Fundamentals of Solid State Physics

Thermal Properties

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Thermal Properties

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

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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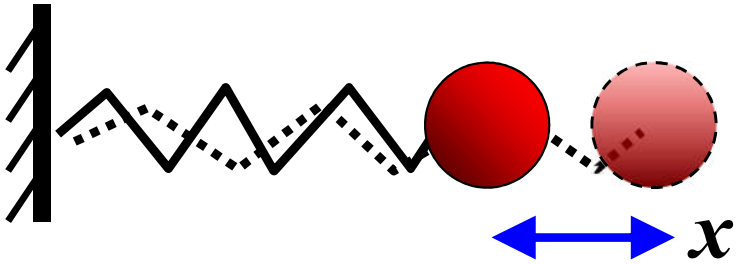
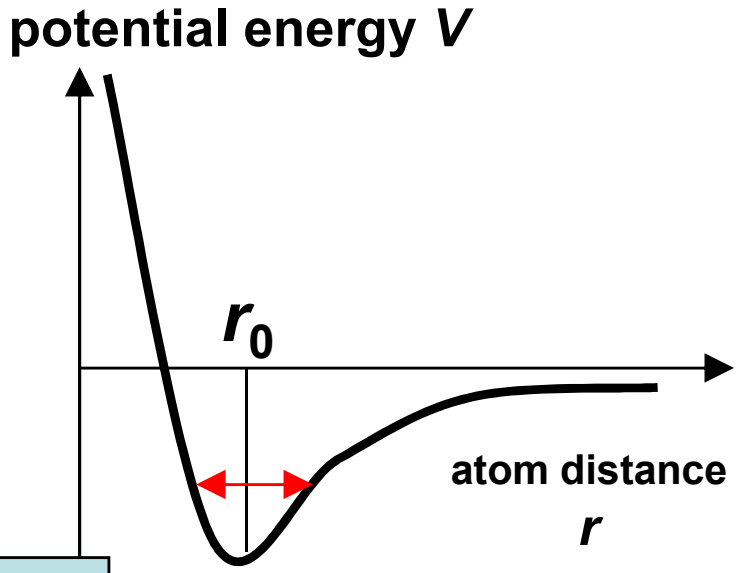
Harmonic Oscillator: Classical Theory

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





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

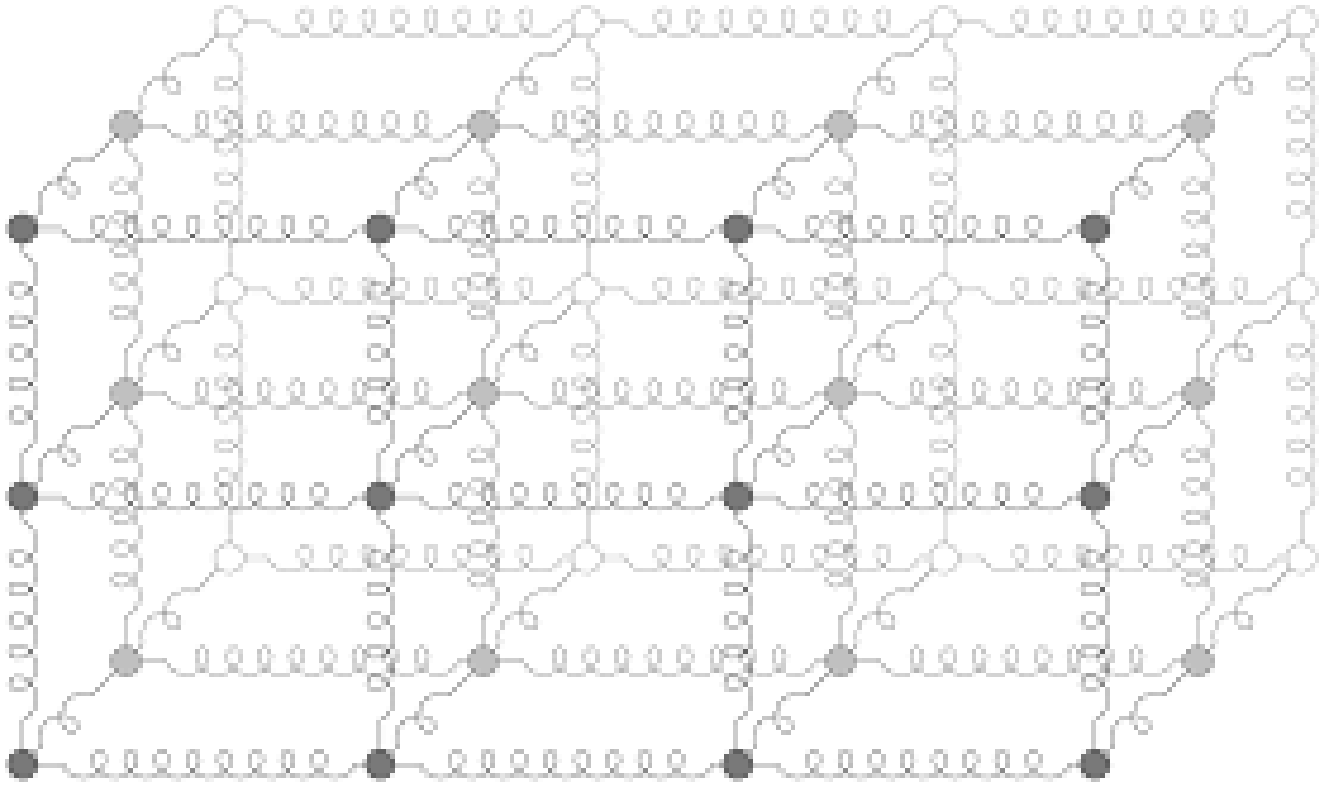
$$E = \frac{1}{2}Kx^2 + \frac{1}{2}mv^2 = \frac{1}{2}k_BT + \frac{1}{2}k_BT = k_BT$$

Thermal vibration around r_0

Energy Equipartition Theorem (能量均分定理)

Internal Energy 内能

- **Total vibration energy of a 3D crystal**
  - **all the springs + all the atoms in 3 directions = 3*NL***



Internal Energy 内能

- **Total vibration energy of a 3D crystal**
  - **all the springs + all the atoms in 3 directions = 3*NL***

$$U = 3NLk_BT$$

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

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

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

Dulong–Petit Law

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

Heat Capacity C_V in different units

- **Example: Copper at room temperature**
  - **Dulong–Petit Law ($3k_B$)**

$$C_V = 3k_B = 4.14 \times 10^{-23}\ \text{J/K/atom}$$ per atom

$$C_V = 3k_B N_A = 24.9\ \text{J/K/mol}$$ per mole

$$C_V = 24.9\ \text{J/K/mol} \div 0.064\ \text{kg/mol} = 389\ \text{J/K/kg}$$ per unit mass

