

Chapter 5 Crystal Thermodynamics

5.1 Phonon heat capacity

5.2 Experimental Determination of Phonon Spectrum

5.3 Anharmonic Effects

5.1 phonon heat capacity

I. Density of states

Consider an atomic chain consisting of N lattice sites:

$$q = \frac{2\pi}{Na} l = \frac{2\pi}{L} l$$

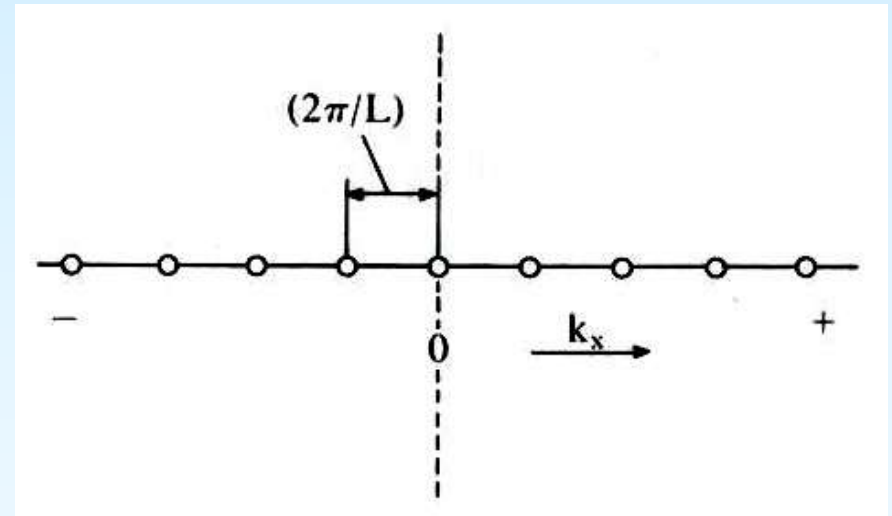
where l is an integer

$$L = Na \text{ —the length of the chain}$$

the q -points are regularly arranged in a 1d chain, with distance $2\pi/L$ to each other.

5.1 phonon heat capacity

For large L , the distance becomes small, and the q -points are nearly continuous; each q -value (a single point) represents a vibration mode.



For an arbitrary distance dq , number of modes dn in between is:

$$dn = \frac{L}{2\pi} dq$$

q is related to frequency ω via the dispersion relation, we can thus get the # of vibration modes in the range of $(\omega, \omega + d\omega)$.

1. Definition

Density of modes (states): # of vibration modes per unit frequency interval

$$g(\omega) = \frac{dn}{d\omega}$$

2. D.O.S. of an atomic chain

$$g(\omega)d\omega = dn$$

$$dn = \frac{L}{2\pi} dq$$

$$g(\omega)d\omega = \frac{L}{2\pi} dq$$

5.1 phonon heat capacity

$$g(\omega) = \frac{L}{2\pi} \left/ \left(\frac{d\omega}{dq} \right) \right.$$

for a given ω value, there exist two symmetric q values:

$$g(\omega) = \frac{L}{\pi} \left/ \left(\frac{d\omega}{dq} \right) \right.$$

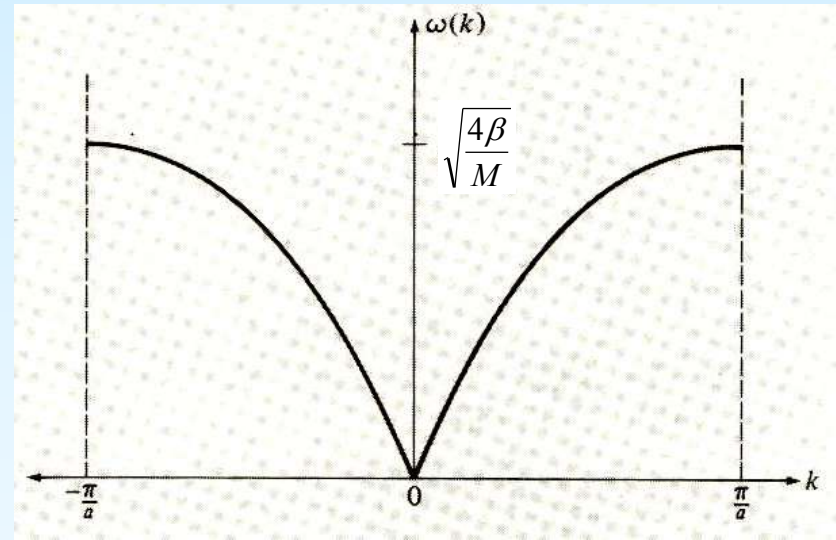
dispersion:

$$\omega = 2 \sqrt{\left(\frac{\beta}{M} \right)} \left| \sin \frac{qa}{2} \right|$$

$$\frac{d\omega}{dq} = 2 \sqrt{\left(\frac{\beta}{m} \right)} \frac{a}{2} \cos \frac{qa}{2} = \frac{a}{2} \omega_m \cos \frac{qa}{2}$$

in which,

$$\omega_m = \sqrt{\frac{4\beta}{M}}$$





5.1 phonon heat capacity

$$g(\omega) = \frac{2L}{\pi a \omega_m \cos \frac{qa}{2}}$$

$$= \frac{2N}{\pi \omega_m \cos \frac{qa}{2}}$$

$$= \frac{2N}{\pi \sqrt{\omega_m^2 - \omega^2}}$$

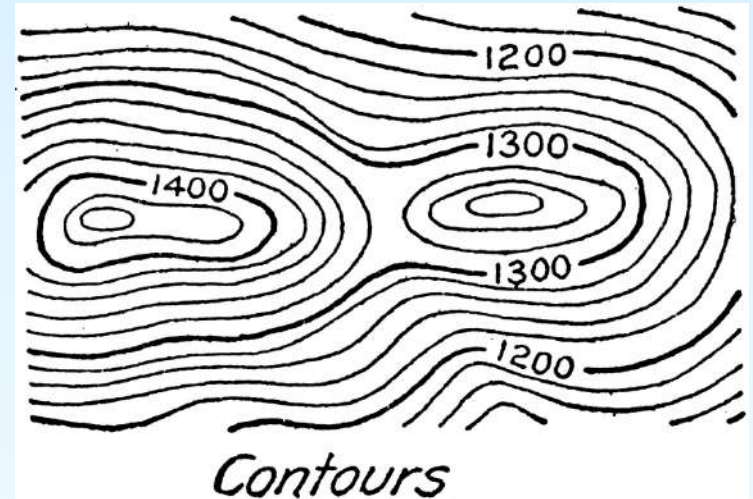
- $\omega = 0$, $g(\omega)$ is finite
- $\omega = \omega_m$, $g(\omega) \rightarrow \infty$
- $\omega > \omega_m$, $g(\omega) = 0$

3. Diatomic chain

for each branch $\omega_+(q)$ $\omega_-(q)$

corresponds: $g_+(\omega)$, $g_-(\omega)$

$$g(\omega) = g_+(\omega) + g_-(\omega)$$

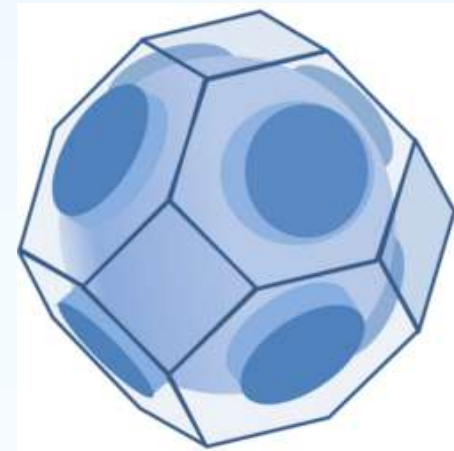


4. General crystals

q-points with the same frequencies

constitutes closed *contours*, or a

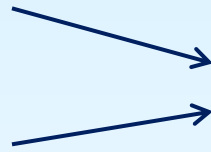
isosurface.



