Outline

Objectives

- To learn the origin of **anharmonicity** of lattice vibrations.

- To learn the **impacts** of anharmonicity on solids.

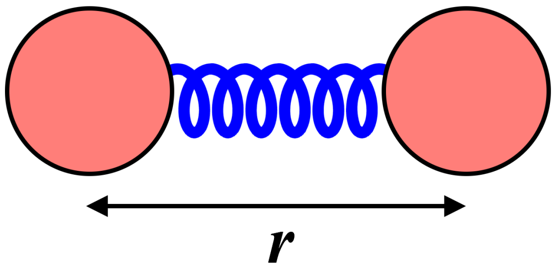
Anharmonic Interactions
(非谐作用)

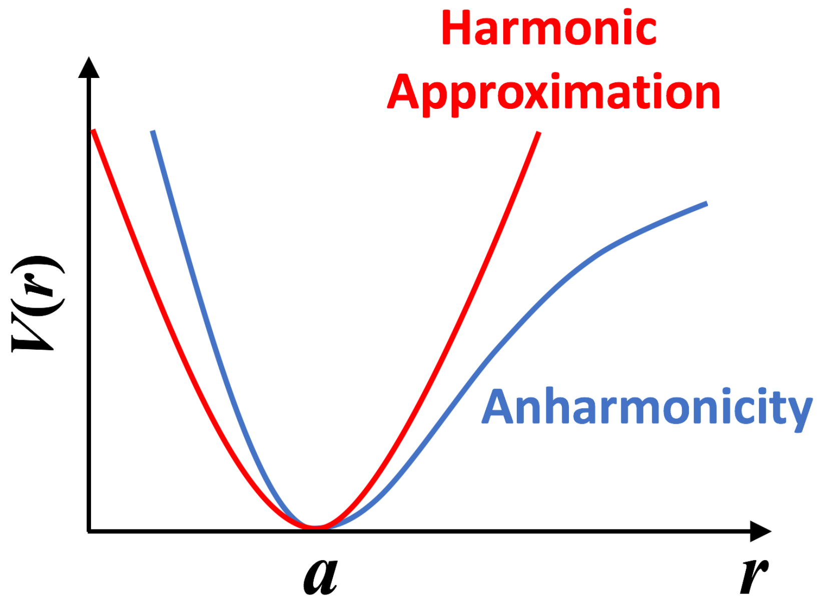
Chapter 3.4: Anharmonicity (非谐效应)

➢ Anharmonic Interactions (非谐作用)

❖ Interatomic potential around the equilibrium positions:

$$V(r) = V(a+\delta) = V(a) + \left(\frac{\mathrm{d}V}{\mathrm{d}r}\right)_a \delta + \frac{1}{2}\left(\frac{\mathrm{d}^2V}{\mathrm{d}r^2}\right)_a \delta^2 + \frac{1}{3!}\left(\frac{\mathrm{d}^3V}{\mathrm{d}r^3}\right)_a \delta^3 + \cdots$$