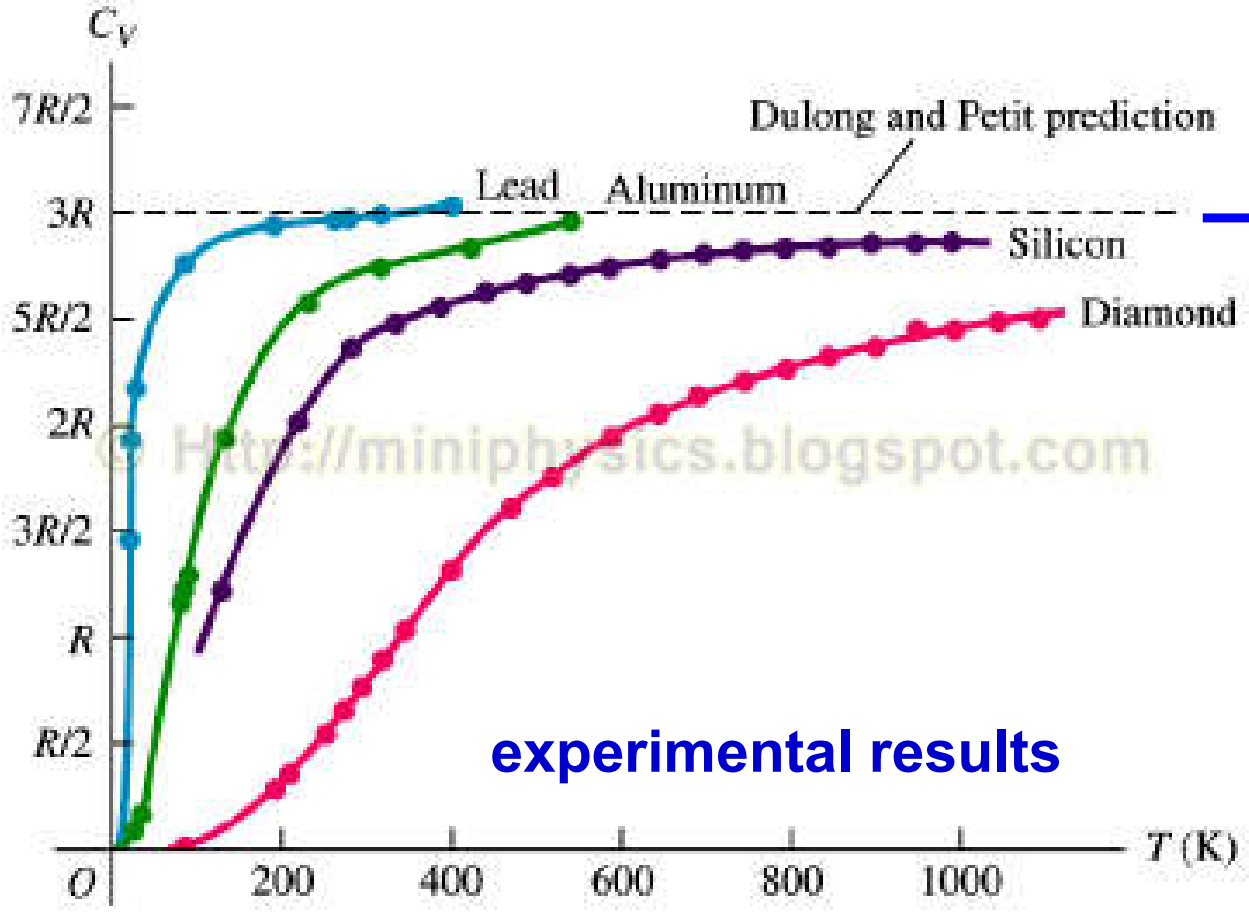
$$C_V = 389\ \text{J/K/kg} \times 8960\ \text{kg/m}^3 = 3.49 \times 10^6\ \text{J/K/m}^3$$ per unit volume

Molar mass of Cu = 64 g/mol
Density of Cu = 8.96 g/cm^3

Heat Capacity C_V

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

Dulong–Petit Law

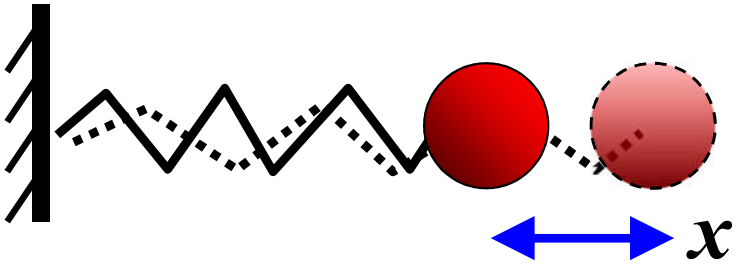


experimental results

The classical model is only valid at high temperatures, but cannot explain the results at low temperatures

Harmonic Oscillator: Quantum Theory

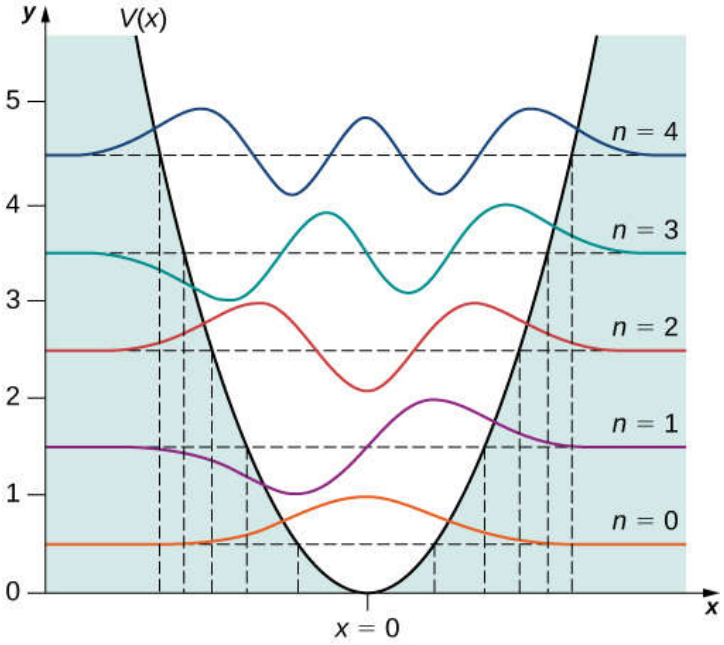
$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)+V(x)\cdot\psi(x)=E\psi(x)$$



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

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

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



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 ($\hbar\omega$)

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

  - average n in each state follows Bose-Einstein distribution

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

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

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

quasi-continuous states

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, $T \gg 0$ K**

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

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

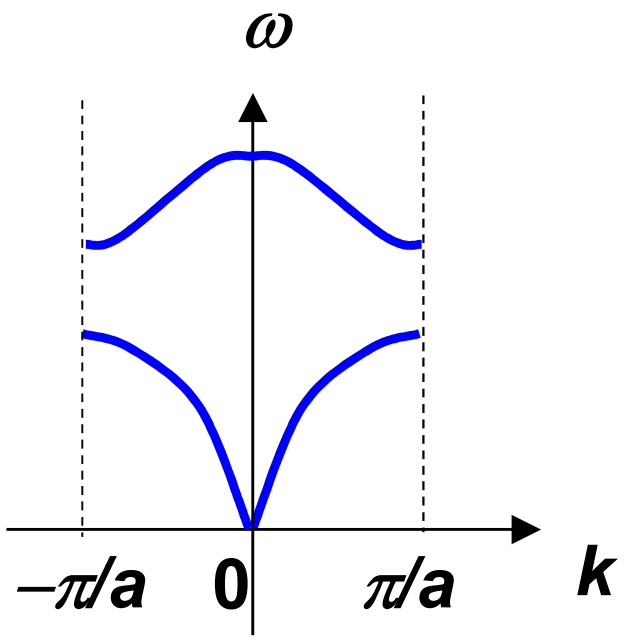
Dulong–Petit Law

Heat Capacity C_V

- **At low and medium temperatures**

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

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



Calculate DOS based on the phonon diagram

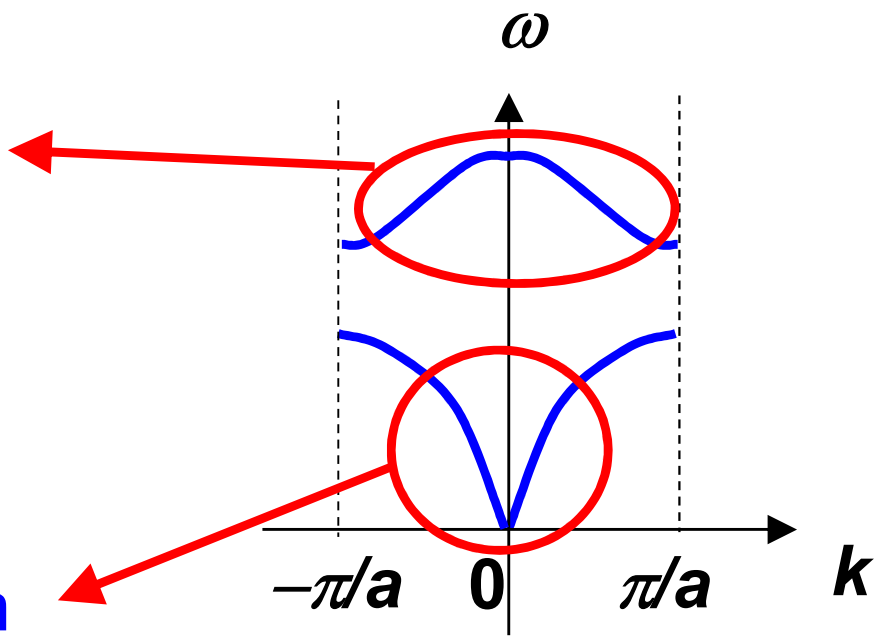
Heat Capacity C_V

- 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:

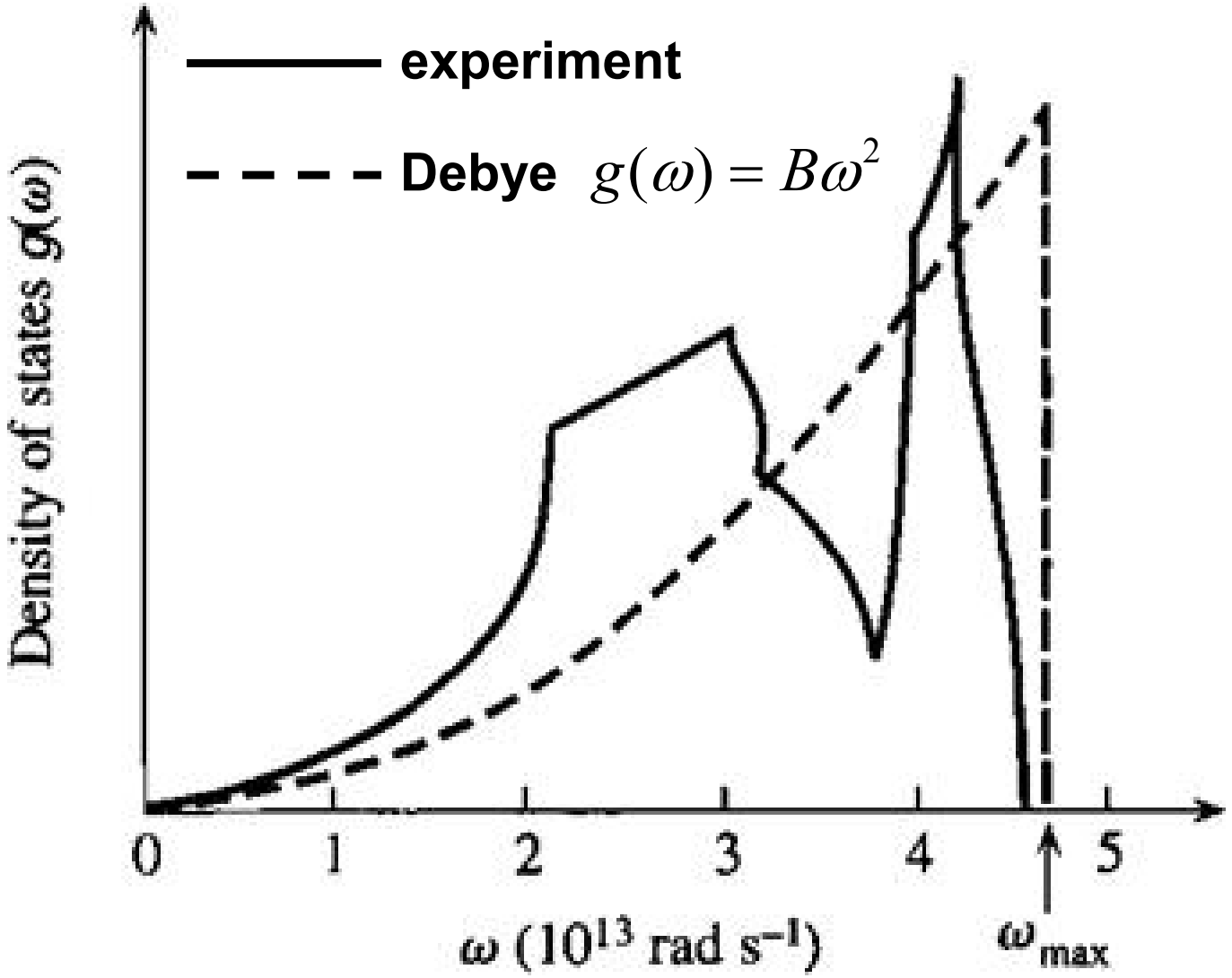
assume linear ω-k relation

The Debye Model (德拜模型)

$$g(\omega) = B\omega^2$$

Phonon Density of States $g(\omega)$

DOS for copper



Heat Capacity C_V

- **The Debye Model for the acoustic branch**

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

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

At very low temperature, *T* --> 0 K

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

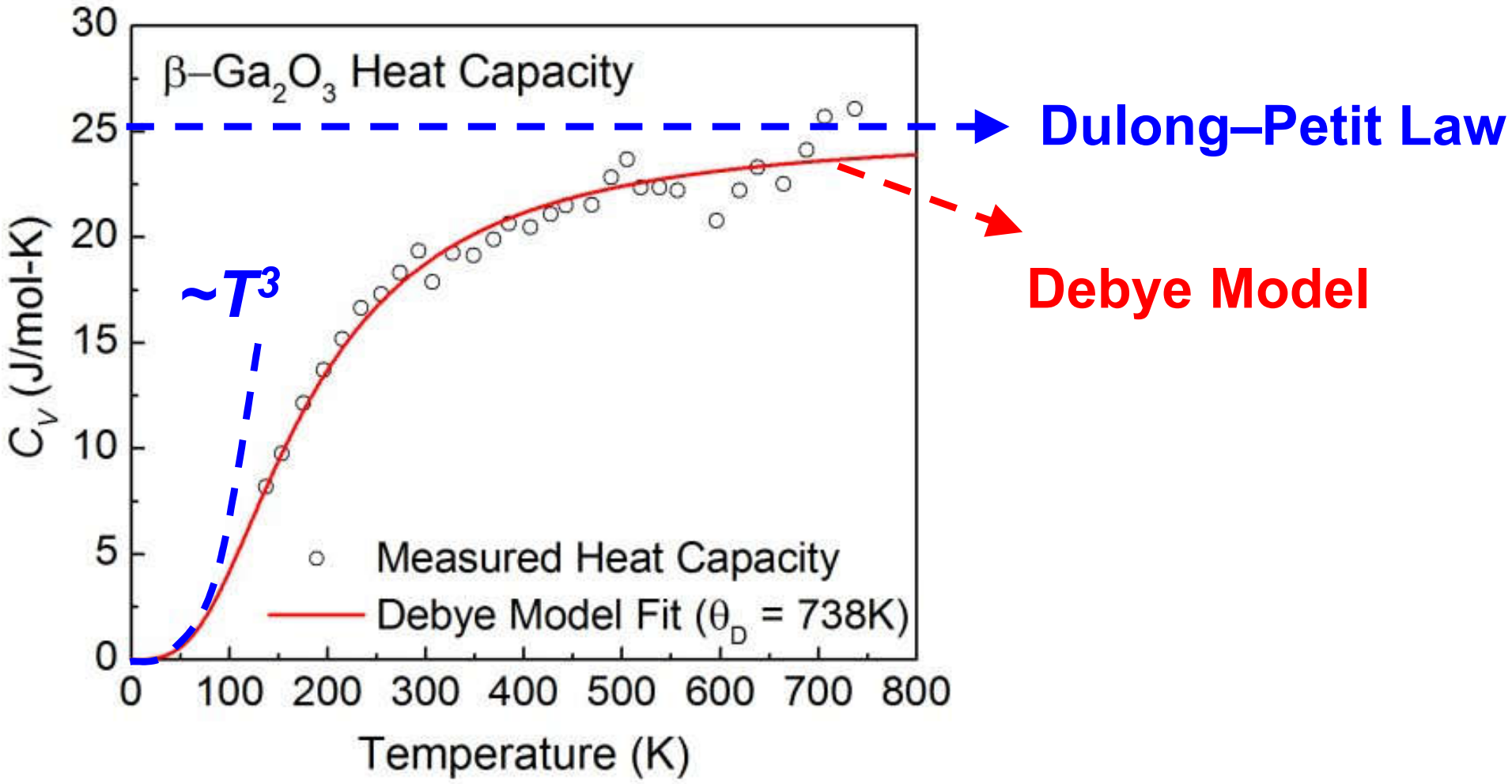
- **The Debye Model** for the acoustic branch
- **Debye Temperature** is around room temperature for most materials