For a given branch j

$$\omega_j(\bar{q}) = \omega$$

$$\omega_j(\bar{q} + d\bar{q}) = \omega + d\omega$$



two isoenergetic
contours/isosurfaces

Count # of all modes between these two isosurfaces: dn_j

Equal. $g_j(\omega)d\omega \Rightarrow$ determine $g_j(\omega)$

Sum over all branches, one gets the total density of states:

$$g(\omega) = \sum_j g_j(\omega)$$

Example: A cube with length L

According to periodic boundary condition,

$$q_i = \frac{l_i 2\pi}{N_i a_i} = l_i \frac{2\pi}{L}$$

volume per q -point: $\left(\frac{2\pi}{L}\right)^3$

A unit volume in q -point space contains:

$$\left(\frac{L}{2\pi}\right)^3 = \frac{V}{8\pi^3} \text{ allowed } q$$

V ——volume of the crystal

Isosurfaces are spheres, with radius q .

The # of modes in this sphere:

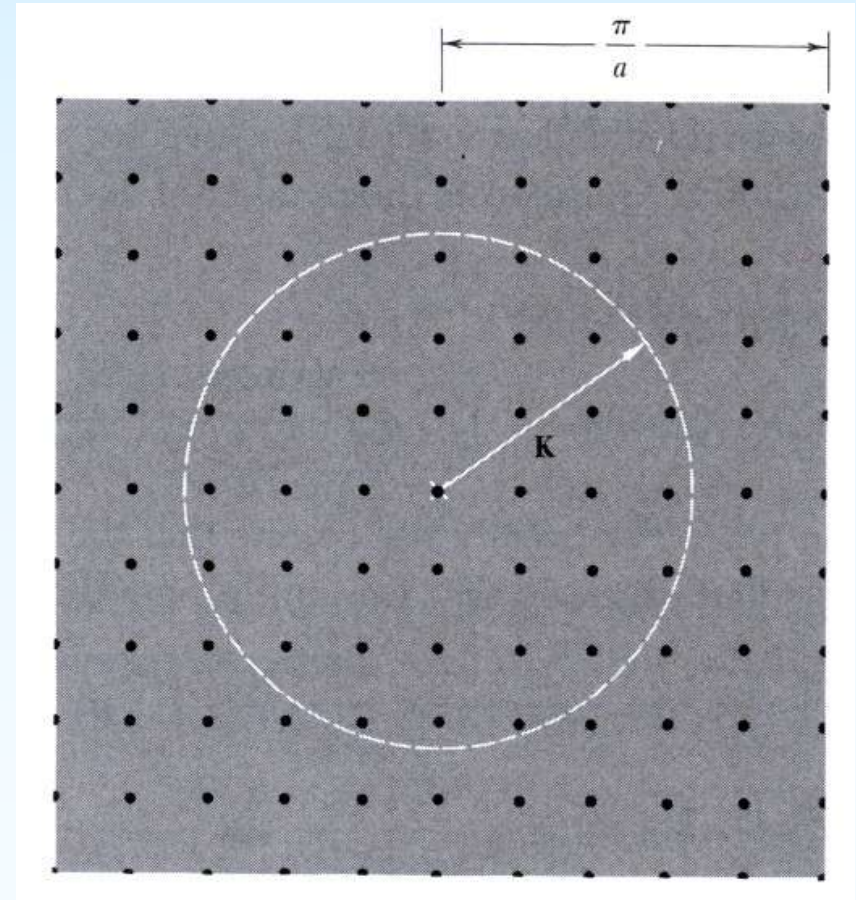
$$n = \frac{4\pi}{3} q^3 \bigg/ \left(\frac{2\pi}{L} \right)^3$$

$$= \frac{V}{(2\pi)^3} \frac{4\pi}{3} q^3$$

For q , modes between $q \sim q+dq$:

$$dn = \frac{V}{(2\pi)^3} \frac{4\pi}{3} 3q^2 dq$$

$$= \frac{V}{(2\pi)^3} 4\pi q^2 dq$$



$$g_j(\omega)d\omega_j = \frac{V}{(2\pi)^3} 4\pi q^2 dq$$

$$g_j(\omega) = \frac{V}{(2\pi)^3} 4\pi q^2 \left/ \left(\frac{d\omega_j}{dq} \right) \right.$$

$\frac{d\omega_j}{dq}$ can be obtained from dispersion relation

For arbitrary isosurface, and any branch, vibration modes are uniformly distributed in \vec{q} space. Corresponding DOS is:

$$\rho(q) = \frac{1}{\frac{1}{N_1} \vec{b}_1 \cdot \left(\frac{1}{N_2} \vec{b}_2 \times \frac{1}{N_3} \vec{b}_3 \right)} = \frac{N}{\Omega_r} = \frac{N\Omega_d}{(2\pi)^3} = \frac{V}{(2\pi)^3}$$

5.1 phonon heat capacity

$$dn = \frac{V}{(2\pi)^3} \times (\text{volume between } \omega \text{ and } \omega + d\omega)$$

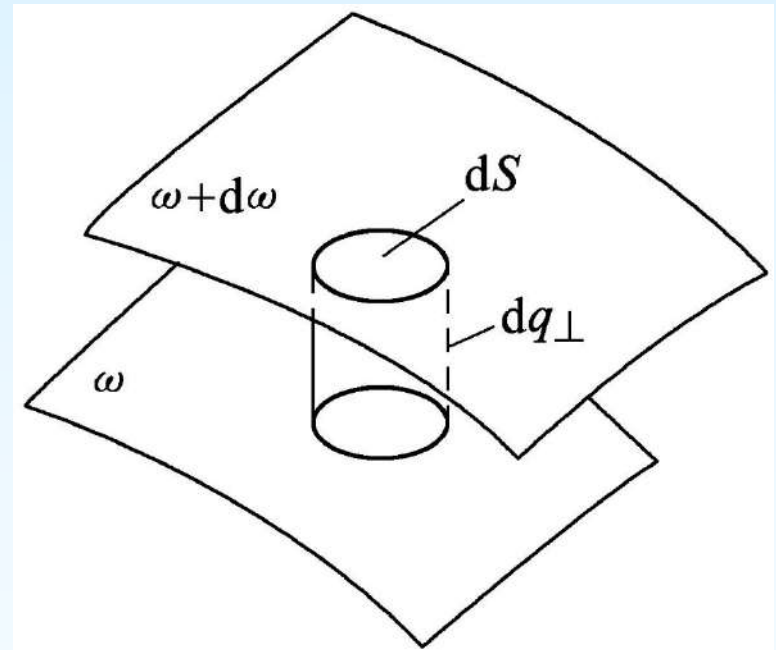
$$dn = \frac{V}{(2\pi)^3} \int_S dS dq_{\perp}$$

dS --surface element,

dq_{\perp} --distance between two surfaces

$$d\omega_j = dq_{\perp} |\nabla_q \omega_j(\mathbf{q})|$$

$\nabla_q \omega_j(\mathbf{q})$ ——gradient along direction normal to the surface



$$dn = \frac{V}{(2\pi)^3} \int_S \frac{dS}{|\nabla_q \omega_j(q)|} d\omega_j$$

$$g_j(\omega) = \frac{dn}{d\omega_j} = \frac{V}{(2\pi)^3} \int_S \frac{dS}{|\nabla_q \omega_j(q)|}$$

Total Density of States:

$$g(\omega) = \sum_j g_j(\omega)$$

which satisfies:

$$\int g(\omega) d\omega = 3PN$$

II. Heat Capacity

1. lattice heat capacity

Specific heat of solid is defined: $C_V = \left(\frac{\partial \bar{\mathcal{E}}}{\partial T} \right)_V$

$\bar{\mathcal{E}}$: average internal energy of solid, including energies of lattice vibration and electron motions

According to classical theory, every degree of freedom corresponds to ave. energy $k_B T$, with $k_B T/2$ *kinetic* energy and $k_B T/2$ *potential* energy; suppose there are N atoms, the total energy is $\bar{\mathcal{E}} = 3Nk_B T$.

