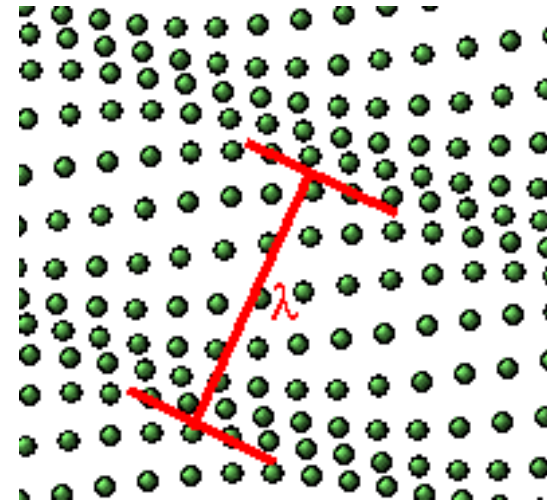


Chap 13 Phonons

- classical theory of vibration
 - 1-dim, 3-dim
- quantum theory of vibration
- phonon specific heat
 - Einstein model, Debye model
- thermal expansion
- neutron scattering



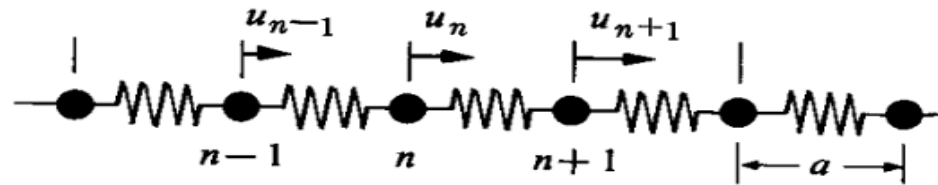
Dept of Phys



M.C. Chang

One dimensional vibration

- consider only longitudinal motion
- consider only NN coupling



$$M \frac{d^2 u_n}{dt^2} = \alpha(u_{n+1} - u_n) - \alpha(u_n - u_{n-1})$$

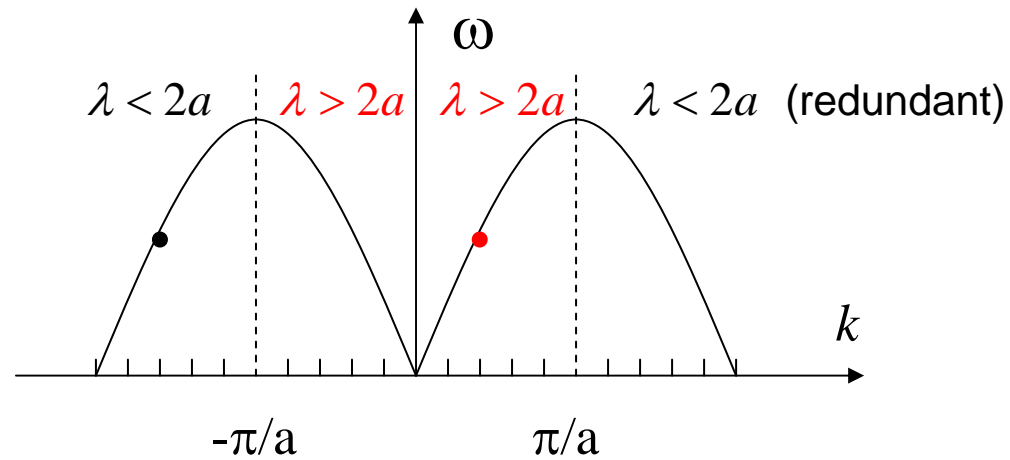
PBC: Assume $u_n = A e^{i(kX_n - \omega t)}$, where $X_n = na$,
then we'll get

$$M(-\omega^2) e^{ikna} = -\alpha \left[2e^{ikna} - e^{ik(n+1)a} - e^{ik(n-1)a} \right],$$