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

	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 - Example



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

Heat Capacity C_V

- **The Einstein Model assumes all the phonons in an optical branch have frequency ω_0**

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

heat capacity (for 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

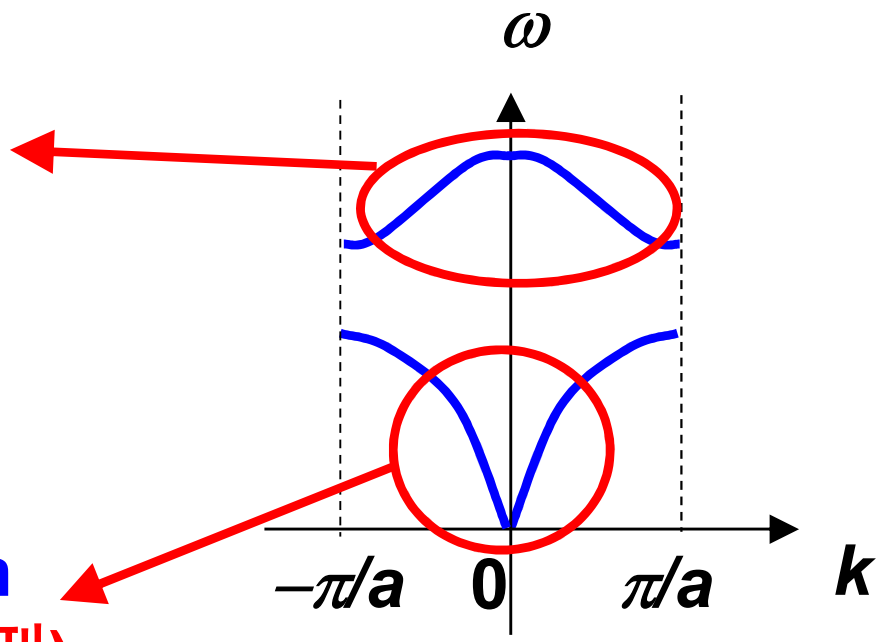
- **Heat capacity is the combination of all the acoustical and optical phonons**

$$C_V = C_{V,acoustic} + C_{V,optical}$$

For optical phonons:

assume all the phonons have the same ω_0

The Einstein Model (爱因斯坦模型)



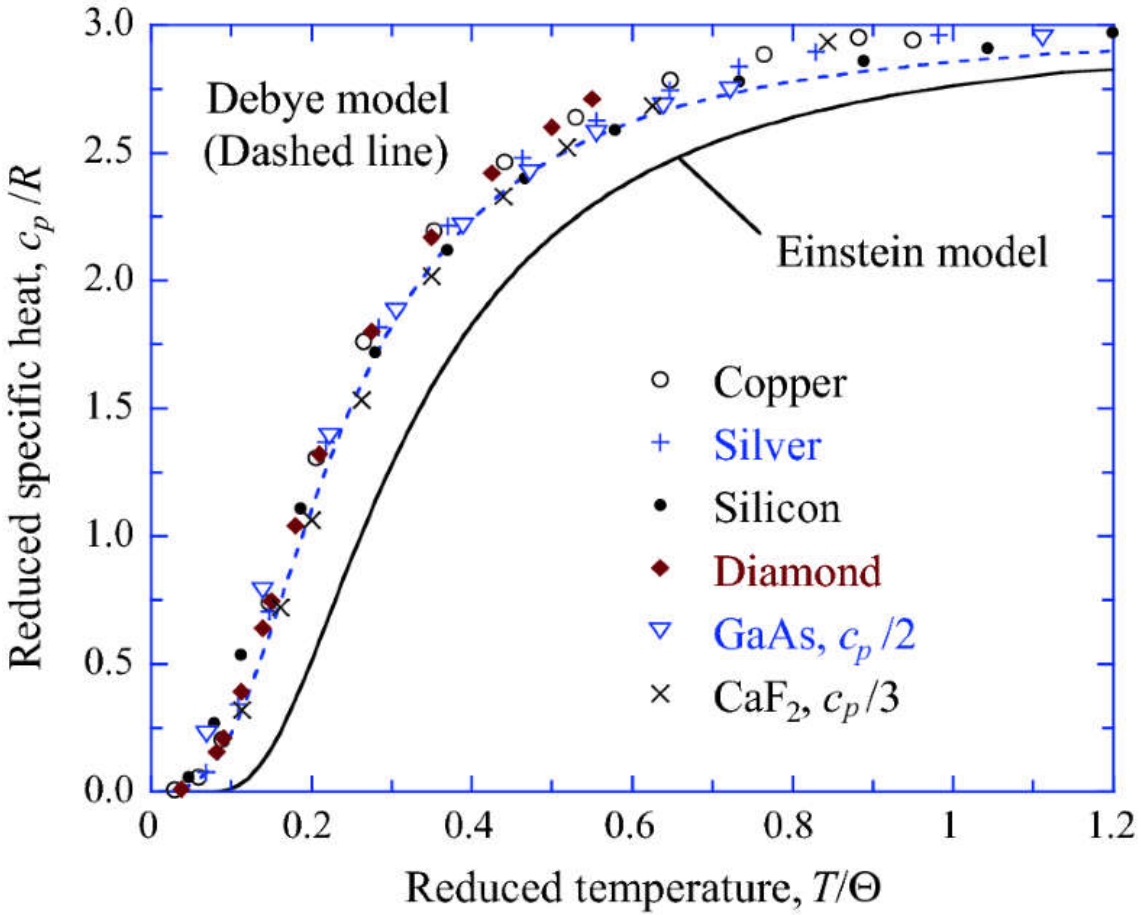
For acoustic phonons:

assume linear ω-k relation

The Debye Model (德拜模型)

