Outline

- **Chapter 3.1** Classical Lattice Vibrations (晶格振动的经典理论)
- **Chapter 3.2** Phonons (声子)
- **Chapter 3.3** Phonon Heat Capacity (声子热容)
- **Chapter 3.4** Anharmonicity (非谐效应)

Objectives

- To learn the **classical theory** of heat capacity in solids.
- To learn the **quantum theory** of heat capacity in solids.
- To understand the **Einstein mode**l and **Debye model**.

Classical Theory of Heat Capacity in Solids
(固体热容的经典理论)

➢ Heat Capacity (热容)

❖ **Heat capacity** is the amount of heat ($\boldsymbol{Q}$) needed to raise the temperature of an object to a certain range. In unit of **J/K**.

- **Heat Capacity at Constant Volume (定容热容):** $$\boldsymbol{C_V = \left(\frac{\partial Q}{\partial T}\right)_V}$$
- **Heat Capacity at Constant Pressure (定压热容):** $$\boldsymbol{C_P = \left(\frac{\partial Q}{\partial T}\right)_P}$$
- **Specific Heat Capacity (比热容)**: The heat capacity per unit mass of a material.
- **Molar Heat Capacity (摩尔热容)**: The heat capacity per unit amount of a pure material.

➢ Heat Capacity in Solids (固体热容)

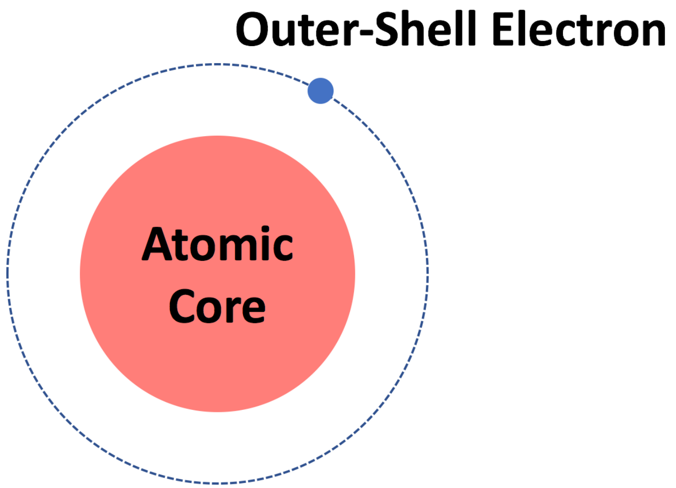
❖ The contributions to heat capacity in solids:

- **Lattice Vibrations** (晶格振动)

Have a **major contribution** at normal (not too low) temperatures.

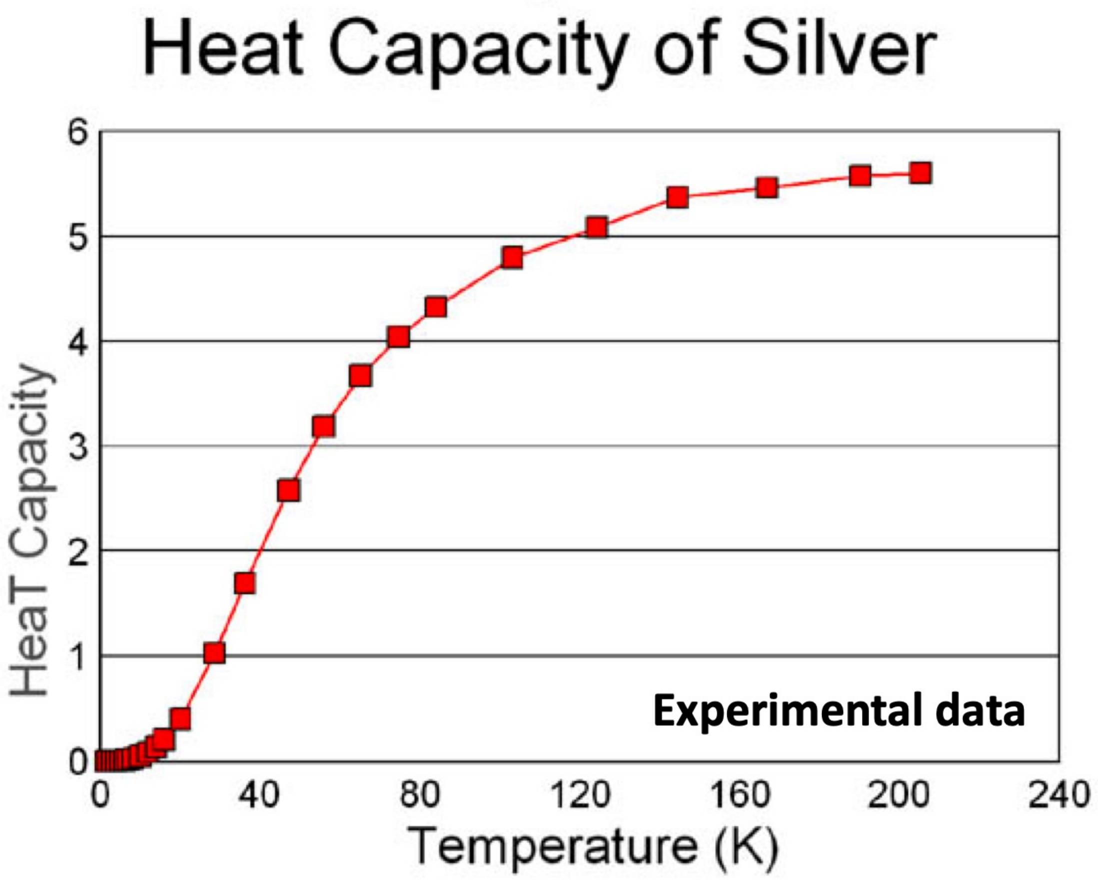
- **Electron Motions (电子运动)**

Have little contribution except **at extremely low temperature (e.g., $T < 3\text{K}$)**.



Heat Capacity in Solids (固体热容)

- Temperature dependence of heat capacity in solids:



Chapter 3.3: Phonon Heat Capacity (声子热容)

➢ Classical Theory of Heat Capacity in Solids (固体热容的经典理论)

❖ Dulong-Petit Law (杜隆-珀蒂定律)

For a 3D lattice with $\boldsymbol{N}$ atoms, the heat capacity is:

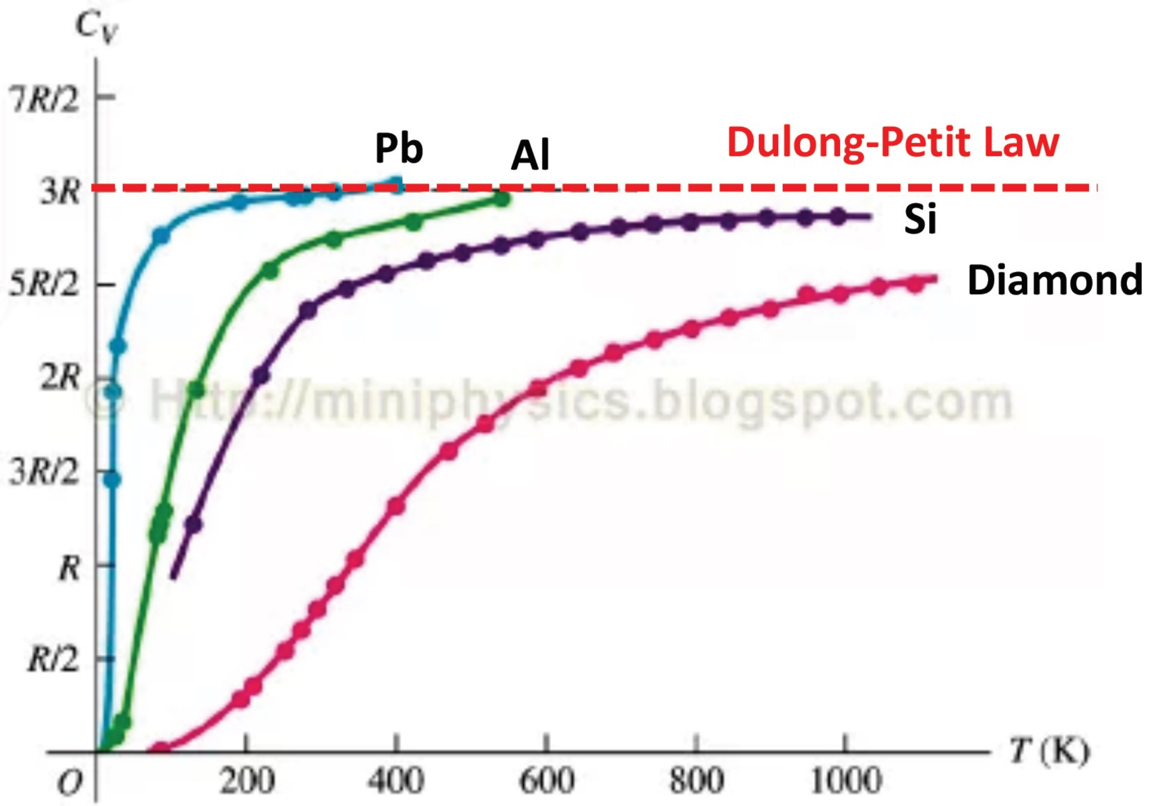
$$\boldsymbol{C_V = 3Nk_{\mathrm{B}}}$$

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial \overline{E}}{\partial T}\right)_V$$

$\overline{E} = 3Nk_{\mathrm{B}}T$ denotes the **average internal energy** (平均内能) of the lattice.

➢ Classical Theory of Heat Capacity in Solids (固体热容的经典理论)

❖ Dulong-Petit Law (杜隆-珀蒂定律)



The gas constant
$R = N_A k_B$

Quantum Theory of Heat Capacity in Solids
(固体热容的量子理论)

➢ Quantum Theory of Heat Capacity in Solids (固体热容的量子理论)

❖ For a 3D lattice with $\boldsymbol{N}$ atoms, in the harmonic approximation, the lattice vibrations can be described in terms of $\boldsymbol{3N}$ independent vibration modes (harmonic oscillators), of which the energies are quantized:

$$\boldsymbol{E_{n_j} = \left(n_j + \frac{1}{2}\right)\hbar\omega_j \qquad n_j = 0, 1, 2, 3, \cdots}$$

$$\boldsymbol{j = 1, 2, 3, \cdots, 3N}$$

➢ Quantum Theory of Heat Capacity in Solids (固体热容的量子理论)

❖ The **average energy** of the jth vibration mode:

$$\overline{E}_j = \frac{1}{2}\hbar\omega_j + \langle n_j \rangle \hbar\omega_j = \frac{1}{2}\hbar\omega_j + \frac{\hbar\omega_j}{\mathrm{e}^{\beta\hbar\omega_j} - 1}$$

Here $\beta = \frac{1}{k_{\mathrm{B}}T}$

❖ The **total average energy** of the lattice vibrations:

$$\overline{E} = \sum_{j=1}^{3N} \overline{E}_j$$

➢ Quantum Theory of Heat Capacity in Solids (固体热容的量子理论)

❖ The heat capacity as a result of lattice vibrations can be obtained as:

$$\boldsymbol{C_V = \left(\frac{\partial \overline{E}}{\partial T}\right)_V = \sum_{j=1}^{3N} \frac{d\overline{E}_j}{dT} = \boxed{\int_0^{\omega_{\max}} k_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} g(\omega)\mathrm{d}\omega}}$$

$g(\omega)$ denotes the **density of states (态密度)** of the vibration modes and satisfies:

$$\int_0^{\omega_{\max}} g(\omega)\mathrm{d}\omega = 3N$$

➢ Quantum Theory of Heat Capacity in Solids (固体热容的量子理论)

❖ The characteristics of $\boldsymbol{C_V}$ in **limiting cases (极限情况)**:

- High-temperature limit ($\boldsymbol{\beta\hbar\omega} \ll \mathbf{1}$):

$$C_V \approx \int_0^{\omega_{\max}} k_{\mathrm{B}}(\beta\hbar\omega)^2 \frac{1}{(1+\beta\hbar\omega-1)^2} g(\omega)\mathrm{d}\omega = \boldsymbol{3Nk_B}$$

(Dulong-Petit Law)

- Low-temperature limit ($\boldsymbol{\beta\hbar\omega} \gg \mathbf{1}$):

$$C_V \approx \int_0^{\omega_{\max}} k_{\mathrm{B}} \frac{(\beta\hbar\omega)^2}{\mathrm{e}^{\beta\hbar\omega}} g(\omega)\mathrm{d}\omega$$

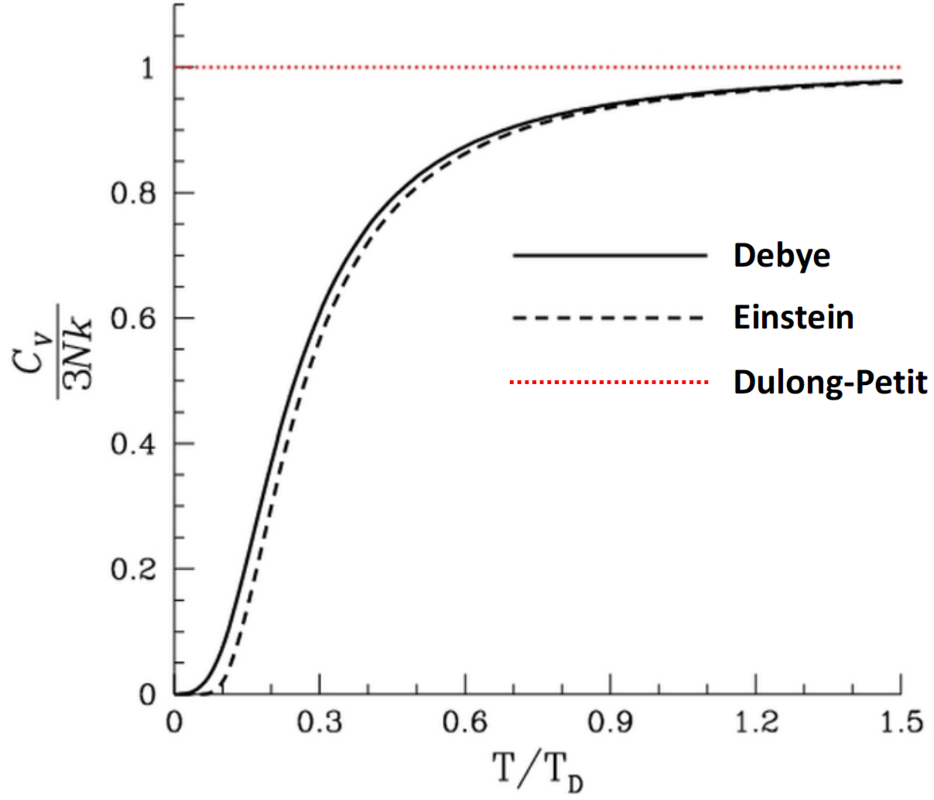
$\boldsymbol{C_V \to 0}$ **when** $\boldsymbol{T \to 0}$ **(or** $\boldsymbol{\beta \to \infty}$**)**

➢ Quantum Theory of Heat Capacity in Solids (固体热容的量子理论)

❖ To **quantitatively** calculate C_V, the key is to obtain $g(\omega)$ that is usually difficult to accurately evaluate in real materials.