suppose $N=N_A$ (1 mole of atoms)

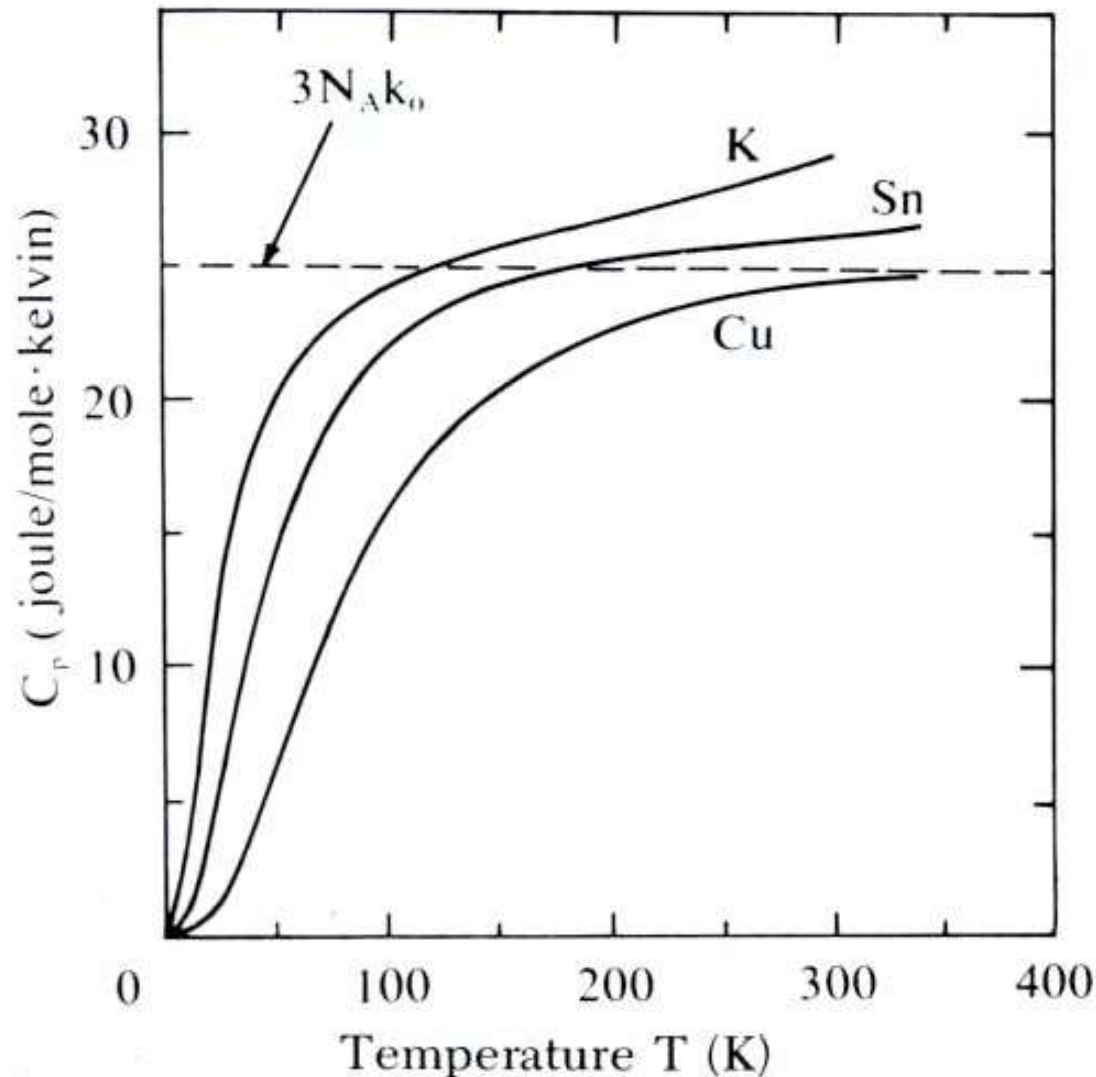
therefore mole capacity is:

$$C_V = \left(\frac{\partial \bar{\mathcal{E}}}{\partial T} \right)_V = 3N_A k_B$$

which has nothing to do with specific material or any temperature dependence.

——**Dulong-Petit's law**

5.1 phonon heat capacity



Experiments show, C_V **violates** the Dulong-Petit's law.

This demonstrates that the classical theory of equipartition of energy is *no longer valid*, and the **quantum theory** of crystal vibration is needed.

lattice vibrations are quantized, at temperature T , the vibration with frequency ω has energy:

$$\varepsilon = \left(n + \frac{1}{2} \right) \hbar \omega$$

average phonon #: $\bar{n}_i(\mathbf{q}) = \frac{1}{e^{\hbar \omega_i(\bar{q})/k_B T} - 1}$

Ignore the zero point energy: $\frac{1}{2} \hbar \omega$

D.O.S $g(\omega)$, satisfy: $\int_0^{\omega_m} g(\omega) d\omega = 3N$

In which, ω_m ----max angular frequency,
 N ----# of primitive unit cell

Average Energy:

$$\bar{\varepsilon} = \int_0^{\omega_m} \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} g(\omega) d\omega$$

Heat Capacity:

$$C_V = \left(\frac{\partial \bar{\varepsilon}}{\partial T} \right)_V =$$

$$\int_0^{\omega_m} k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} g(\omega) d\omega$$

$g(\omega) \Rightarrow$ calculate the *phonon heat capacity*

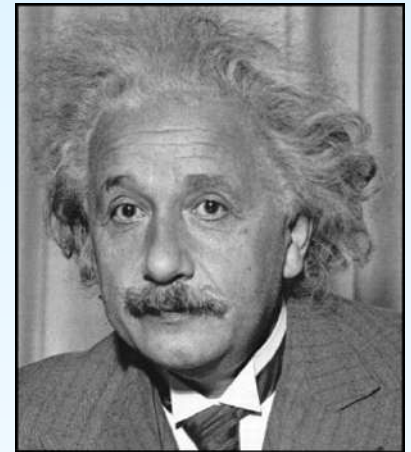
2. Einstein Model

Suppose all the vibration modes are with **the same frequency** ω_E .

Average energy of the crystal:

$$\bar{\varepsilon}(\omega) = 3N \frac{\hbar\omega_E}{e^{\hbar\omega_E/k_B T} - 1}$$

where N is # of primitive cells (PN is # of atoms)



heat capacity:

$$C_V = \left(\frac{\partial \bar{\varepsilon}}{\partial T} \right)_V = 3NPk_B \left(\frac{\hbar\omega_E}{k_B T} \right)^2 \frac{e^{\hbar\omega_E/k_B T}}{\left(e^{\hbar\omega_E/k_B T} - 1 \right)^2}$$

Einstein Temperature: Θ_E $\hbar\omega_E = k_B\Theta_E$

$$C_V = 3PNk_B \left(\frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2}$$

Determination of Θ_E : Select a proper value, such that the calculated specific heat agrees with the experimental data, in an extensive range of temperatures.

- $T \gg \Theta_E$, **at high temperature**

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

$$C_V = 3PNk_B \left(\frac{\Theta_E}{T} \right)^2 \left(\frac{T}{\Theta_E} \right)^2 = 3PNk_B$$

agrees with Dulong-Petit's law.