$$g(\omega) = B\omega^2$$

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

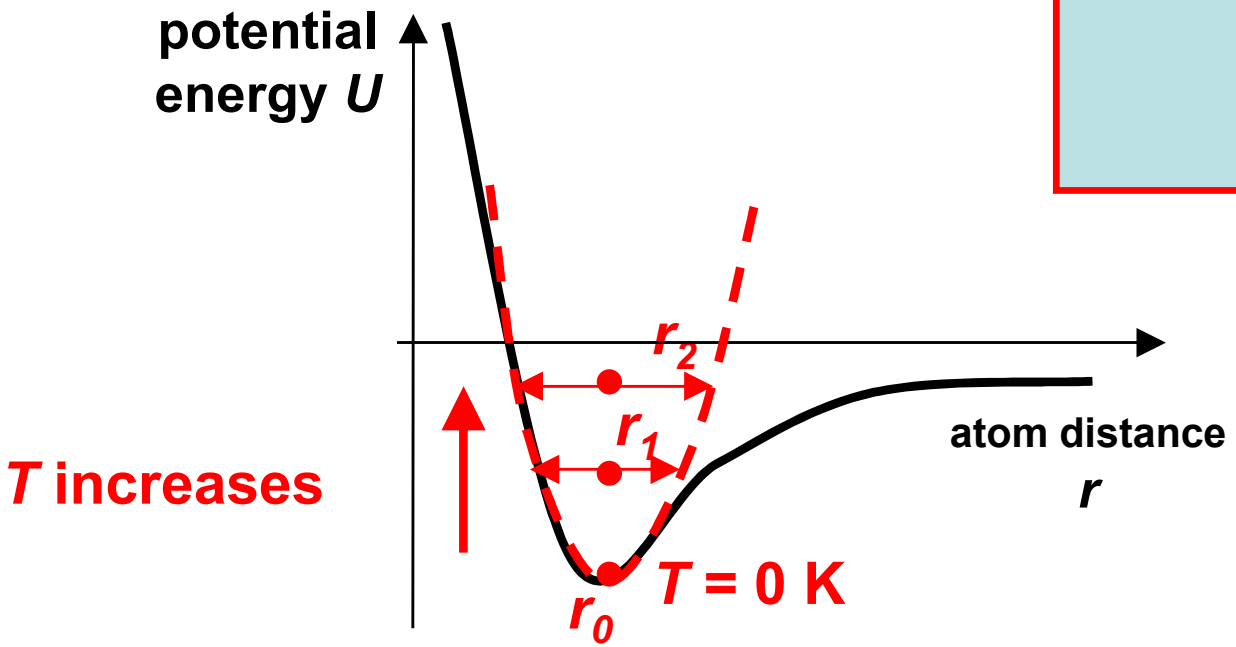
Thermal Properties

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

Thermal Expansion 热膨胀

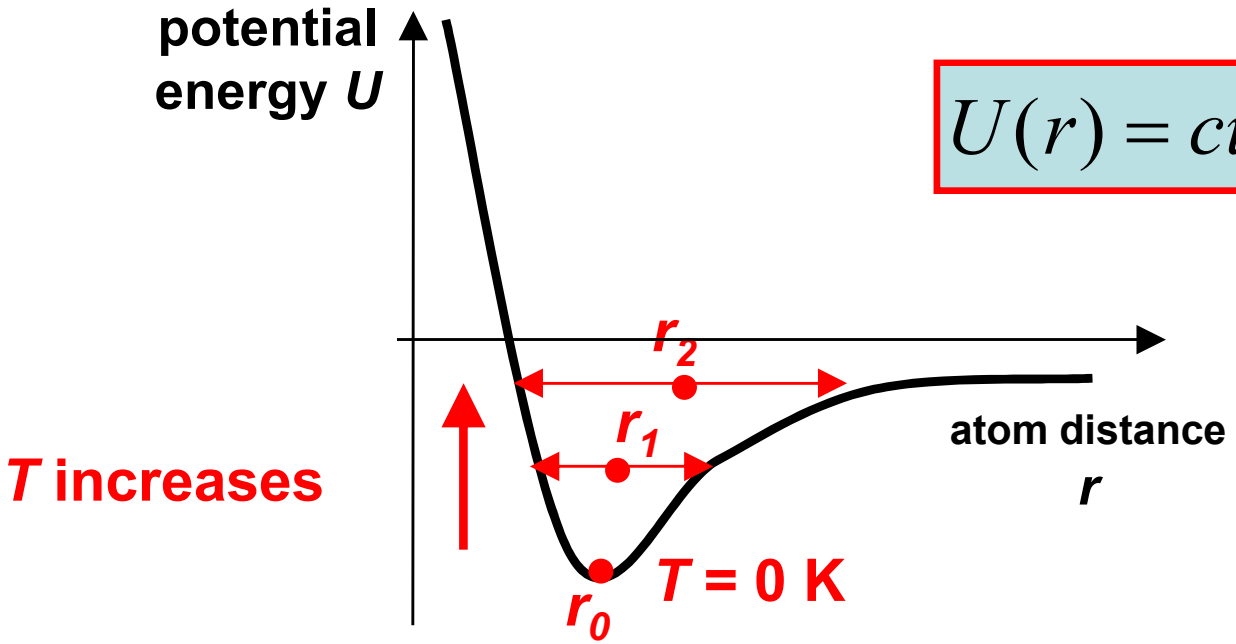
- **Thermal expansion cannot be explained by the harmonic approximation**

$$U(r) = U_0 + \frac{1}{2}K(r - r_0)^2$$
$$= U_0 + \frac{1}{2}K \cdot u^2$$



Thermal Expansion 热膨胀

- Thermal expansion cannot be explained by the harmonic approximation
- Thermal expansion originates from the *anharmonic* nature of the potential
- Vibration increases with temperature

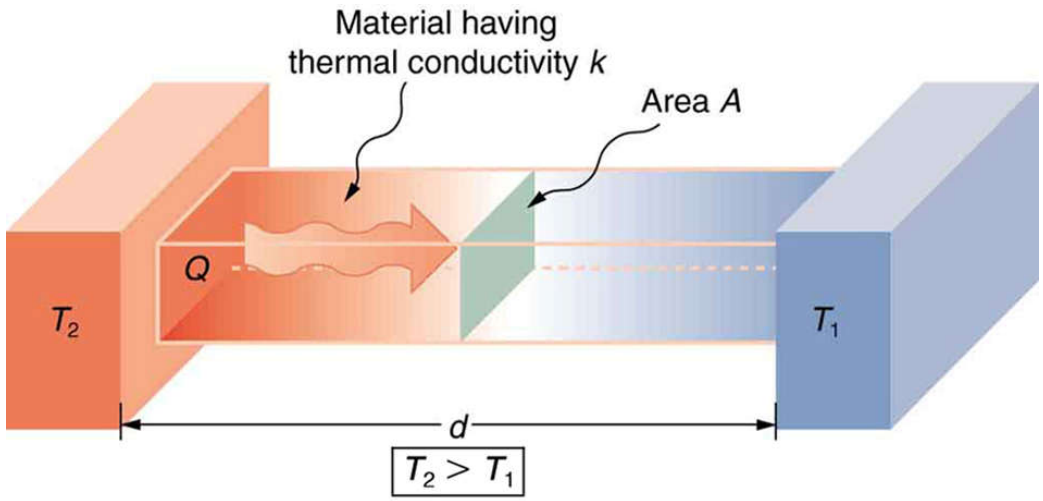


$$U(r) = cu^2 - gu^3 - fu^3 - \ldots$$

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**

$$l = v_g \tau_p$$

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

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?

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 of Free Electrons

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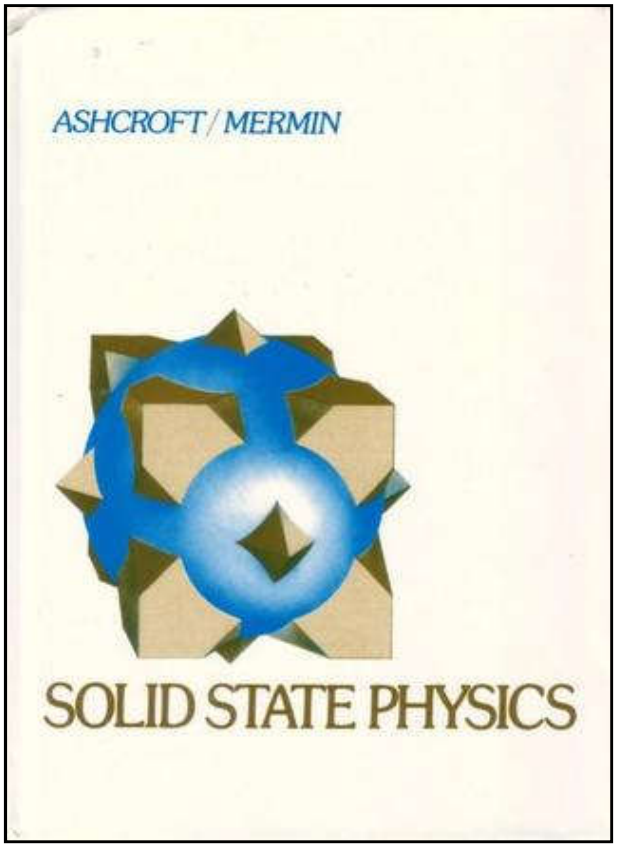
Review