Two important models proposed to simplify the calculations of C_V:

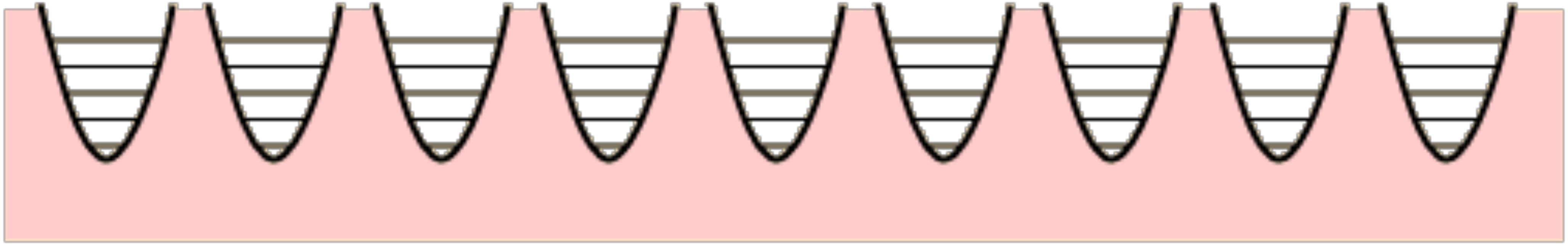
- **The Einstein model** (爱因斯坦模型)
- **The Debye model** (德拜模型)



The Einstein Model
(爱因斯坦模型)

➢ The Einstein Model (爱因斯坦模型)

❖ The Einstein model assumes that all the vibration modes of the lattice have the same frequency (**Einstein frequency 爱因斯坦频率**), i.e., $\hbar\boldsymbol{\omega}_{\boldsymbol{j}} = \hbar\boldsymbol{\omega}_{\mathbf{E}}$.



In the Einstein model, **each atom** of the lattice represents an **independent harmonic oscillator!**

- **The Einstein Model (爱因斯坦模型)**

  - The **total average energy** of the lattice vibrations (omitting the zero-point energy):

$$\overline{E} = \sum_{j=1}^{3N} \overline{E}_j = 3N\overline{E}_j = 3N \frac{\hbar\omega_{\mathrm{E}}}{\mathrm{e}^{\beta\hbar\omega_{\mathrm{E}}} - 1}$$

➢ The Einstein Model (爱因斯坦模型)

❖ The heat capacity can be obtained as:

$$C_V = \left(\frac{\partial \overline{E}}{\partial T}\right)_V = 3Nk_\mathrm{B} f_\mathrm{E}\left(\frac{\hbar\omega_\mathrm{E}}{k_\mathrm{B}T}\right)$$

where $f_\mathrm{E}\left(\frac{\hbar\omega_\mathrm{E}}{k_\mathrm{B}T}\right)$ denotes the **Einstein heat capacity function** (爱因斯坦热容函数):

$$f_\mathrm{E}\left(\frac{\hbar\omega_\mathrm{E}}{k_\mathrm{B}T}\right) = \left(\frac{\hbar\omega_\mathrm{E}}{k_\mathrm{B}T}\right)^2 \frac{\mathrm{e}^{\hbar\omega_\mathrm{E}/k_\mathrm{B}T}}{\left(\mathrm{e}^{\hbar\omega_\mathrm{E}/k_\mathrm{B}T}-1\right)^2}$$

➢ **The Einstein Model (爱因斯坦模型)**

❖ By introducing the **Einstein temperature** (爱因斯坦温度) $T_E = \hbar\omega_{\mathrm{E}}/k_{\mathrm{B}}$, we obtain:

$$\boxed{C_V = 3Nk_{\mathrm{B}}\left(\frac{T_{\mathrm{E}}}{T}\right)^2 \frac{\mathrm{e}^{T_{\mathrm{E}}/T}}{(\mathrm{e}^{T_{\mathrm{E}}/T} - 1)^2}}$$

➢ The Einstein Model (爱因斯坦模型)

❖ The limiting cases:

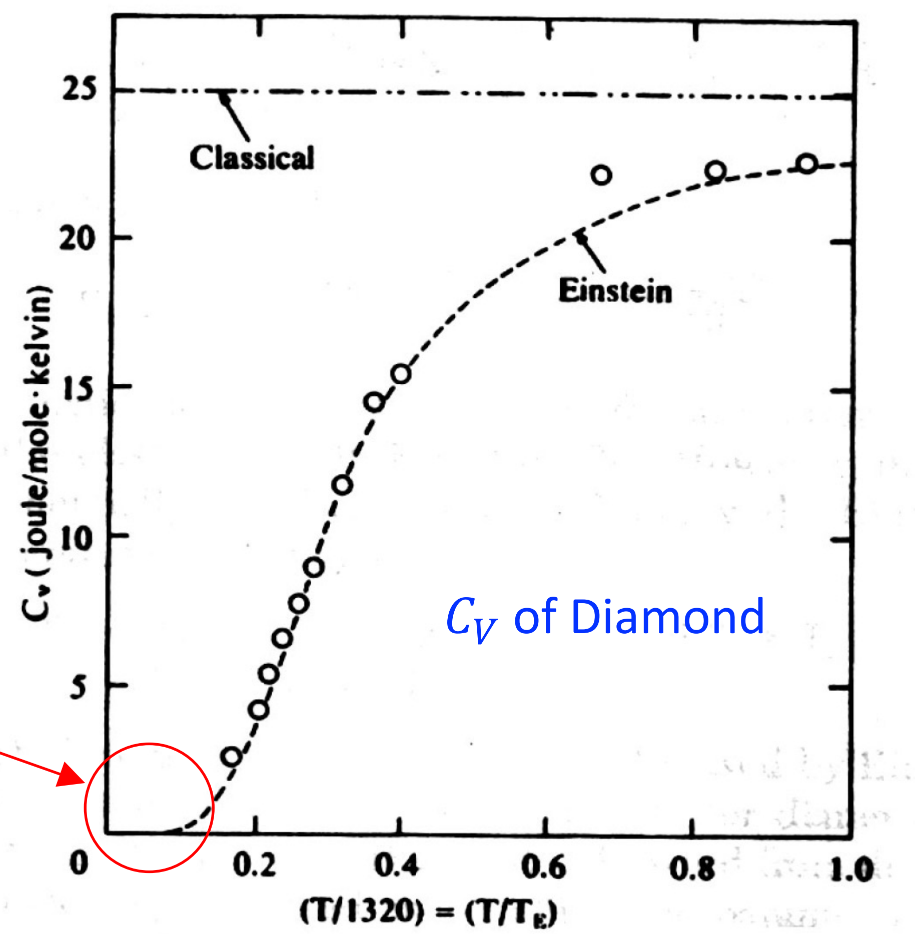
- High-temperature limit ($\boldsymbol{T_{\mathrm{E}}/T \ll 1}$): $\boldsymbol{C_V \approx 3Nk_{\mathrm{B}}}$