- $T \ll \Theta_E$, low temperature

$$e^{\Theta_E/T} \gg 1 \quad e^{\Theta_E/T} - 1 \approx e^{\Theta_E/T}$$

$$C_V = 3PNk_B \left(\frac{\Theta_E}{T} \right)^2 e^{-\Theta_E/T}$$

$$= 3PNk_B \left(\frac{\hbar\omega_E}{k_B T} \right)^2 e^{-\frac{\hbar\omega_E}{k_B T}}$$

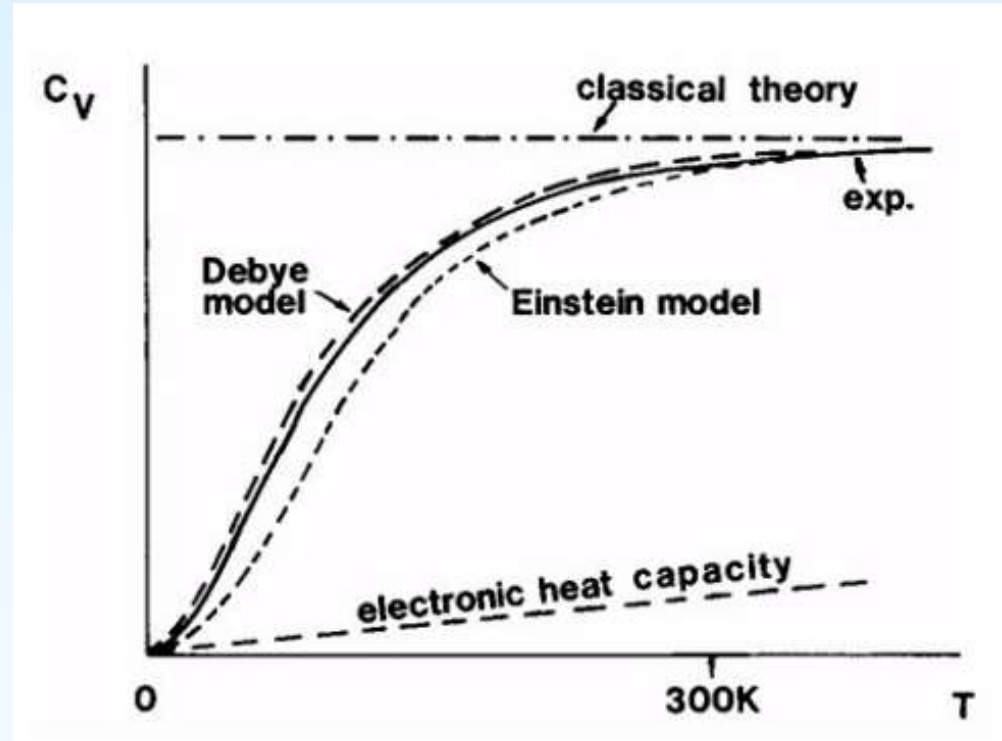
5.1 phonon heat capacity

$$T \rightarrow 0$$

$$C_V \rightarrow 0$$

asymptotic behavior
(from experiments):

$$T^3$$



Einstein model **oversimplified** the **difference in frequency** of various lattice waves (vibration modes)

3. Debye model

Regard Bravais lattices as *isotropic continuous* media, and the crystal vibration an elastic wave with longitudinal and transverse waves presumably moving in the *same velocity*.

Volume of the crystal V , for elastic wave in an isotropic media

$$\omega = vq \quad d\omega = v dq$$

In each branch, # of vibration modes in the range of $q \sim q + dq$

$$dn = \frac{V}{(2\pi)^3} 4\pi q^2 dq$$

of vibration modes in the range of $\omega \sim \omega + d\omega$:

$$dn = \frac{V}{(2\pi)^3} \frac{4\pi q^2}{v} d\omega = \frac{V}{2\pi^2} \frac{\omega^2}{v^3} d\omega$$

For each q , there corresponds **3 elastic waves** (1 *longitudinal*, 2 *transverse* modes).

Therefore, # of modes in $\omega \sim \omega + d\omega$:

$$dn = \frac{3}{2\pi^2} \frac{V}{v^3} \omega^2 d\omega$$

$$g(\omega)d\omega = dn = \frac{3}{2\pi^2} \frac{V}{v^3} \omega^2 d\omega$$

Density of States:

$$g(\omega) = \frac{3}{2\pi^2} \frac{V}{v^3} \omega^2$$

Average Energy:

$$\begin{aligned} \bar{\varepsilon} &= \int_0^{\omega_m} \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \cdot \frac{3V}{2\pi^2 v^3} \omega^2 d\omega \\ &= \frac{3V}{2\pi^2 v^3} \int_0^{\omega_m} \frac{\hbar\omega^3}{e^{\hbar\omega/k_B T} - 1} d\omega \end{aligned}$$

Heat Capacity:

$$C_V = \frac{3}{2\pi} \frac{V}{v^3} \cdot \int_0^{\omega_m} k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\hbar\omega/k_B T} \omega^2}{(e^{\hbar\omega/k_B T} - 1)^2} d\omega$$

For N atoms, $3N$ canonical frequencies:

$$\int_0^{\omega_m} g(\omega) d\omega = \int_0^{\omega_m} \frac{3}{2\pi^2} \frac{V}{v^3} \omega^2 d\omega = 3N$$

$$\omega_m = \left(\frac{6\pi^2 N}{V} \right)^{\frac{1}{3}} v$$

set $\mathbf{x} = \frac{\hbar\omega}{k_B T}$ $\mathbf{x}_m = \frac{\hbar\omega_m}{k_B T}$

$$C_V = 3k_B \frac{V}{2\pi^2} \left(\frac{k_B T}{\hbar v} \right)^3 \int_0^{\mathbf{x}_m} \frac{e^{\mathbf{x}} \mathbf{x}^4}{(e^{\mathbf{x}} - 1)^2} d\mathbf{x}$$

Debye Temperature: Θ_D

$$\Theta_D = \frac{\hbar \omega_m}{k_B}$$

$$\frac{\Theta_D}{T} = x_m = \frac{\hbar \omega_m}{k_B T} = \frac{\hbar}{k_B T} \left(\frac{6\pi^2 N}{V} \right)^{\frac{1}{3}} v$$

$$\bar{\varepsilon} = 9Nk_B T \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx$$

$$C_V = 3k_B \frac{V}{2\pi^2} \frac{6\pi^2 N}{V} \left(\frac{T}{\Theta_D} \right)^3 \cdot \int_0^{x_m} \frac{e^x x^4}{(e^x - 1)^2} dx$$

$$C_V = 9Nk_B \left(\frac{T}{\Theta_D} \right)^3 \cdot \int_0^{\Theta_D/T} \frac{e^x x^4}{(e^x - 1)^2} dx$$

Debye temperature is a *characteristic* temperature of the system

• $T \gg \Theta_D \quad e^x \approx 1 + x$

$$\bar{\varepsilon} = 9Nk_B T \left(\frac{T}{\Theta_D} \right)^3 \frac{1}{3} \left(\frac{\Theta_D}{T} \right)^3 = 3Nk_B T$$

$$C_V = \left(\frac{\partial \bar{\varepsilon}}{\partial T} \right)_V = 3Nk_B$$

tends to classical limit





• $T \ll \Theta_D$ $x_m = \frac{\Theta_D}{T} \rightarrow \infty$

$$\int_0^{\infty} \frac{x^3}{(e^x - 1)^2} dx = \frac{\pi^4}{15} \quad \int_0^{\infty} \frac{e^x x^4}{(e^x - 1)^2} dx = \frac{4}{15} \pi^4$$