- 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

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

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

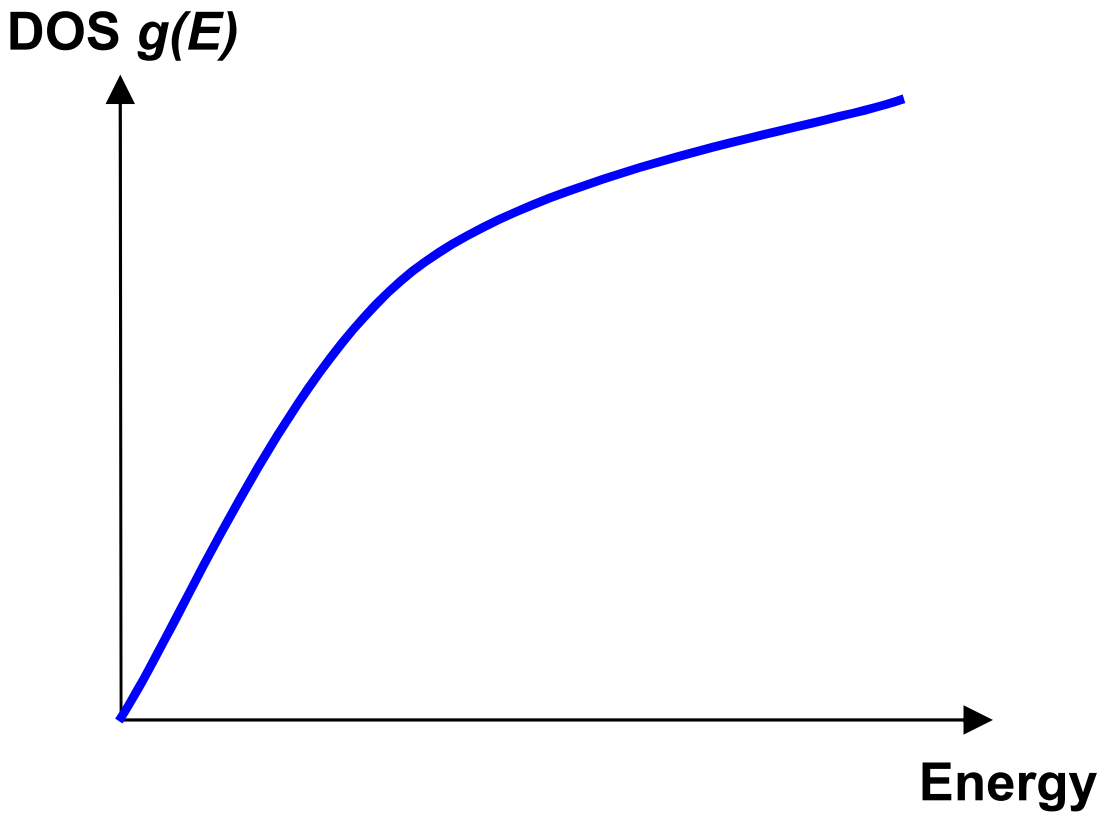
$$\rightarrow \quad n = \frac{1}{3\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} E^{3/2}$$