- Low-temperature limit ($\boldsymbol{T_{\mathrm{E}}/T \gg 1}$): $\boldsymbol{C_V \approx 3Nk_{\mathrm{B}}\left(\frac{T_{\mathrm{E}}}{T}\right)^2 \mathrm{e}^{-T_{\mathrm{E}}/T}}$

➢ The Einstein Model (爱因斯坦模型)

❖ Problem with the Einstein model:

The Einstein model works very well except at very low temperature where **it fails to predict $C_V \propto T^3$**.



C_V of Diamond

The Debye Model
(德拜模型)

➢ The Debye Model (德拜模型)

❖ The Debye model overcomes the problem with the Einstein model by assuming a **linear dispersion** of the vibration frequency, i.e., **elastic waves (弹性波)**.

$$\boldsymbol{\omega = cq}$$

where $\boldsymbol{c}$ denotes the group velocity of the lattice waves.

❖ In a 3D lattice, there are 1 branch of longitudinal waves (纵波) and 2 branches of transverse waves (横波):

$$\omega = c_{\mathrm{L}} q \quad \text{(1 branch)}$$

$$\omega = c_{\mathrm{T}} q \quad \text{(2 branches)}$$

➢ The Debye Model (德拜模型)

❖ The **density of states** can be obtained as:

$$\boldsymbol{g(\omega) = \frac{3V}{2\pi^2 \bar{c}^3}\omega^2}$$

$\boldsymbol{V}$ denotes the total volume of the crystal and $\frac{1}{\bar{c}^3} = \frac{1}{3}\left(\frac{1}{c_{\mathrm{L}}^3} + \frac{2}{c_{\mathrm{T}}^3}\right)$

➢ The Debye Model (德拜模型)

❖ A maximum of the vibration frequency (**Debye frequency 德拜频率**), i.e., $\boldsymbol{\omega}_{\mathbf{D}}$, has to be introduced such that the following equation is satisfied:

$$\int_0^{\omega_{\mathrm{D}}} g(\omega)\mathrm{d}\omega = \frac{3V}{2\pi^2\bar{c}^3}\int_0^{\omega_{\mathrm{D}}} \omega^2 \mathrm{d}\omega = 3N$$

$$\longrightarrow \quad \boldsymbol{\omega}_{\mathbf{D}} = \bar{\boldsymbol{c}}\left[6\boldsymbol{\pi}^2\left(\frac{\boldsymbol{N}}{\boldsymbol{V}}\right)\right]^{1/3}$$

➢ The Debye Model (德拜模型)

❖ The heat capacity can be obtained as:

$$C_V = 3Nk_\mathrm{B}f_\mathrm{D}\left(\frac{\hbar\omega_\mathrm{D}}{k_\mathrm{B}T}\right)$$

where $f_\mathrm{D}\left(\frac{\hbar\omega_\mathrm{D}}{k_\mathrm{B}T}\right)$ denotes the **Debye heat capacity function (德拜热容函数)**:

$$f_\mathrm{D}\left(\frac{\hbar\omega_\mathrm{D}}{k_\mathrm{B}T}\right) = 3\left(\frac{k_\mathrm{B}T}{\hbar\omega_\mathrm{D}}\right)^3 \int_0^{\hbar\omega_\mathrm{D}/k_\mathrm{B}T} \frac{\mathrm{e}^x x^4}{(\mathrm{e}^x - 1)^2}\,\mathrm{d}x$$

➢ The Debye Model (德拜模型)

❖ By introducing the **Debye temperature** (德拜温度) $\boldsymbol{T_{\mathrm{D}}} = \boldsymbol{\hbar\omega_{\mathrm{D}}/k_{\mathrm{B}}}$, we obtain:

$$\boxed{\boldsymbol{C_V = 9Nk_{\mathrm{B}}\left(\frac{T}{T_{\mathrm{D}}}\right)^3 \int_0^{T_{\mathrm{D}}/T} \frac{\mathrm{e}^x x^4}{(\mathrm{e}^x - 1)^2}\,\mathrm{d}x}}$$

The Debye Model (德拜模型)

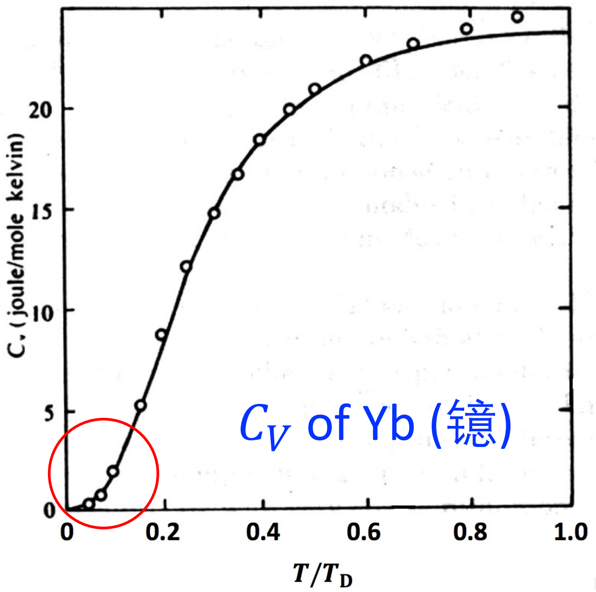
- The limiting cases:

  - High-temperature limit ($T_\mathrm{D}/T \ll 1$): $C_V \approx 3Nk_\mathrm{B}$

  - Low-temperature limit ($T_\mathrm{D}/T \gg 1$): $C_V = \dfrac{12\pi^4}{5} Nk_\mathrm{B} \left(\dfrac{T}{T_\mathrm{D}}\right)^3$

- **The Debye Model (德拜模型)**
  - The **Debye T^3 law (德拜T^3定律):**

$$\boxed{C_V \propto T^3 \text{ when } T \to 0}$$



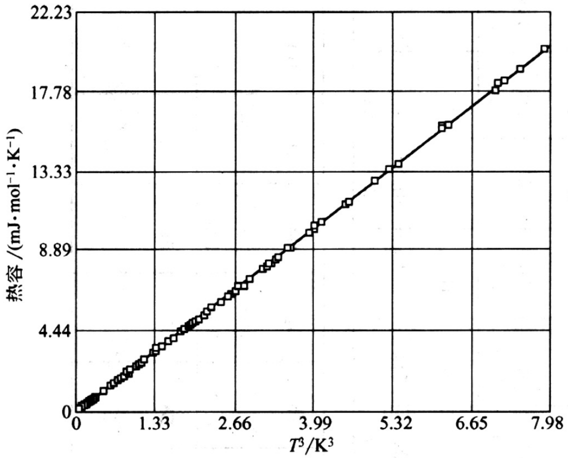


图 9 固态氩的低温比热容对 T^3 的依赖关系曲线。在这个温度区间，实验结果与德拜的 T^3 律符合极佳。这里取 $\theta=92.0$K。引自 L. Finegold 和 N. E. Phillips。