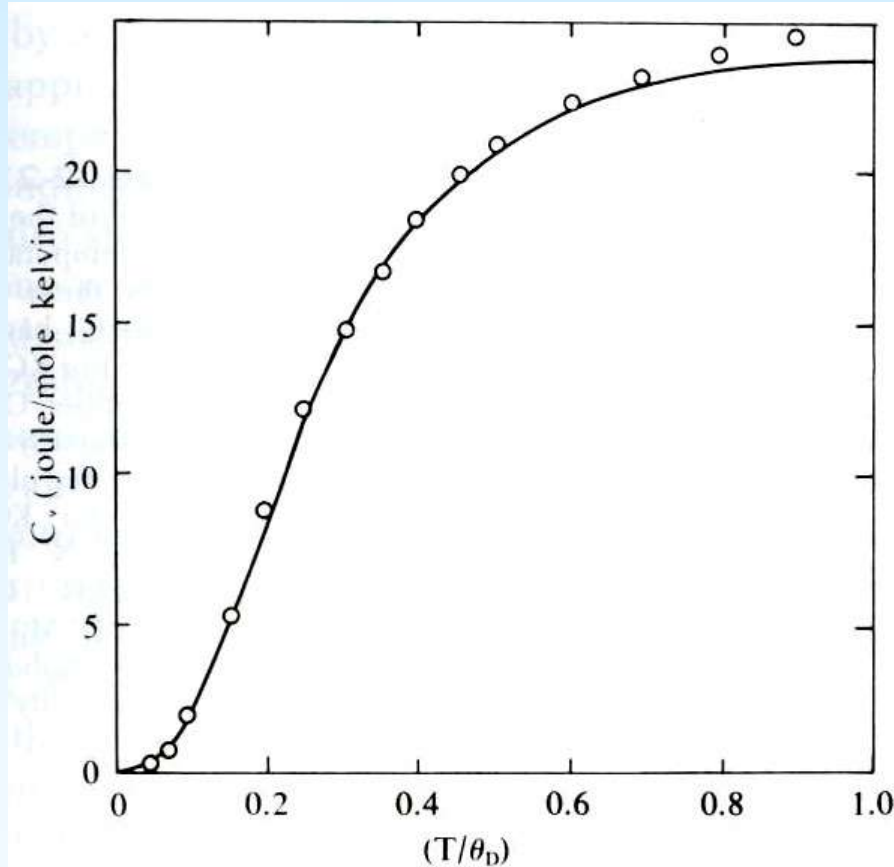
$$\bar{\varepsilon} = 9Nk_B T \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\infty} \frac{x^3}{e^x - 1} dx$$

$$= 9Nk_B T \left(\frac{T}{\Theta_D} \right)^3 \frac{\pi^4}{15} = \frac{3}{5} \pi^4 \frac{Nk_B T^4}{\Theta_D^3}$$

$$C_V = \left(\frac{\partial \bar{\varepsilon}}{\partial T} \right)_V = \frac{12}{5} \pi^4 Nk_B \left(\frac{T}{\Theta_D} \right)^3$$

In extremely temperature, specific heat changes as T^3 .

5.1 phonon heat capacity

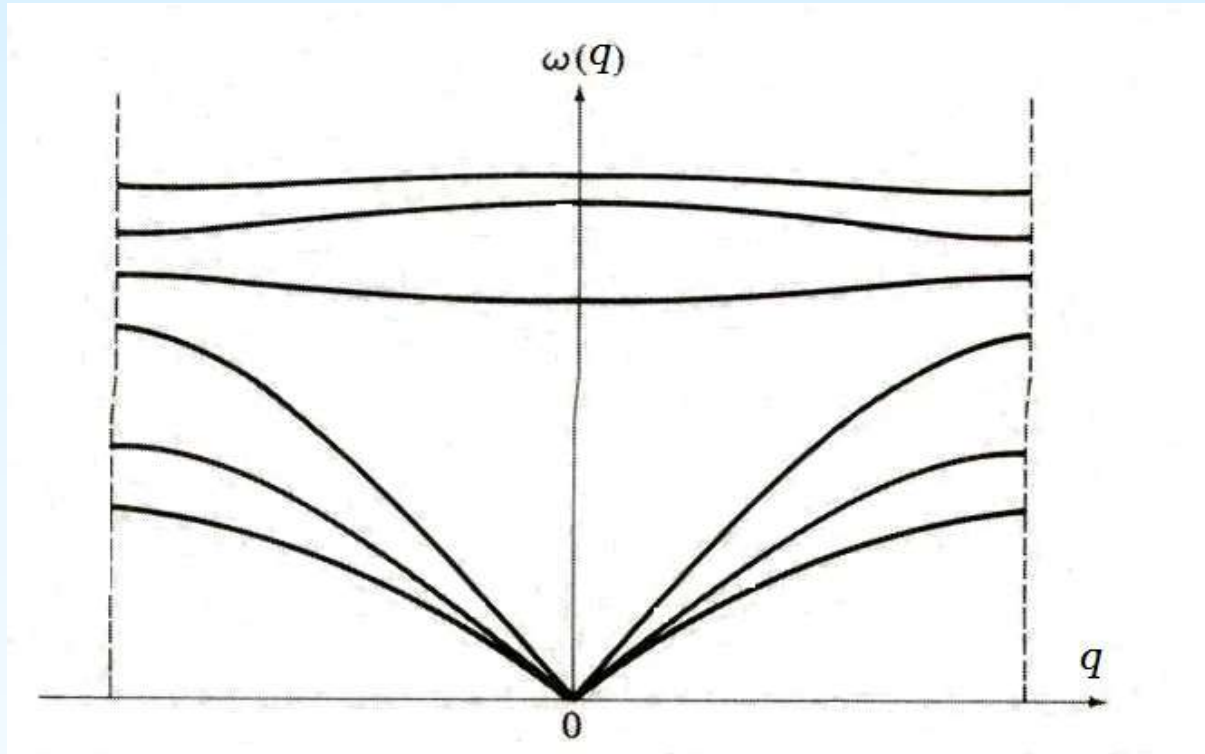


The curve of the specific heat of a solid (per mole) as a function of temperature, according to the Debye model in three dimensions. The experimental points are the data for yttrium reported by L. D. Jennings, R. E. Miller, and F. H. Spedding, *J. Chem. Phys.* **20**, 1040 (1952).

determination of Θ_D

1. from elastic const. and wave velocity
2. from specific heat data

4. Comparison of Einstein and Debye Models



Crystal
Vibration

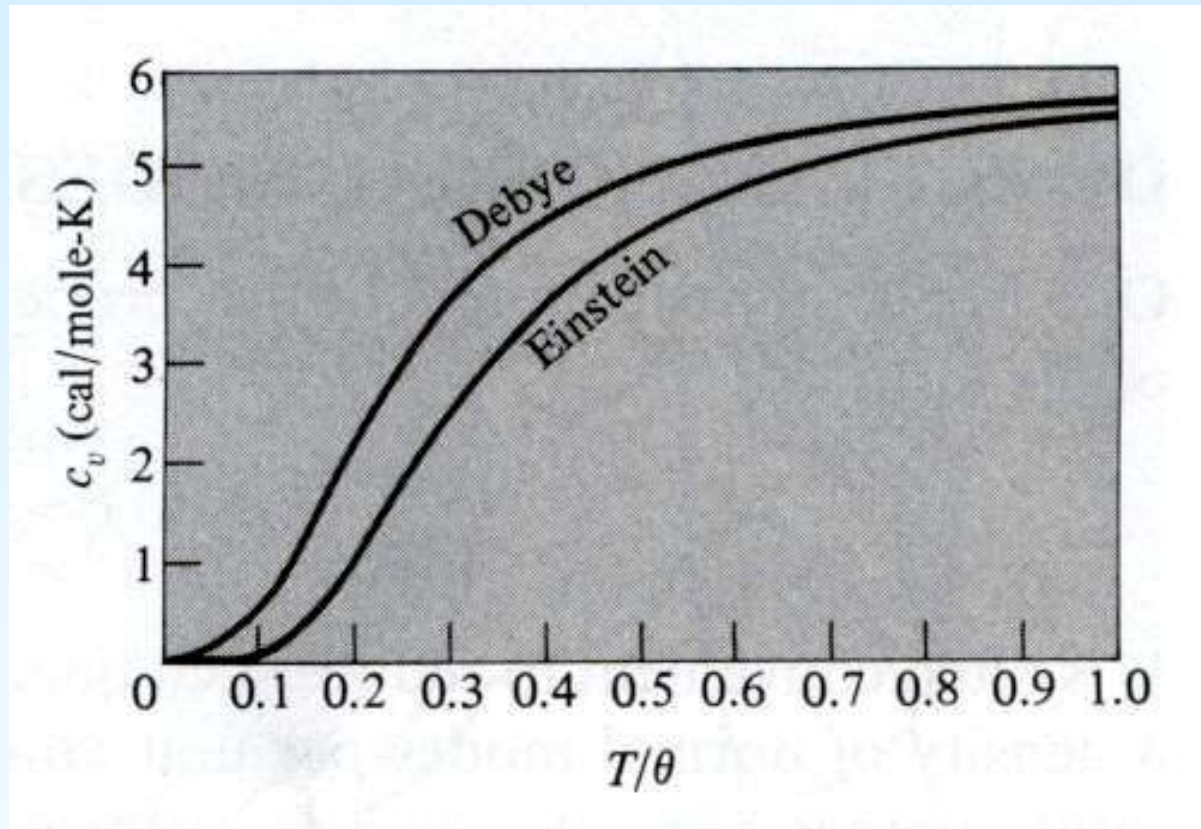
{ optical branch---Einstein model
acoustic branch---Debye model

Einstein Model:

Approximate all branches as *a straight line*, ignore the effects of low energy phonons, and treat all lattice waves as *optical* modes.