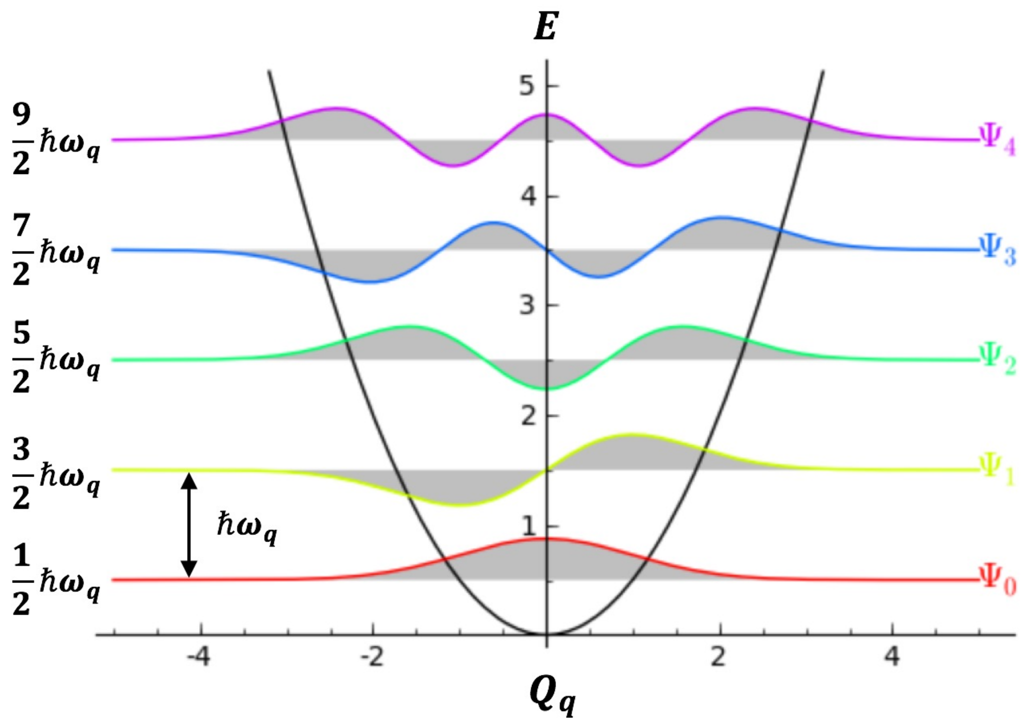


➢ Anharmonic Interactions (非谐作用)

❖ Independent vibration modes in the harmonic approximation:

$$H = \frac{1}{2}\sum_{j=1}^{3N}\left(P_j^2 + \omega_j^2 Q_j^2\right)$$

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



Anharmonic Interactions (非谐作用)

- Problems with the harmonic approximation:
  - No thermal expansion (没有热膨胀)
  - Elastic constant is independent of temperature and pressure (弹性常数不依赖于温度和压力)
  - Heat capacity is constant at high temperature ($T > T_{\mathrm{D}}$) (高温热容是常数)
  - No interaction between phonons or lattice waves (声子或格波之间无相互作用)
  - Thermal conductivity is infinite in the absence of phonon scattering (无声子散射时热导率无穷大)
  - ……

Chapter 3.4: Anharmonicity (非谐效应)

- **Anharmonic Interactions (非谐作用)**

  - Interatomic potential with **anharmonic terms** (非谐项):

$$V(r) = \frac{1}{2}\left(\frac{\mathrm{d}^2 V}{\mathrm{d}r^2}\right)_a \delta^2 + \frac{1}{3!}\left(\frac{\mathrm{d}^3 V}{\mathrm{d}r^3}\right)_a \delta^3 + \frac{1}{4!}\left(\frac{\mathrm{d}^4 V}{\mathrm{d}r^4}\right)_a \delta^4 + \cdots$$

$$= \frac{1}{2}K\delta^2 + \boxed{\frac{1}{3!}K_{(3)}\delta^3 + \frac{1}{4!}K_{(4)}\delta^4 + \cdots}$$

$K > 0 \qquad \boldsymbol{K_{(3)} < 0} \qquad \boldsymbol{K_{(4)} < 0}$

Chapter 3.4: Anharmonicity (非谐效应)

➢ Anharmonic Interactions (非谐作用)

❖ Roles of the anharmonic terms:

- $\frac{1}{3!}K_{(3)}\delta^3$ leads to **thermal expansion** (**热膨胀**).

- $\frac{1}{3!}K_{(4)}\delta^4$ leads to **vibration mode softening** (**振动模软化**).

$$V(r) = \frac{1}{2}K\delta^2 + \frac{1}{4!}K_{(4)}\delta^4 = \frac{1}{2}K'\delta^2$$

