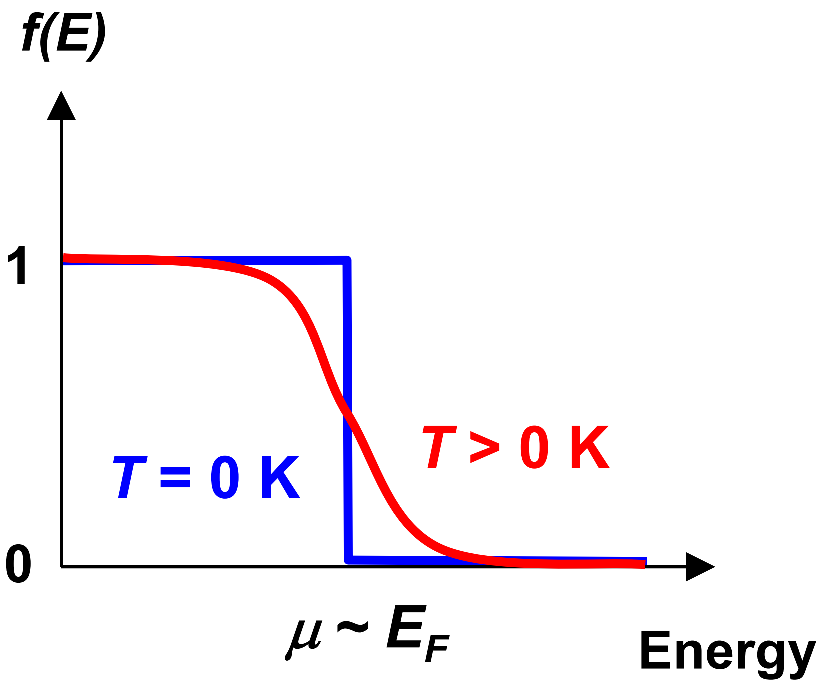
3D Free Electrons

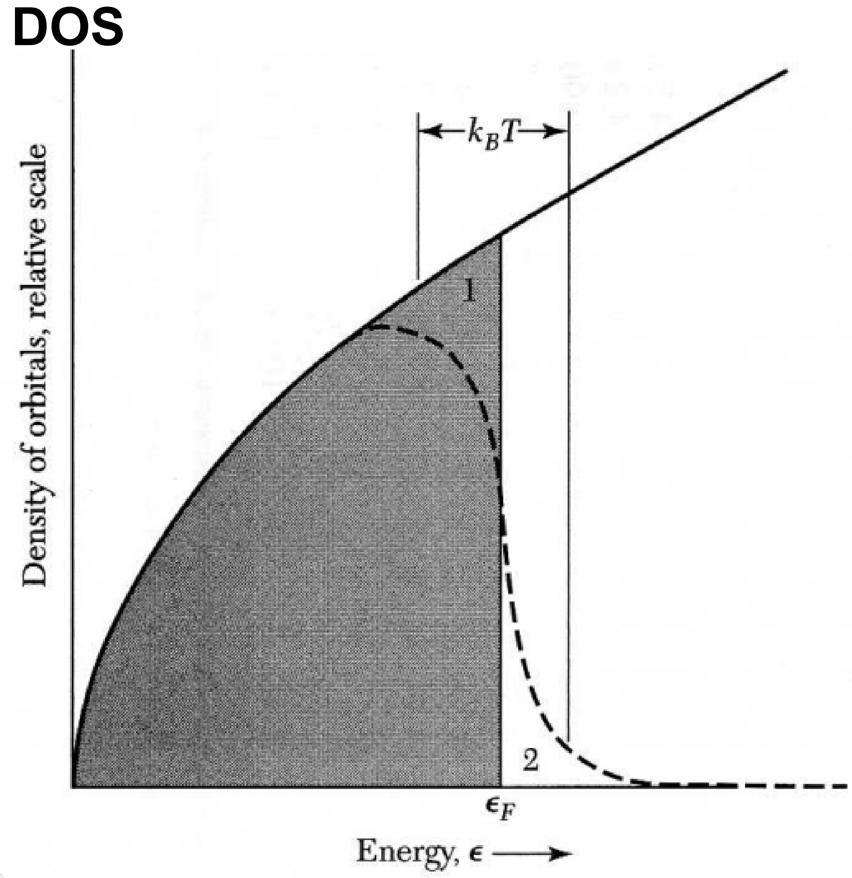
Density of Electrons

Density of electrons = DOS * probability

$$f(E)g(E)$$

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





When T > 0 K, some electrons are excited to higher states (from 1 to 2)