Debye Model:

For *long wavelength acoustic* waves, effective model at low temperatures.



We also adopt the combination of the two models
—— **hybridized model**

$$g(\omega) = g_E(\omega) + g_D(\omega)$$

5.2 Experimental Determination of Phonon Spectrum

The *dispersion* relation between *frequency* and *wave vector*
——vibration spectrum of crystal, *phonon spectrum*

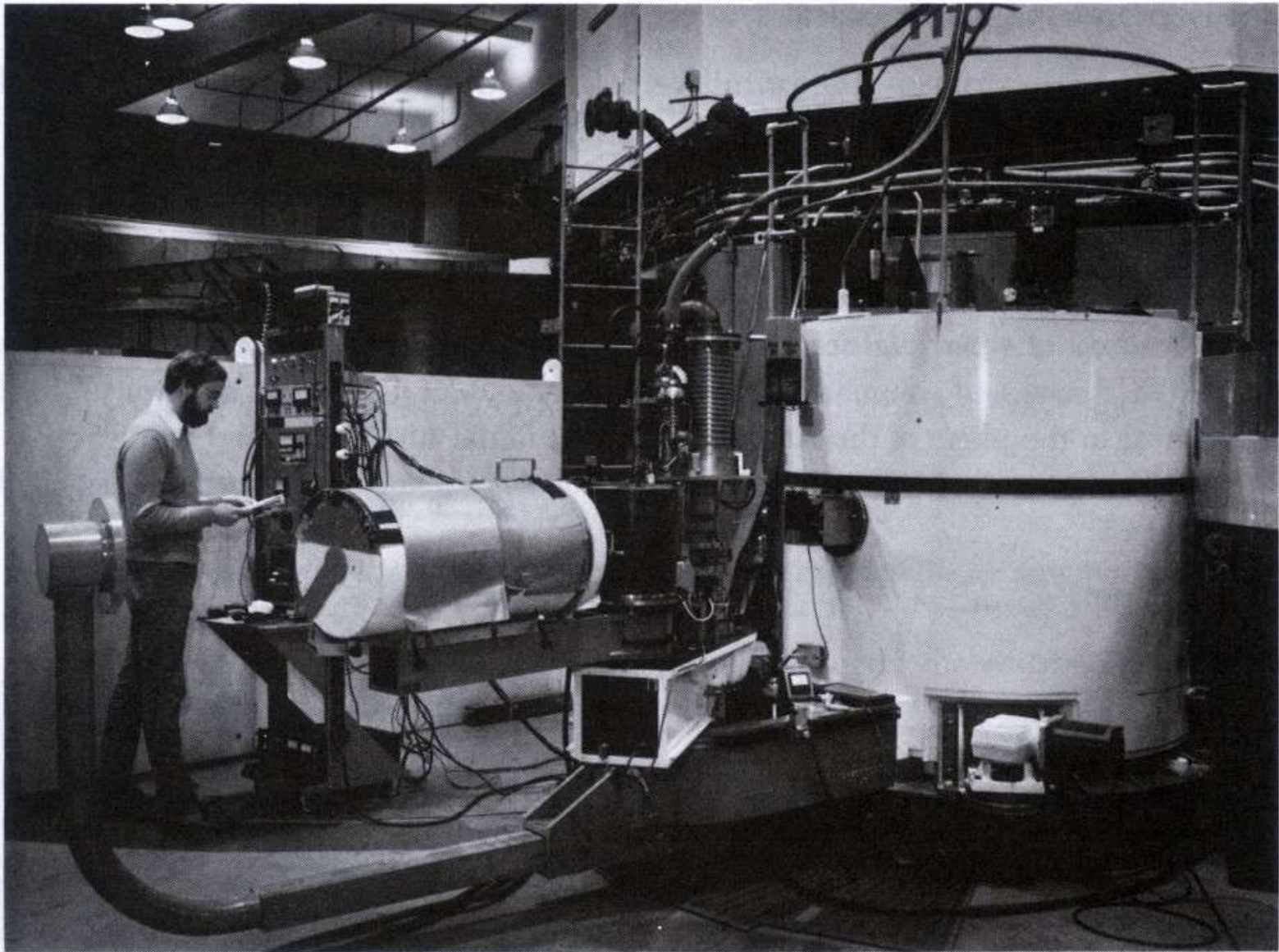
When photons or neutrons are shot into crystals, they can exchange energies with the lattice, and excite/annihilate *phonons*——*inelastic* scattering.

Inelastic X-Ray scattering, neutron scattering, light scattering...

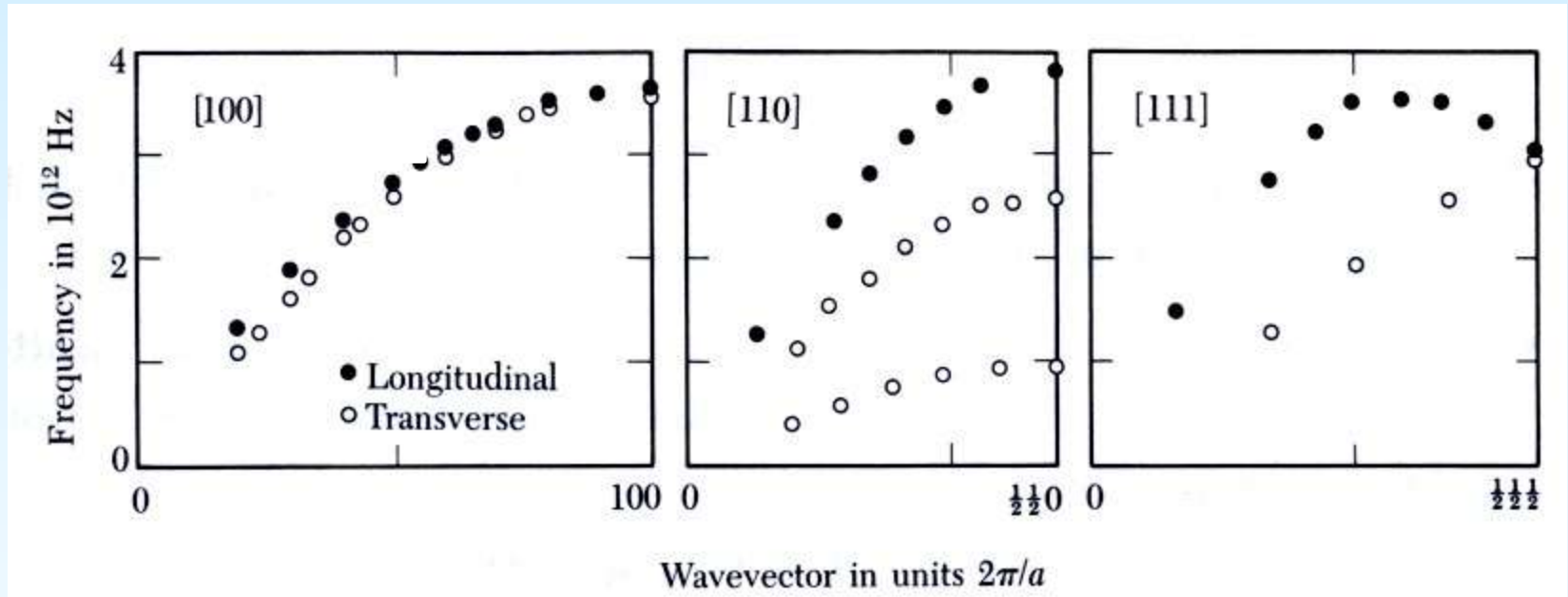
light scattered by *acoustic* phonon——**Brillouin Scattering**

light scattered by *optic* phonon——**Raman Scattering.**

Raman spectrum is very **important** tool for investigating *microstructure* in condensed matter.