***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

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



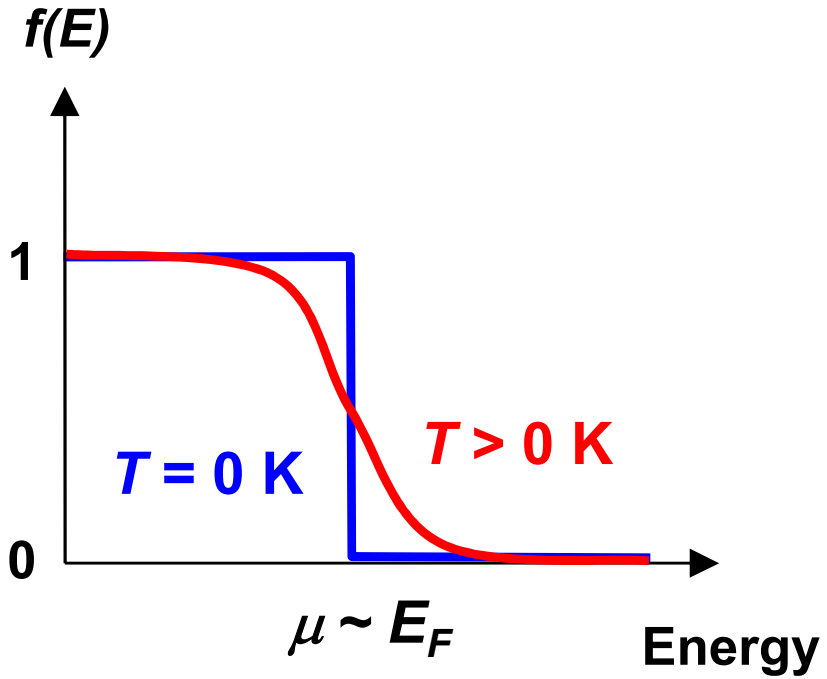
3D Free Electrons

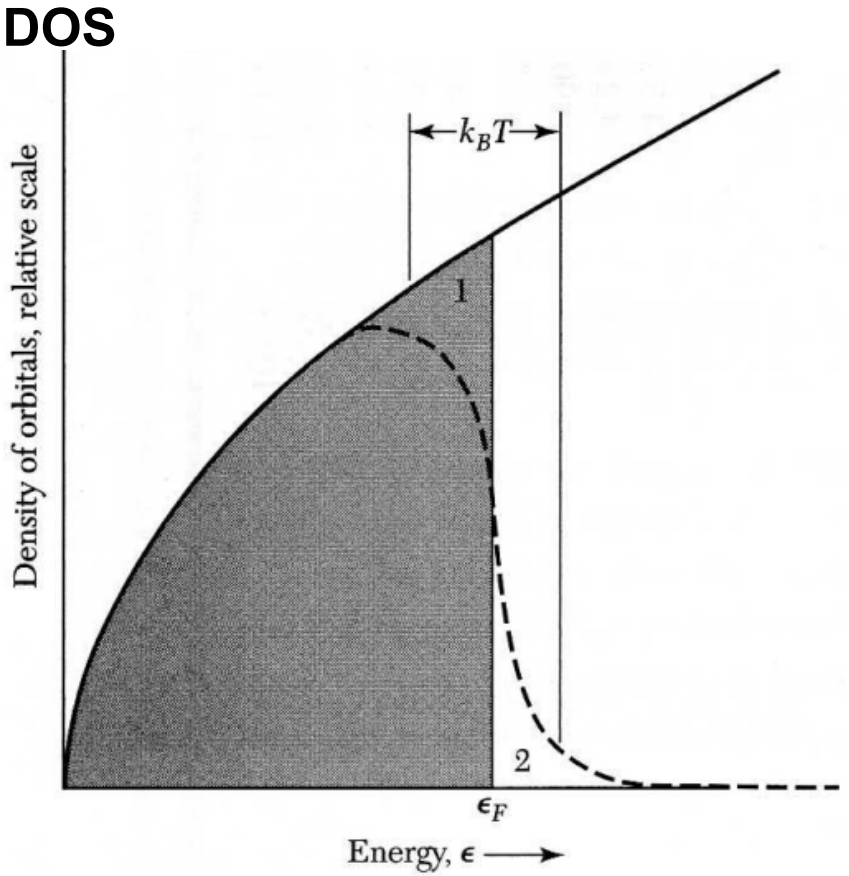
Density of Electrons

Density of electrons = DOS * probability

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

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

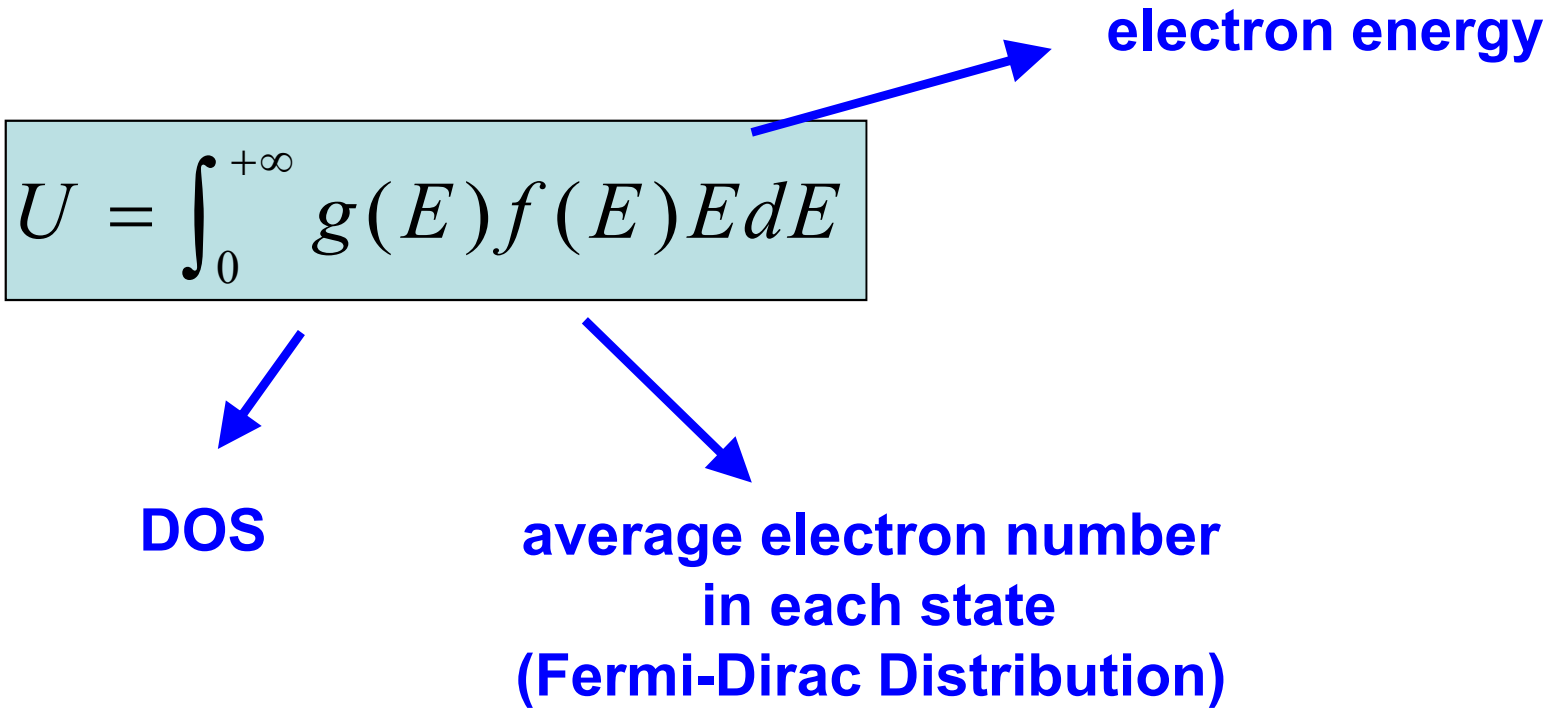




When $T > 0$ K, some electrons are excited to higher states (from 1 to 2)

Internal Energy 内能

- **Internal energy is the energy of all the free electrons**



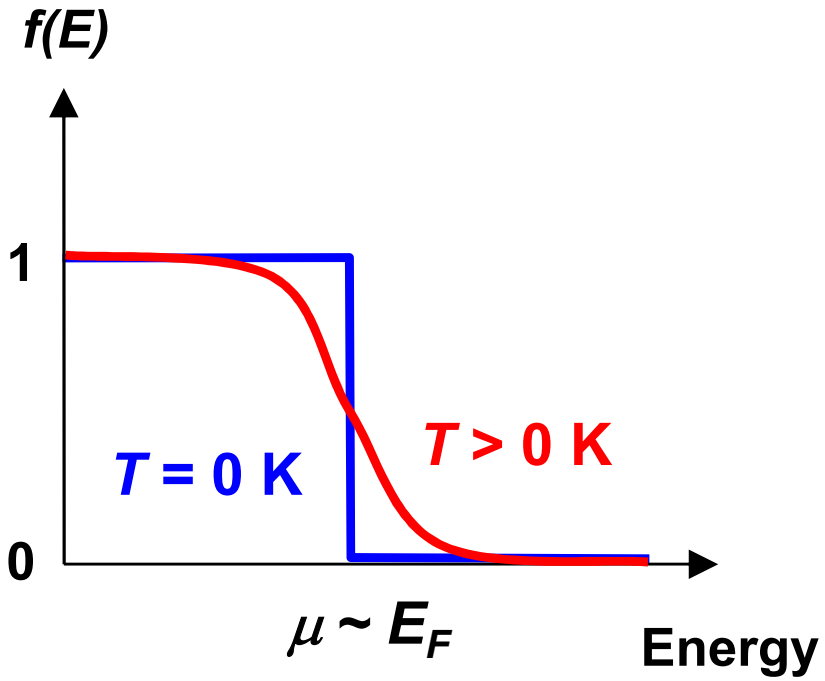
The Sommerfeld Model

Internal Energy 内能

- When $T = 0$ K

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

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



Homework 4.4

Heat Capacity C_V

- When $T > 0$ K

Ashcroft & Mermin, p46

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

heat capacity

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

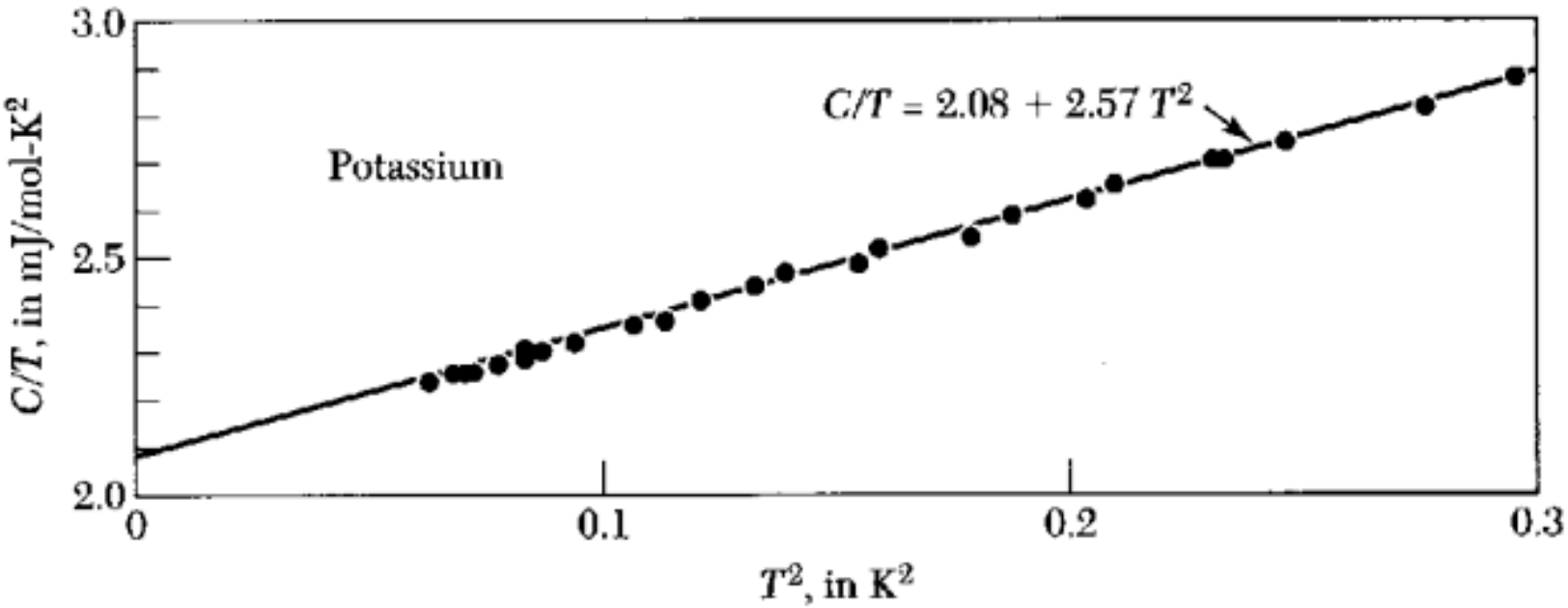
T_F - Fermi temperature (~10^4 K)