Internal Energy 内能

- Internal energy is the energy of all the free electrons

electron energy

$$U = \int_0^{+\infty} g(E) f(E) E dE$$

DOS

average electron number in each state (Fermi-Dirac Distribution)

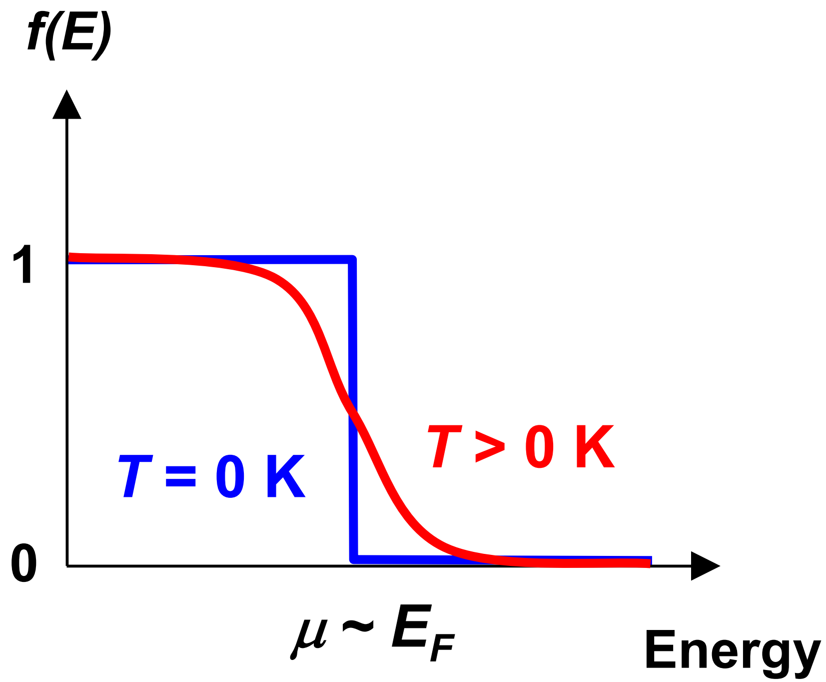
The Sommerfeld Model

Internal Energy 内能

- **When T = 0 K**

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

$$U_0=\int_0^{E_F} g(E)\cdot E dE$$
$$=\frac{3}{5}E_F$$



Homework 4.4

Heat Capacity C_V

- **When T > 0 K**

$$U = U_0 + \frac{\pi^2}{6}(k_B T)^2 g(E_F)$$

heat capacity

$$C_{V,e} = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\pi^2}{2}\frac{T}{T_F} n k_B \propto T$$