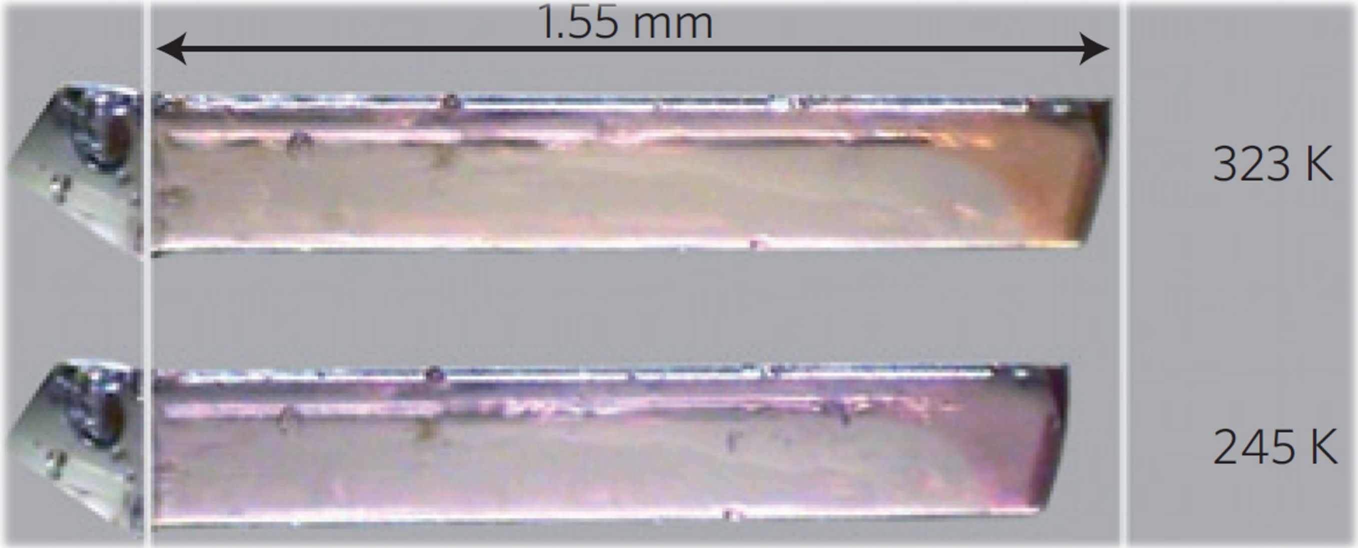
$$\boxed{K' = K + \frac{1}{12}K_{(4)}\delta^2 < \boldsymbol{K}}$$

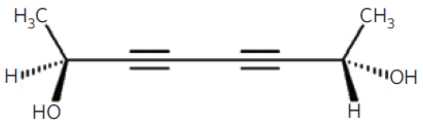
Thermal Expansion
(热膨胀)

Chapter 3.4: Anharmonicity (非谐效应)

➢ Thermal Expansion (热膨胀)

❖ Thermal expansion is the change in volume of solids in response to a change in temperature.





Thermal Expansion of an Organic Crystal

D. Das, T. Jacobs, and L. J. Barbour, **Nature Mater. 9, 36 (2010).**

➢ Thermal Expansion (热膨胀)

❖ Thermal expansion in the presence of anharmonicity:

$$V(r) = \frac{1}{2}K\delta^2 + \frac{1}{3!}K_{(3)}\delta^3$$

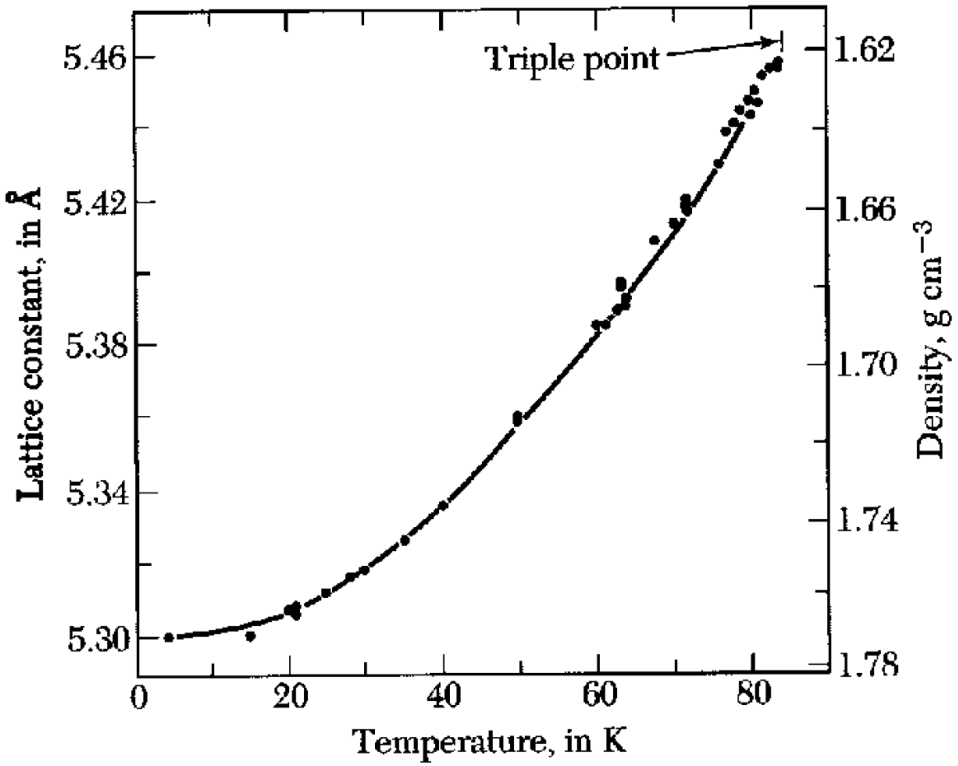
The thermal average of interatomic space:

$$\langle r\rangle = a + \langle\delta\rangle = a + \frac{\int_{-\infty}^{\infty}\delta \mathrm{e}^{-V(\delta)/k_\mathrm{B}T}\mathrm{d}\delta}{\int_{-\infty}^{\infty}\mathrm{e}^{-V(\delta)/k_\mathrm{B}T}\mathrm{d}\delta} = a - \frac{3K_{(3)}}{4K^2}k_\mathrm{B}T$$

Chapter 3.4: Anharmonicity (非谐效应)

➢ Thermal Expansion (热膨胀)

❖ Thermal expansion in the presence of anharmonicity:



Lattice Constant as a Function of Temperature in an Ar Solid

Thermal Conduction
(热传导)

➢ Thermal Conduction (热传导)

- In solids, thermal conduction represents the flow of heat from the regions with higher temperature to those with lower temperature, which can be described by the **Fourier's law (傅里叶定律):**

$$\boldsymbol{j} = -\boldsymbol{\kappa}\frac{\boldsymbol{dT}}{\boldsymbol{dx}}$$

where $\boldsymbol{j}$ denotes the **flux of thermal energy (热流密度),** $\boldsymbol{\kappa}$ the **thermal conductivity** (**热导率**), and $\boldsymbol{T}$ the temperature.

- Thermal conduction in solids has two contributions, i.e., **phonons** (for nonmetals 非金属) and **electrons** (for metals 金属).

➢ Thermal Conduction (热传导)

❖ The **phonon contribution** to thermal conductivity:

$$\boldsymbol{\kappa = \frac{1}{3} c_V v \lambda}$$

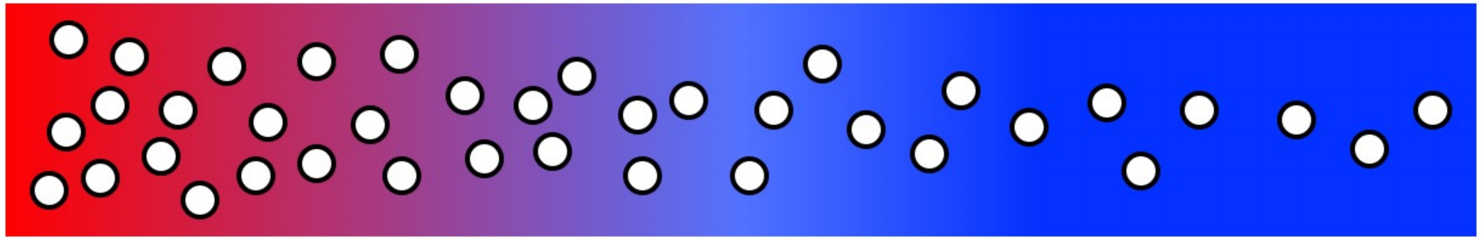
where c_V denotes the **volume-specific heat capacity** (体积比热容), υ the phonon **mean velocity (平均速度)**, and λ the phonon **mean free path** (平均自由程).

❖ The **mean free path** describes the **average distance** that a phonon can travel between two successive scattering events (by other phonons or defects).

➢ Thermal Conduction (热传导)

❖ In nonmetals, thermal conduction is essentially caused by **phonon diffusion (声子扩散)** from high-temperature regions to low-temperature regions.

$$\langle \boldsymbol{n} \rangle = \frac{\mathbf{1}}{\mathbf{e}^{\hbar\omega/k_{\mathrm{B}}T} - \mathbf{1}}$$