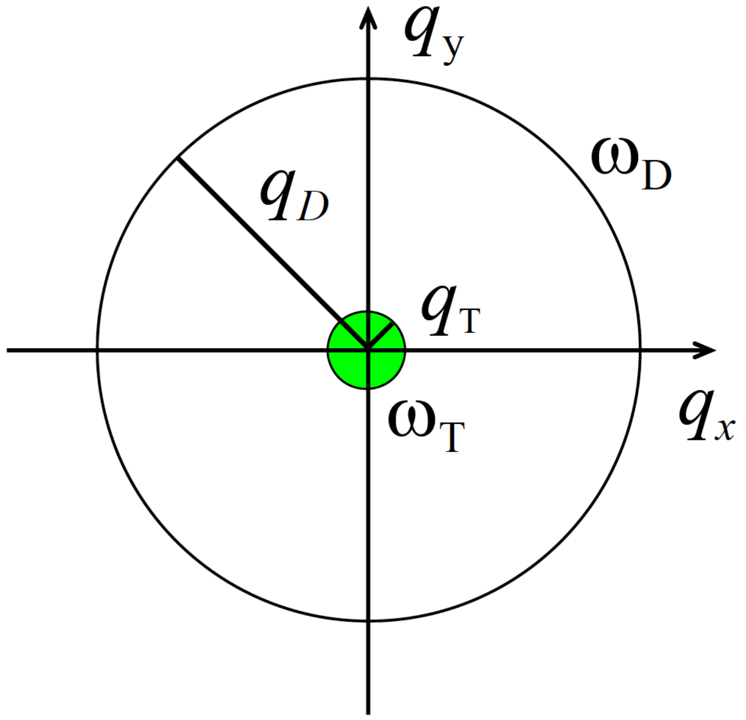
➢ The Debye Model (德拜模型)

❖ The **Debye T^3 law (德拜T^3定律):**

- At very low temperature T, only the long-wave phonons with energy $\hbar\omega < k_B T$ can be excited and have significant contributions to the heat capacity.

- The fraction of the excited long-wave phonons is proportional to the heat capacity:

$$C_V \propto \left(\frac{q_T}{q_D}\right)^3 = \left(\frac{\omega_T}{\omega_D}\right)^3 = \left(\frac{T}{T_D}\right)^3$$

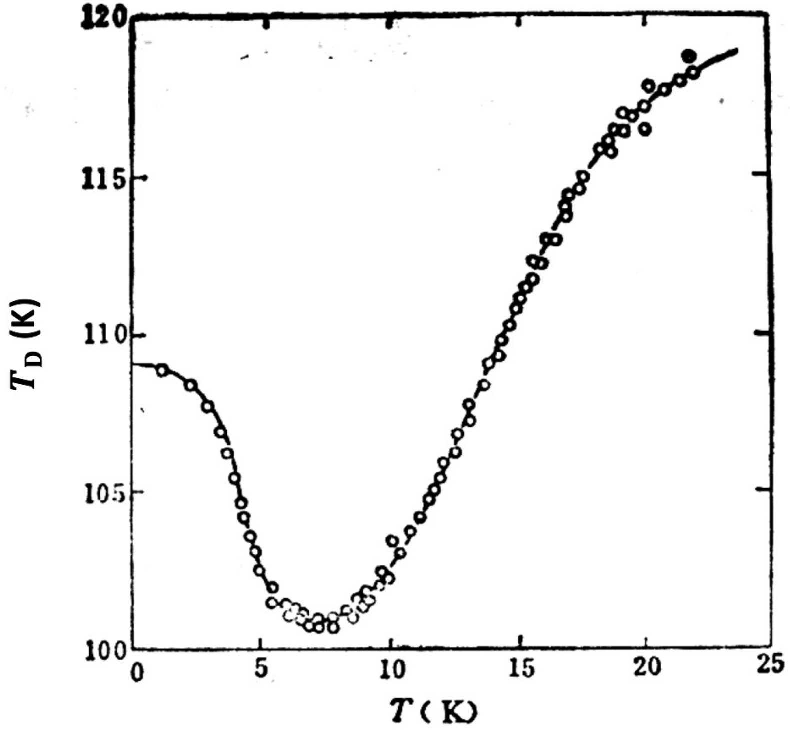


➢ The Debye Model (德拜模型)

❖ Problems with the Debye model:

- For a specific material, the Debye temperature $\boldsymbol{T}_{\mathbf{D}}$ obtained at different temperatures is usually different, indicating that the Debye model is still not very accurate for the calculations of $\boldsymbol{C_V}$.

- **To accurately calculate $\boldsymbol{C_V}$, detailed information of $\boldsymbol{g(\omega)}$ is needed!**



The Debye temperature of In (铟) as a function of temperature.

➢ The Debye Model (德拜模型)

❖ The Debye temperature of some real materials:

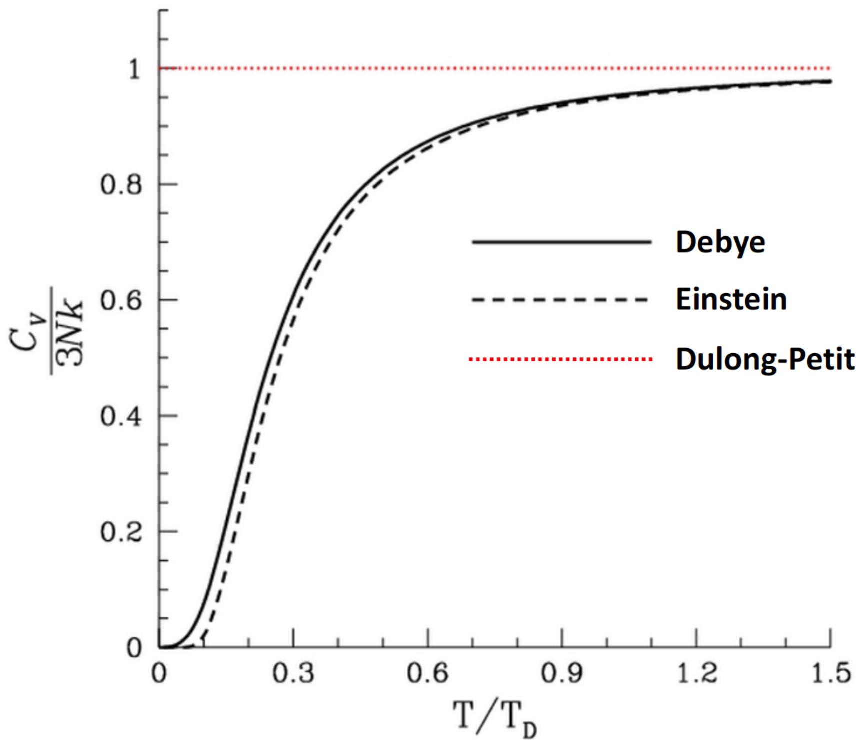
Element	**Au**	**Ag**	**Cu**	**Fe**	**Al**	**Ca**	**Si**	**Hg**	**K**	**C** Diamond	**B**	**Be**
$\boldsymbol{T_{\mathrm{D}}}$ **(K)**	165	225	343	470	428	230	645	71.9	91	2230	1250	1440