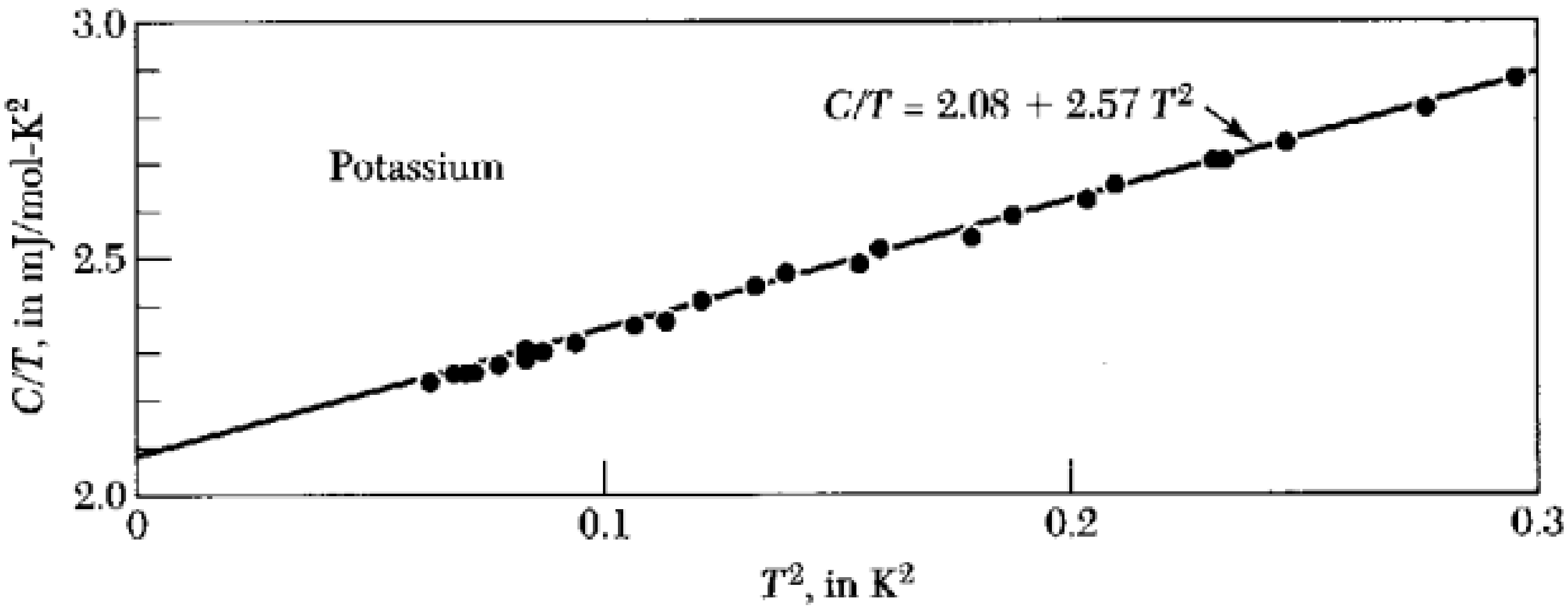
T_F - Fermi temperature (~10^4 K)

Only a few electrons around E_F contribute to $C_{V,e}$.
At room temperature, for free electrons $C_{V,e} \ll Nk_B$
much smaller than C_V from phonons

Heat Capacity C_V

- **For metals at very low temperature *T* ~ 0 K**
  - **Thermal properties = phonon part + free electron part**

$$C_V = C_{V,p} + C_{V,e} = AT^3 + \gamma T \quad \longrightarrow \quad C_V / T = AT^2 + \gamma$$



W. Lien and N. Phillips, *Phys. Rev.* **133,** A1370 (1964)

Thermal Conductivity 热导率

- **Thermal conductivity κ for free electrons**

$$\kappa_e = \frac{1}{3} C_V v_F l = \frac{1}{3} C_V v_F^2 \tau_e$$

Ashcroft & Mermin, p20

C_V - thermal capacity
v_F - Fermi velocity
l - electron mean free path
τ_e - electron relaxation time

Thermal Conductivity 热导率

- **Thermal conductivity κ for metals**

$$\kappa = \kappa_p + \kappa_e = \frac{1}{3} C_{V,p} v_g^2 \tau_p + \frac{1}{3} C_{V,e} v_F^2 \tau_e$$

For conductive metals like Cu or Ag, $v_F \gg v_g$
electron part dominates

Thermal Conductivity 热导率

- **Relationship of thermal conductivity κ and electron conductivity σ for certain metals**
  - **Lorentz number *L***

Homework 8.7

$$L = \frac{\kappa}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 2.44 \times 10^{-8}\ \mathrm{W \cdot \Omega / K^2}$$

Agree with experimental results (Wieddemann and Franz law in 1853)

metals at 300 K	Cu	Ag	Au	Al	Fe	Pb
L (10^{-8} W*Ω/K²)	2.30	2.31	2.35	2.23	2.47	2.45

Q: Which metal has the highest thermal conductivity?

Thermal Conductivity 热导率

	κ (W/m/K)
C (diamond)	2000
Cu	400
C (graphite)	~200
Si	130
glass	1
paper	0.05

Q: High thermal conductivities of diamond and graphite have different origins. Why?

Summary

- Thermal properties are the combinations of properties of lattice vibration (phonons) and free electrons

- For insulators, there are no free electron. Thermal properties of lattice vibration (phonons) dominate.

- For metals,

  thermal properties = phonon part + free electron part

  Thermal capacity $$C_V = C_{V,p} + C_{V,e}$$

  Thermal conductivity $$\kappa = \kappa_p + \kappa_e$$

Thank you for your attention