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

Heat Capacity C_V

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

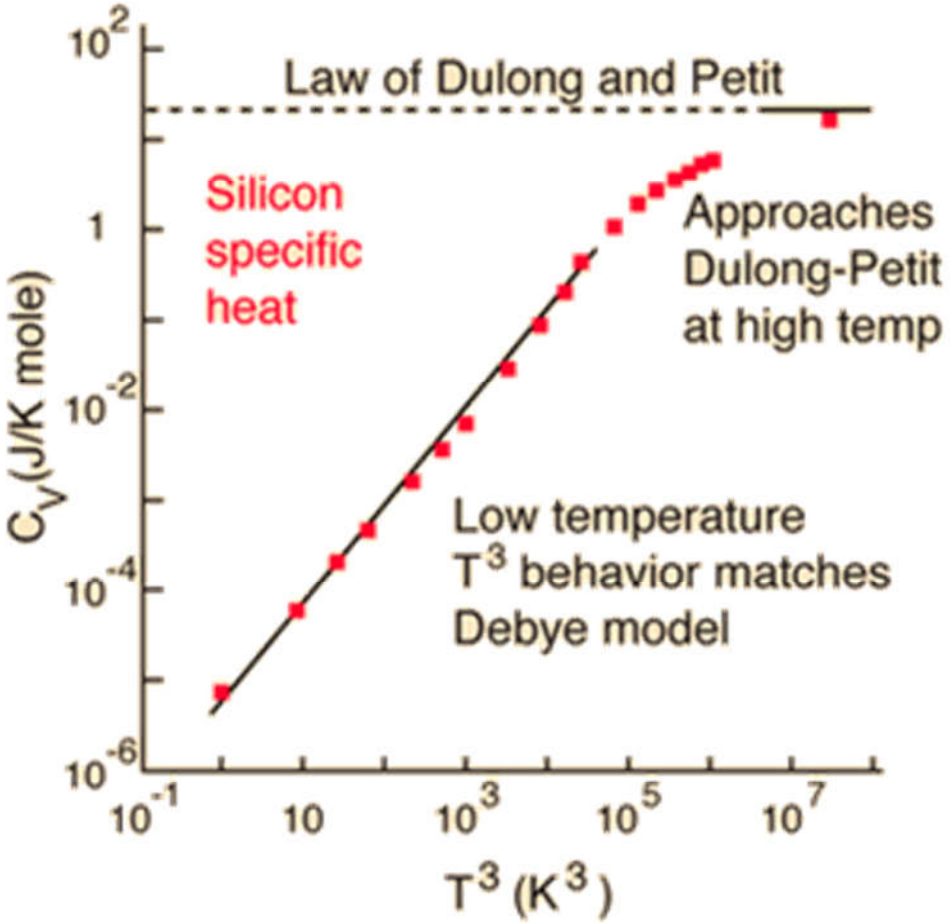
$$C_V = C_{V,p} + C_{V,e} = AT^3 + \gamma T \quad \rightarrow \quad C_V / T = AT^2 + \gamma$$

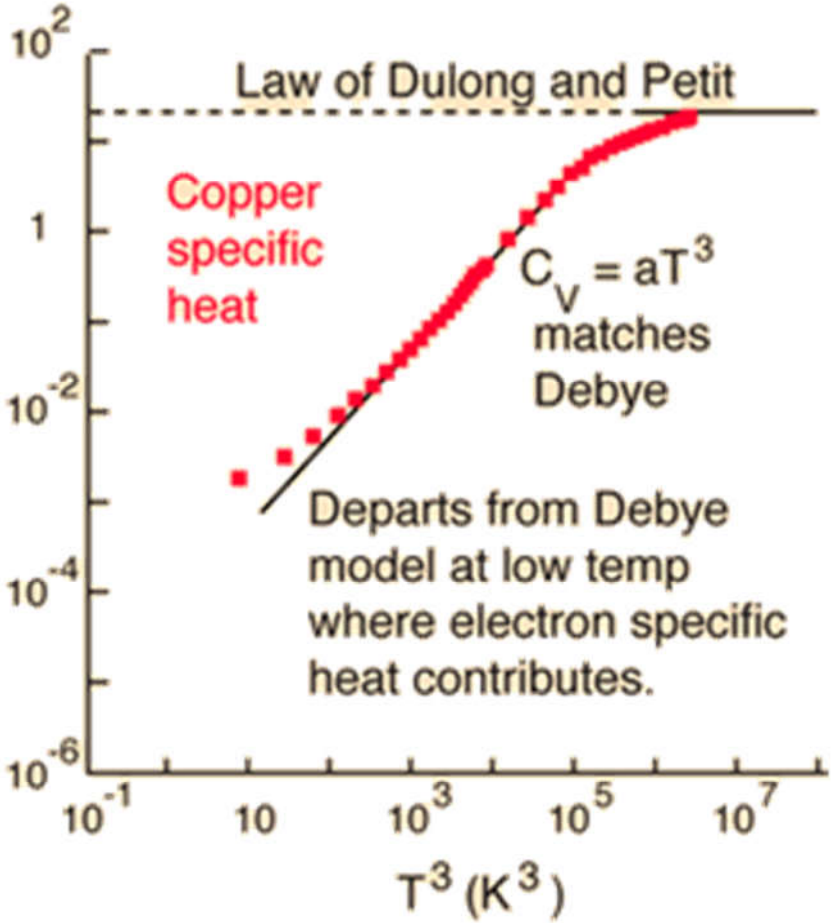


W. Lien and N. Phillips, *Phys. Rev.* **133,** A1370 (1964)

Heat Capacity C_V

- **More examples**
  - **silicon vs. copper**





after Rohlf

http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/Dulong.html

Thermal Conductivity 热导率

- **Thermal conductivity κ for free electrons**

$$\kappa_e = \frac{1}{3} C_{V,e} v_F l = \frac{1}{3} C_{V,e} v_F^2 \tau_e$$

$$l = v_F \tau_e$$

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, $v_F >> v_g$ electron part dominates

Thermal Conductivity 热导率

- Ratio of thermal conductivity κ and electron conductivity σ for certain metals is a constant
  - Lorentz number *L*

$$L = \frac{\kappa}{\sigma T}$$

Wieddemann and Franz law in 1853

metals at 300 K	Cu	Ag	Au	Al	Fe	Pb
L (10^{-8} W*Ω/K^2)	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

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

metals at 300 K	Cu	Ag	Au	Al	Fe	Pb
L (10^{-8} W*Ω/K^2)	2.30	2.31	2.35	2.23	2.47	2.45

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

Homework 8.7

Not correct for most other materials, because only the free electron part satisfies this.

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