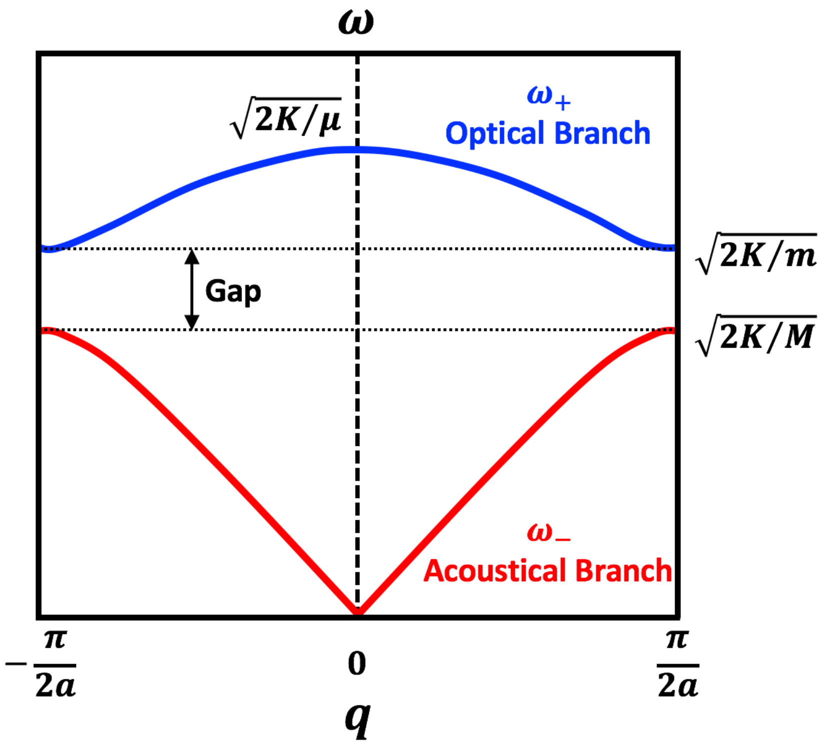
Most materials have a Debye temperature of $\boldsymbol{T_{\mathrm{D}} \approx 200 \sim 400\ \mathrm{K}}$, which corresponds to a Debye frequency of $\boldsymbol{\omega_{\mathrm{D}} \approx 10^{13}\ \mathrm{s}^{-1}}$.

The classical theory of lattice vibrations works when $\boldsymbol{T > T_{\mathrm{D}}}$!

➢ The Debye Model (德拜模型)

❖ Comparison between the three models of heat capacity :





➢ The Debye Model (德拜模型)

❖ Comparison between the three models of heat capacity :

Model	Debye	Einstein	Dulong-Petit
Merit 优点	1. Working at both low and high temperature; 2. Working at very low temperature ($T \to 0$).	Working at both low and high temperature.	Working at high temperature ($T > T_{\mathrm{D}}$).
Drawback 缺点	Not accurate enough for real materials.	1. Not working at very low temperature ($T \to 0$); 2. Not very accurate for real materials.	1. Not working at low temperature ($T < T_{\mathrm{D}}$); 2. Not accurate for real materials.

Density of States
(态密度)

➢ Density of States (态密度)

❖ In general, density of states (**DOS**) is defined as the **number of states per interval of energy** (单位能量间隔内的状态数).

❖ In particular, the DOS for lattice vibrations is defined as the number of vibration modes Δn per interval of frequency $\Delta\omega$:

$$g(\omega) = \lim_{\Delta\omega \to 0} \frac{\Delta n}{\Delta\omega} = \frac{\mathrm{d}n}{\mathrm{d}\omega}$$

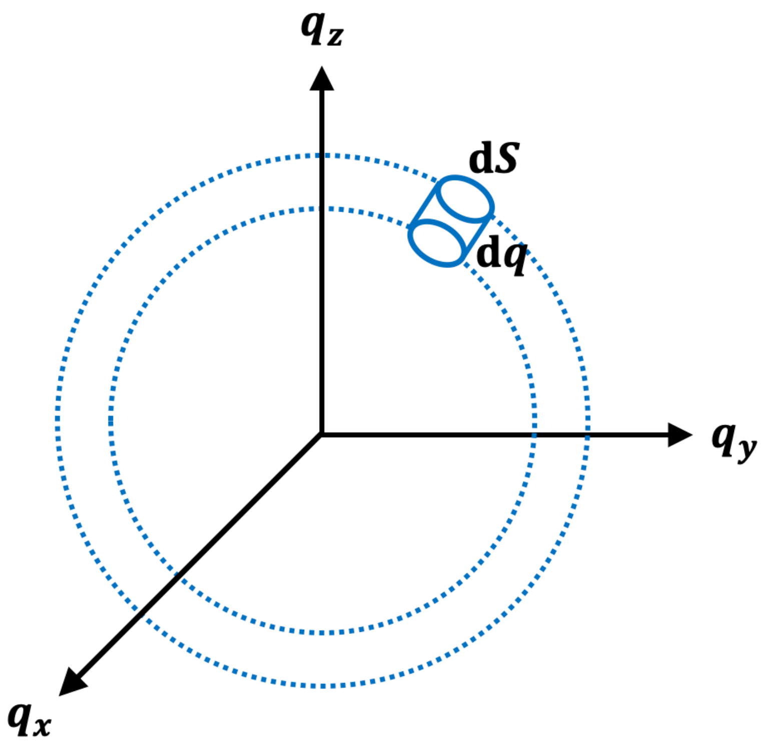
Density of States (态密度)

❖ In the case of 3D:

$$\mathrm{d}n = \frac{V}{(2\pi)^3} \oiint \mathrm{d}S\mathrm{d}q$$

$$\mathrm{d}\omega = \mathrm{d}q\left|\nabla_q \omega_q\right|$$

$$\boldsymbol{g(\omega)} = \frac{\boldsymbol{V}}{(\boldsymbol{2\pi})^3} \oiint \frac{\mathbf{d}\boldsymbol{S}}{\left|\boldsymbol{\nabla}_q \boldsymbol{\omega}_q\right|}$$



V denotes the total volume of the crystal.