A triple axis neutron spectrometer at Brookhaven. (Courtesy of B. H. Grier.)

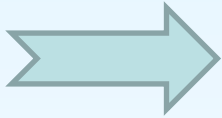


90K, Na crystal, determined dispersion relation
 along *three* directions

5.3 Anharmonic Effects

Harmonic Approximation:

Force on the atom is proportional to its displacement, potential energy is kept up to δ^2 .



Crystal vibration can be described as a series of independent harmonic oscillators, which do not interact with each other, nor exchange energy with each other.

Cannot convey energy, nor establish thermal equilibrium.

Realistic Crystal:

- ✓ Strictly, the interaction between atoms are **not completely** harmonic, the crystal vibration modes are **not completely** independent, but can instead talk to each other.
- ✓ **Phonon-phonon interaction exists**, which enable them to exchange energies. A phonon with a specific frequency could be transfered into another phonon with different frequency, and the distribution of phonons achieves thermal equilibrium after a period of time.
- ✓ **Anharmonic terms** accounts for the existence of thermal equilibrium of crystals.

I. Lattice Free Energy and Equation of State

1. thermodynamic relations

lattice free energy : $F = U - TS$

pressure : $P = -\left(\frac{\partial F}{\partial V}\right)_T$

entropy : $S = -\left(\frac{\partial F}{\partial T}\right)_V$

heat capacity : $C_V = T\left(\frac{\partial S}{\partial T}\right)_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$

energy : $U(T) = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V$

2. Free Energy

lattice free energy: $F = U(V) - \underline{k_B T \ln Z}$ phonon contribution

$U(V)$ —crystal cohesive energy at $T = 0$, a function of volume V , *independent* of temperature T

Z —phonon partition function :

$$Z = \sum e^{-\varepsilon_i/k_B T}$$

For lattice wave ω_i :
$$Z_i = \sum_{n_i=0}^{\infty} e^{-\left(n_i + \frac{1}{2}\right) \frac{\hbar \omega_i}{k_B T}} = \frac{e^{-\frac{1}{2} \frac{\hbar \omega_i}{k_B T}}}{1 - e^{-\frac{\hbar \omega_i}{k_B T}}}$$

Partition function
for all vibration modes:

$$Z = \prod_i Z_i = \prod_i \frac{e^{-\hbar \omega_i / 2 k_B T}}{1 - e^{-\hbar \omega_i / k_B T}}$$

$$F = U(V) + \left\{ -k_B T \sum_i \left[-\frac{1}{2} \frac{\hbar \omega_i}{k_B T} - \ln(1 - e^{-\hbar \omega_i / k_B T}) \right] \right\}$$

$$= U(V) + \sum_i \left[\frac{1}{2} \hbar \omega_i + k_B T \ln(1 - e^{-\hbar \omega_i / k_B T}) \right]$$

Sum over all branches and \vec{q} values (modes).

3. Equation of States

Nonlinear vibration changes the volume and frequency ω_i ,
 ω_i is a function of V .

$$P = -\left(\frac{\partial F}{\partial V} \right)_T = -\left(\frac{\partial U}{\partial V} \right)_T - \sum_i \left[\frac{1}{2} \hbar + \frac{\hbar e^{-\hbar \omega_i / k_B T}}{1 - e^{-\hbar \omega_i / k_B T}} \right] \frac{d\omega_i}{dV}$$

$$= -\left(\frac{\partial U}{\partial V}\right)_T - \sum_i \left[\frac{1}{2} \hbar \omega_i + \frac{\hbar \omega_i}{e^{\hbar \omega_i / k_b T} - 1} \right] \frac{d \ln \omega_i}{dV}$$

$$= -\left(\frac{\partial U}{\partial V}\right)_T - \frac{1}{V} \sum_i \bar{\varepsilon}_i \frac{d \ln \omega_i}{d \ln V}$$

in which: $\bar{\varepsilon}_i = \frac{1}{2} \hbar \omega_i + \frac{\hbar \omega_i}{e^{\hbar \omega_i / k_B T} - 1}$

set $\gamma = -\frac{d \ln \omega_i}{d \ln V}$

—— **Gruneisen parameter,**
*independent of ω_i , related with
nonlinear vibration.*

$$\mathbf{P} = -\frac{dU}{dV} + \gamma \frac{\bar{\varepsilon}}{V}$$

II. Thermal Expansion

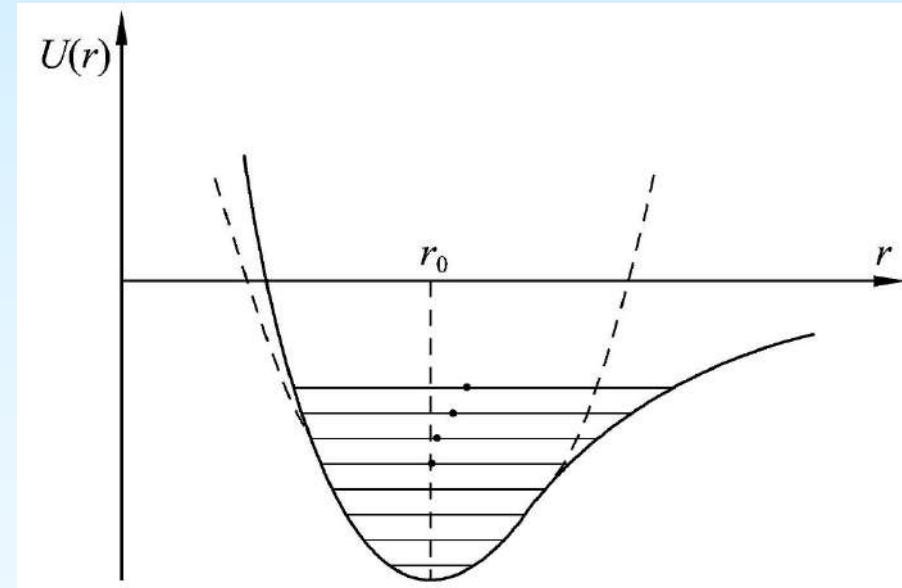
Volume changes with T , under a fixed pressure.

1. Qualitative analysis

Given a symmetric potential around equilibrium position, then

⇒ equilibrium position independent of amplitude of vibration or temperature.

Realistic potential curve is not strictly a parabola, *steeper* on the left and *smoother* on the right side. Atoms tend to move rightwards when vibration amplitudes increase.



Anharmonic potential is non-symmetric, inducing some “repulsive” interactions when atoms vibrate, accounting for the thermal expansion phenomenon.