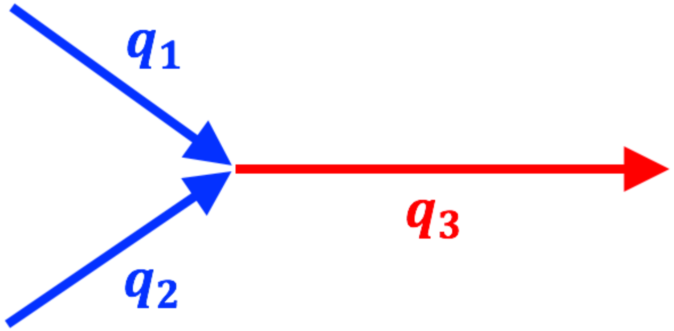


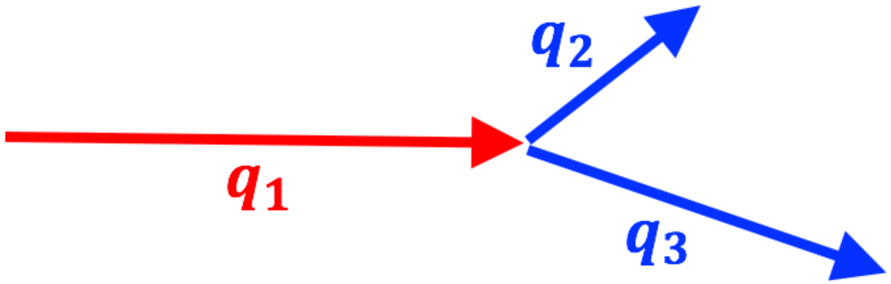
Higher Temperature
Larger $\langle n \rangle$

Lower Temperature
Smaller $\langle n \rangle$

- **Thermal Conduction (热传导)**

  - **Phonon collision (声子碰撞)** as a result of **anharmonicity**:





Two phonons **merge** to form a single phonon.

A single phonon **splits** into two phonon.

➢ Thermal Conduction (热传导)

❖ **Conservation law (守恒律)** for phonon collision:

Conservation of energy (能量守恒): $\hbar\boldsymbol{\omega}_{\boldsymbol{q}_1} + \hbar\boldsymbol{\omega}_{\boldsymbol{q}_2} = \hbar\boldsymbol{\omega}_{\boldsymbol{q}_3}$

Conservation of quasi-momentum (准动量守恒): $\hbar\boldsymbol{q}_1 + \hbar\boldsymbol{q}_2 = \hbar\boldsymbol{q}_3 + \hbar\boldsymbol{G}_n$

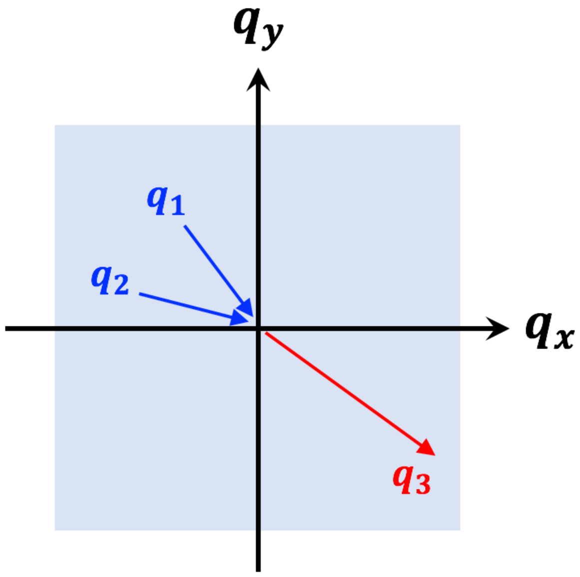
G_n denotes a vector of reciprocal lattice.

Chapter 3.4: Anharmonicity (非谐效应)

➢ Thermal Conduction (热传导)

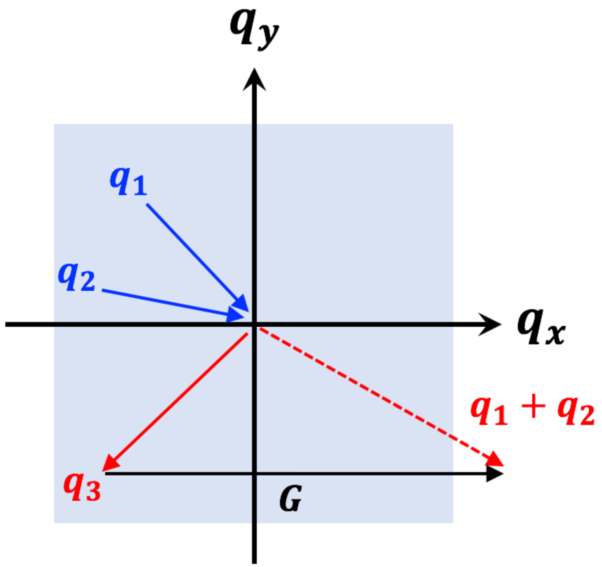
❖ **Normal process (正常过程)** and **Umklapp process (倒逆过程)** of phonon collision:

Normal process
(**N-process**)



$$\hbar q_1 + \hbar q_2 = \hbar q_3$$

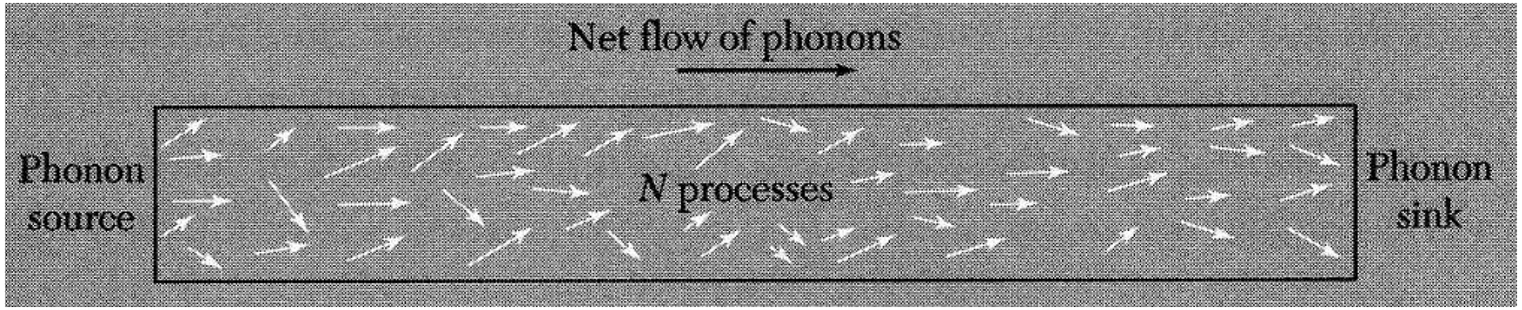
Umklapp process
(**U-process**)



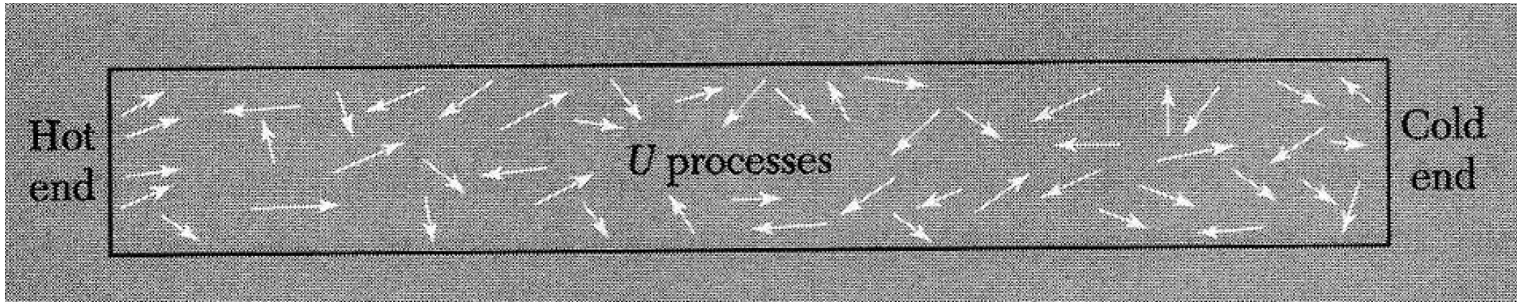
$$\hbar q_1 + \hbar q_2 = \hbar q_3 + \hbar G$$

➢ Thermal Conduction (热传导)

❖ **Normal process (正常过程)** and **Umklapp process (倒逆过程)** of phonon collision:



No thermal resistance (无热阻) in the N-process



Have thermal resistance (有热阻) in the U-process

Summary (总结)

➢ Summary (总结)

❖ **Anharmonic interactions.**

❖ **Thermal expansion.**

❖ **Thermal conduction:**

1) Phonon diffusion;

2) Phonon collision.