➢ Density of States (态密度)

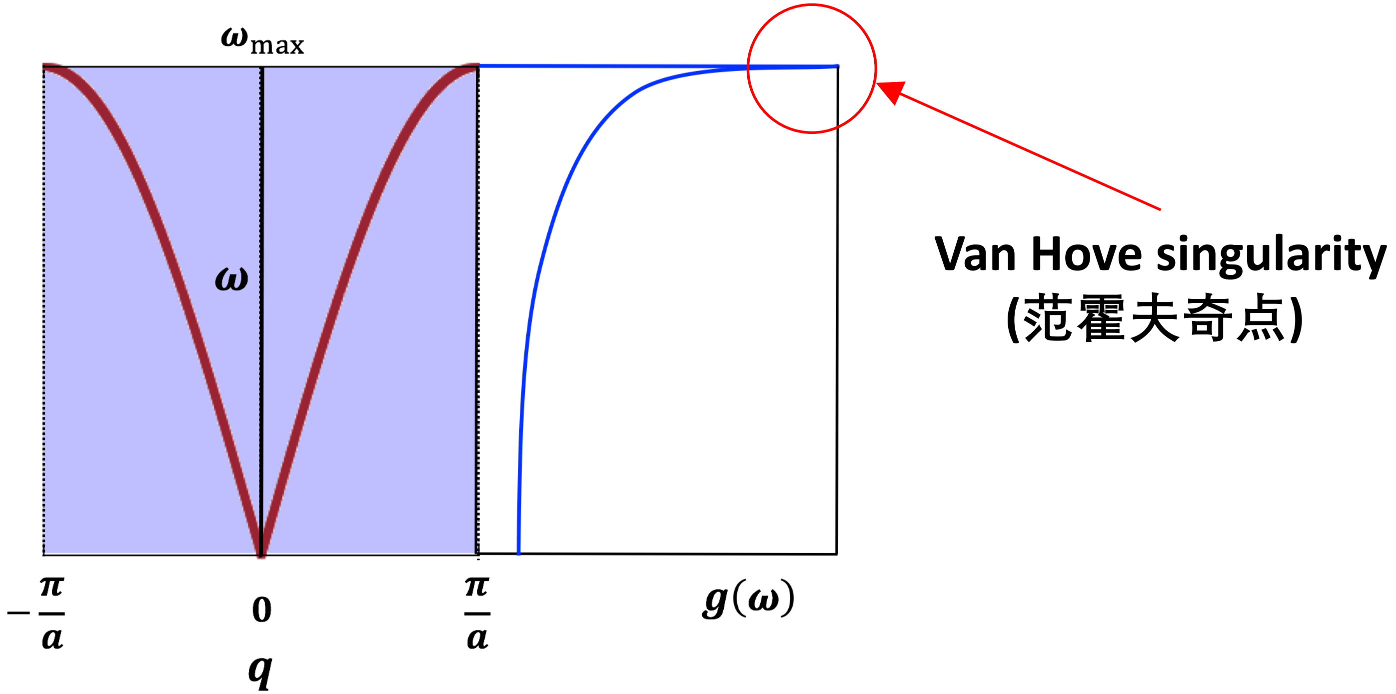
❖ **Example:** DOS of a 1D monoatomic chain

$$g(\omega)=\frac{\mathrm{d}n}{\mathrm{d}\omega}=\frac{\mathrm{d}n}{\mathrm{d}q}\frac{\mathrm{d}q}{\mathrm{d}\omega}$$

$$=2\times\frac{Na}{2\pi}\frac{1}{\mathrm{d}\omega/\mathrm{d}q}$$

$$=\frac{2N}{\pi}\left(\omega_{\max}^2-\omega^2\right)^{-\frac{1}{2}}$$

$$\omega=\omega_{\max}\left|\sin\left(\frac{1}{2}aq\right)\right|$$



➢ **Density of States (态密度)**

❖ **Example:** DOS of real materials

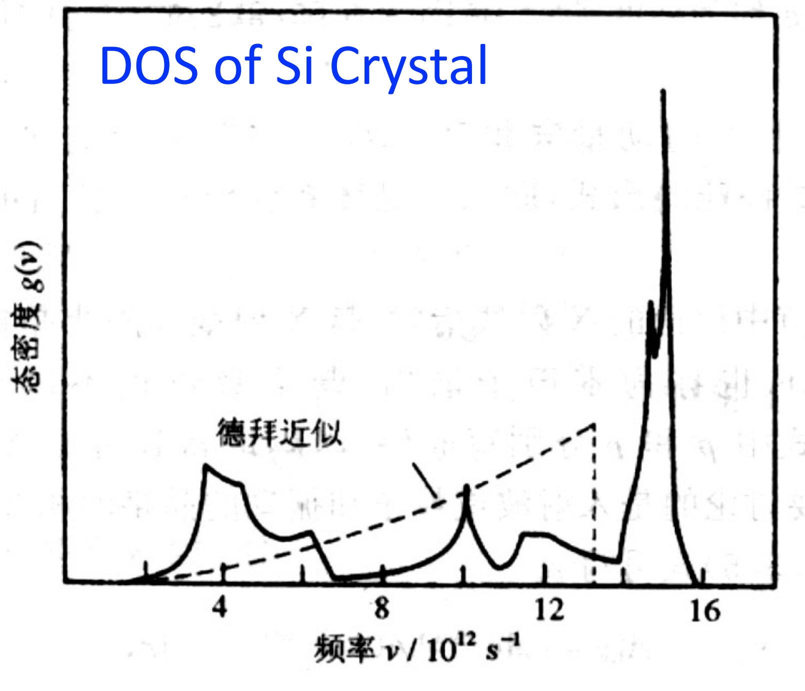
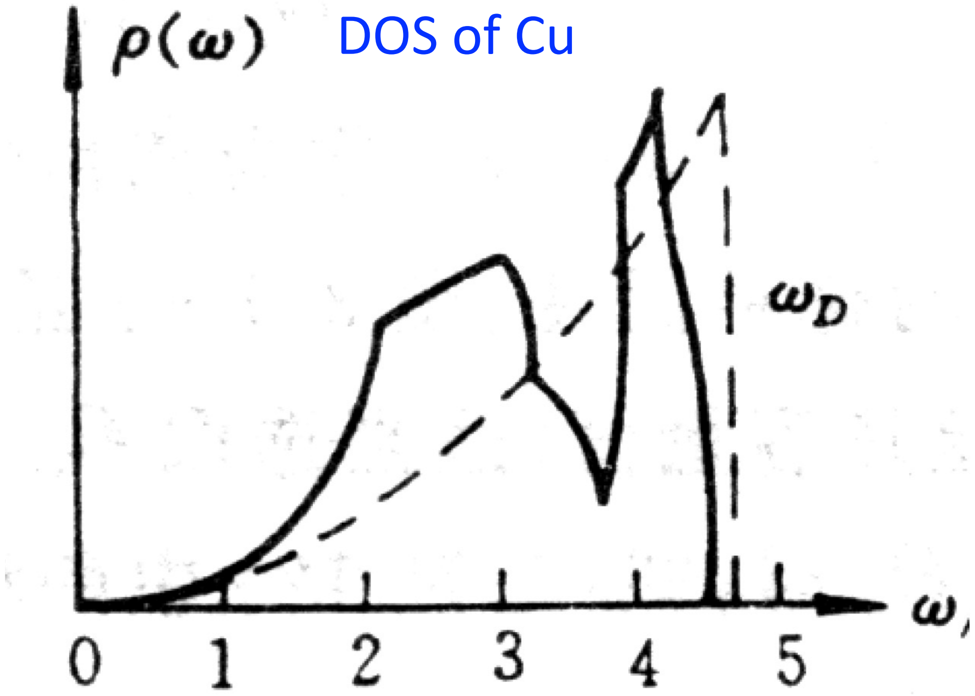


图 5.7　硅的声子态密度，其中 $\nu=\omega/2\pi$



➢ **Density of States (态密度)**

❖ DOS of **noncrystalline solids** (**非晶固体**的态密度)