2. quantitative analysis

volume expansion
coefficient:

$$\alpha = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{K} \left(\frac{\partial P}{\partial T} \right)_V$$

$$K = -V_0 \left(\frac{\partial P}{\partial V} \right)_T$$

K is bulk modulus

linear expansion
coefficient:

$$\alpha_l = \frac{1}{l_0} \left(\frac{\partial l}{\partial T} \right)_P$$

isotropic cubic system: $\alpha_l = \alpha/3 = \frac{1}{3K} \left(\frac{\partial P}{\partial T} \right)_V$

According to equation of state:

$$P = -\frac{dU}{dV} + \gamma \frac{\bar{\varepsilon}}{V}$$

For most solids, volume change is small, expand $\frac{dU}{dV}$ around equilibrium V_0 :

$$\frac{dU}{dV} = \left(\frac{dU}{dV} \right)_{V_0} + (V - V_0) \left(\frac{d^2U}{dV^2} \right)_{V_0} + \dots$$

First term vanishes, retain up to the second term:

$$\frac{dU}{dV} = \frac{V - V_0}{V_0} \left[V_0 \left(\frac{d^2U}{dV^2} \right)_{V_0} \right] = K \frac{V - V_0}{V_0} \quad \rightarrow$$

$$P = -K \frac{V - V_0}{V_0} + \gamma \frac{\bar{\varepsilon}}{V}$$

thermal expansion is the relation between V and T at $P = 0$,

$$P = 0 \quad \longrightarrow \quad \frac{V - V_0}{V_0} = \frac{\gamma \bar{\varepsilon}}{K V}$$

$$dV = V - V_0$$

$$\alpha = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right)_P = \frac{\gamma C_V}{K V}$$

$$\alpha_l = \frac{\gamma C_V}{3K V}$$

Grüneisen's law, thermal expansion of solids is proportional to the specific heat (per volume).

III. Thermal Conductivity

1. phonon scattering

Lattice waves are no longer independent due to anharmonic effects, leading to *phonon scattering*.

The process of phonon collision obeys **energy conservation** and **quasi-momentum conservation**:

$$\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3$$

$$\vec{q}_1 + \vec{q}_2 = \vec{q}_3 + \vec{G}_h$$

(1) Normal process

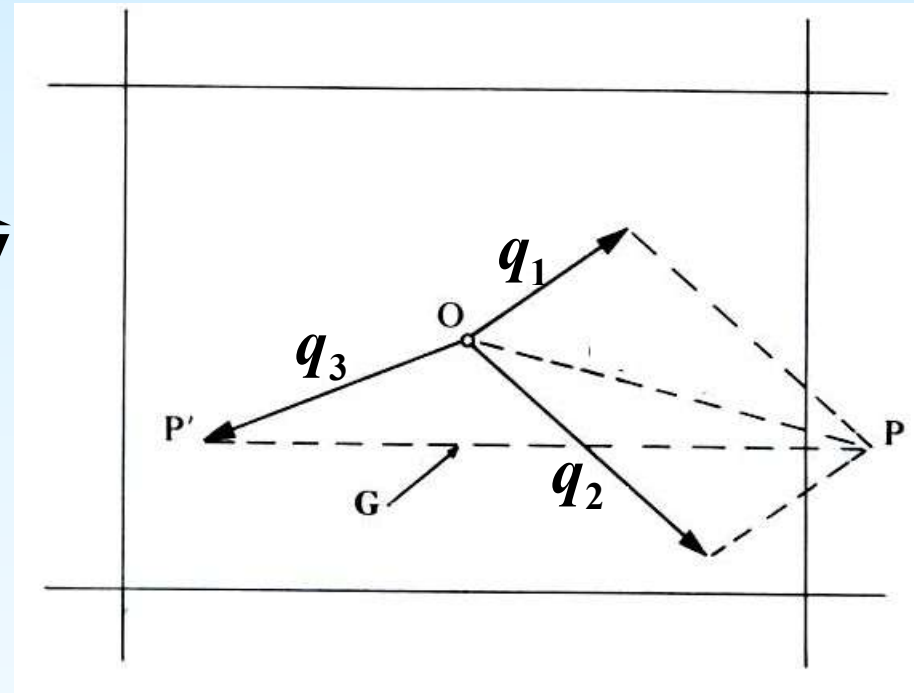
Wave vectors q_1 , q_2 are relatively small, resulting q_3 is still in the *1st* BZ, thus called **normal process**.

Total energy/wave vector keeps unchanged, only the *energy* and *quasi-momentum* of the two phonons are transferred to a *3rd* one, **net heat flow** does not decrease, nor does its direction change.

If all phonon collisions are normal processes, the lattice thermal conductivity diverges and resistivity is zero, i.e., **normal process** contributes *nothing* to thermal resistivity.

(2) Umklapp process

$\vec{q}_1 + \vec{q}_2$ exceeds 1st BZ, due to the periodicity of lattice, wave vector \vec{q} describes the same vibration state as $\vec{q} + \vec{G}_n$. $\vec{q}_1 + \vec{q}_2$ can be moved back to 1st BZ by adding some reciprocal lattice vector.



- ✓ Such process is called **umklapp process**, a large angle scattering. The direction of phonon movement is changed greatly, making a shorter **mean free path**, and give rise to some finite thermal resistivity.

2. Thermal Conductivity

Suppose different temperatures at two ends of the rod: T_1, T_2

$$T_2 > T_1$$

Heat flow, following the temperature gradient, move from the hot end to the cold one, with energy density proportional to the temperature gradient.

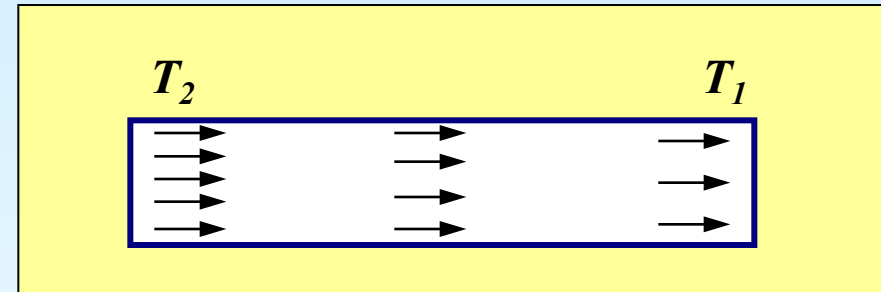
$$J_q = -\kappa \frac{dT}{dx} \quad \text{Fourier's law}$$

where κ denotes thermal conductivity coefficient.

Thermal conductance: electrons (metal), phonon (insulator)

5.3 Anharmonic effects

- Atoms are vibrating more strongly in the **hot** (left) end than those near the **cold** (right) end, leading to a larger density of phonons.
- Phonons move from left to right, carrying heat, and flow along the opposite direction of temperature gradient.



- ✓ Apply the gas molecule dynamic theory to the phonon gas, thermal conductivity reads:

$$\kappa = \frac{1}{3} C_V v l$$

v — phonon *velocity*; l — mean free path, *mean distance a phonon moves between two successive collisions with other phonons.*

Three mechanisms:

(1) Collision between phonons

Phonon-phonon scattering due to anharmonic couplings, especially important at *high* temperatures.

$$\text{High } T: \quad T \gg \Theta_D$$

$$\text{Mean phonon number:} \quad n_q = \frac{1}{e^{\hbar\omega_q/k_B T} - 1} \approx \frac{k_B T}{\hbar\omega_q} \propto T$$

Collision probability proportional to # of phonons,

Corresponding **mean free path** thus is inverse proportional to

$$\text{temperatures:} \quad l \sim \frac{1}{T}$$

(2) Scattering of phonon with crystal defects

Impurities and defects also scatter phonons, since they partially break the lattice periodicity. The larger the mass difference and density of impurities are, the stronger the scattering is, and l becomes shorter.

(3) scattering with the boundaries of specimen

At very low temperatures, (1,2) collisions are scarce.

- only few phonons exist, dilute phonon gas
- phonons with long wavelength at low temperatures, which cannot be effectively scattered by objects like impurities of much smaller size.

At low temperatures, the main mechanism is the boundary scattering. It cause some **geometric effects**, since the phonon has very long wavelength, which is comparable to the size of specimen. Mean free path $l = L$, **independent** of temperatures.

Remember the thermal conductivity: $\kappa = \frac{1}{3} C_V v l$

At **low T**, thermal conductivity determined by heat capacity

$$\kappa \sim T^3$$

At **high T**, thermal conductivity determined by mean free path l

$$\kappa \sim \frac{1}{T}$$