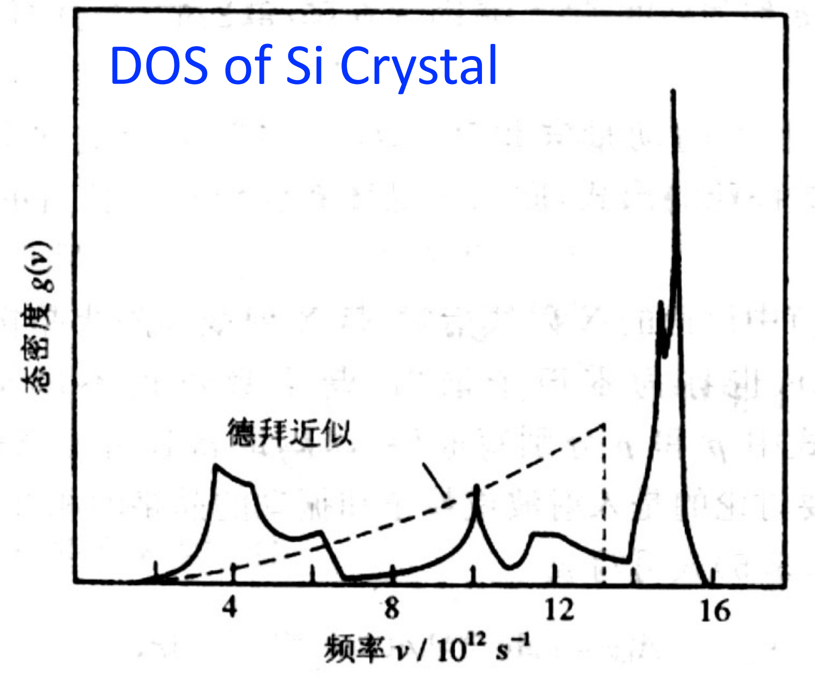
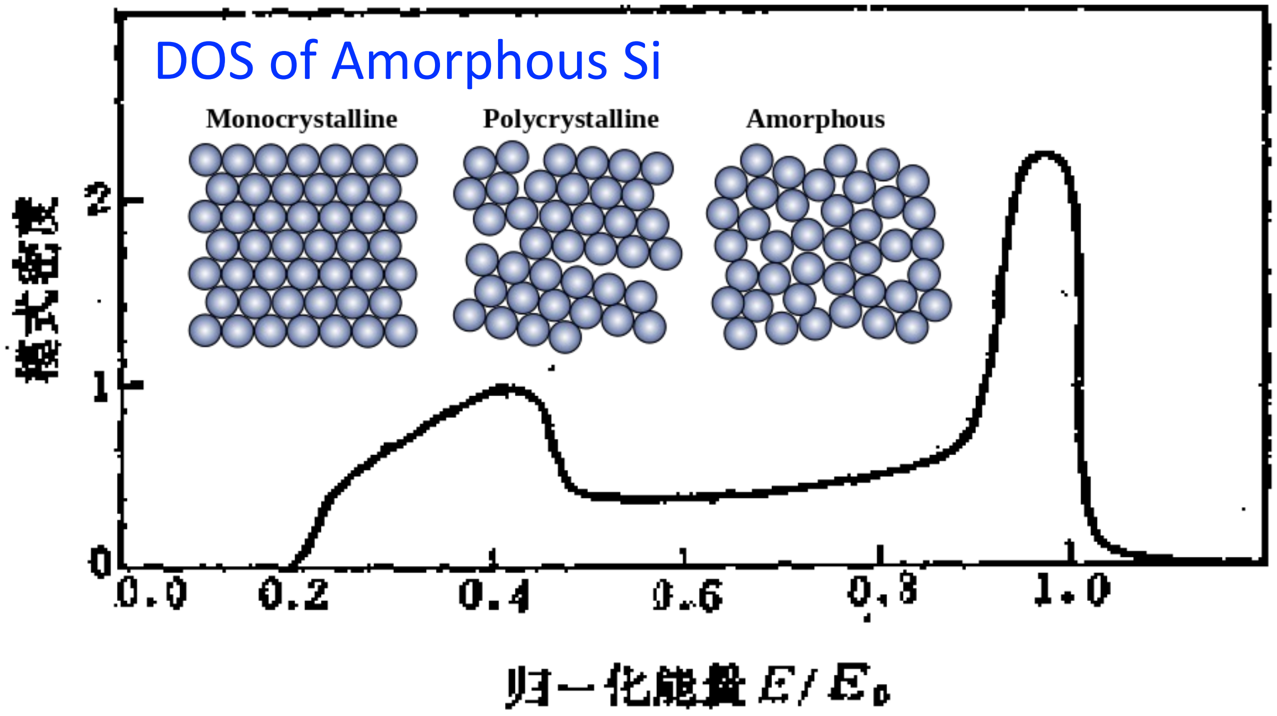


图 5.7 硅的声子态密度，其中 $\nu = \omega/2\pi$



Summary (总结)

➢ Summary (总结)

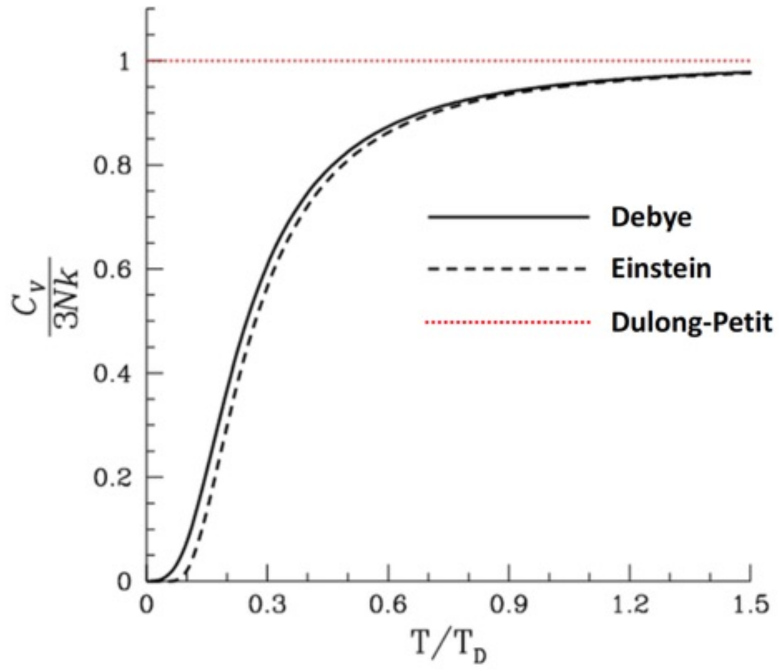
❖ **Classical theory of heat capacity in solids:**

The Dulong-Petit model

❖ **Quantum theory of heat capacity in solids:**

1) The Einstein model

2) The Debye model



Chapter 3.3: 课后作业

设晶体中每个振动模的零点振动能为$\frac{1}{2}\hbar\omega$，使用德拜模型和爱因斯坦模型分别求晶体的零点振动能。

提交时间：3月17日之前

提交方式：手写（写明姓名学号）后拍照，通过本班课代表统一提交电子版