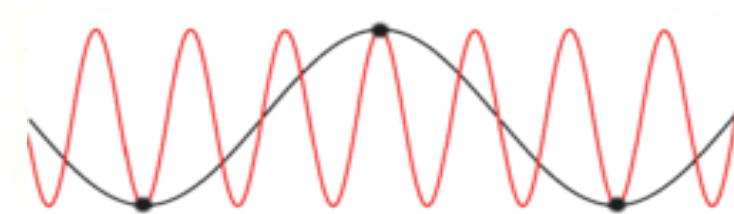
which leads to

$$\omega(k) = \omega_M \left| \sin(ka/2) \right|, \quad \omega_M = 2\sqrt{\alpha/M}$$

Dispersion curve $\omega(k) = \omega_M \left| \sin(ka/2) \right|$



The waves with wave numbers k and $k + 2\pi/a$ describe the same atomic displacement



Therefore, we can restrict k to within the first BZ $[-\pi/a, \pi/a]$

Displacement of the n -th atom

$$u_n(t) = Ae^{i(kX_n - \omega t)}, \quad X_n = na$$

Pattern of vibration:

- $k \sim 0$, $\exp(ikX_n) \sim 1$.

Every atom move in unison. Little restoring force.

- $k \sim \pi/a$, $\exp(ikX_n) \sim (-1)^n$.

Adjacent atoms move in opposite directions. Maximum restoring force.

Velocity of wave:

- $k \sim 0$, $\omega = (\omega_M a/2)k$

Linear dispersion, phase velocity = group velocity

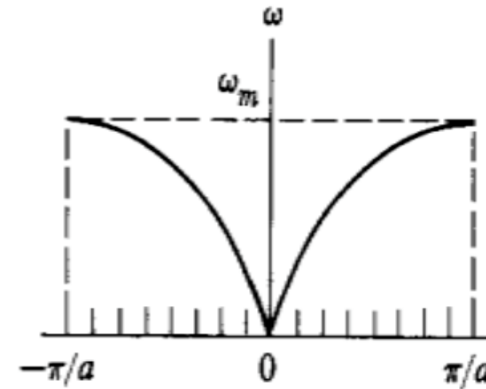
- $k \sim \pi/a$, group velocity ~ 0

Number of “normal modes”:

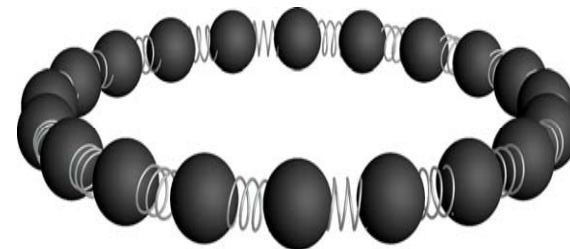
$$u_N = u_0 \Rightarrow \exp(ikNa) = 1$$

$$\therefore k = \frac{m}{N} \frac{2\pi}{a}, \quad m \in \mathbb{Z} \quad \Delta k = 2\pi / Na$$

Within the 1st BZ, there are N k -points.

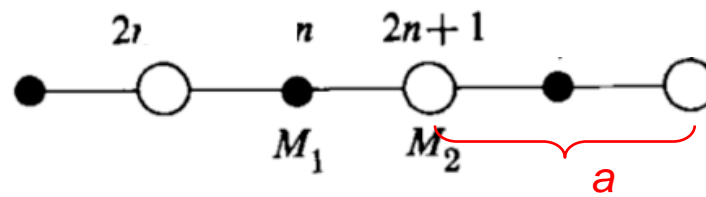


PBC



Each k describes a **normal mode** of vibration (i.e. a vibration with a specific frequency)

Vibration of a crystal with 2 atoms in a unit cell



$$M_2 \frac{d^2 u_{2n+1}}{dt^2} = -\alpha(2u_{2n+1} - u_{2n} - u_{2n+2}),$$

$$M_1 \frac{d^2 u_{2n+2}}{dt^2} = -\alpha(2u_{2n+2} - u_{2n+1} - u_{2n+3}).$$

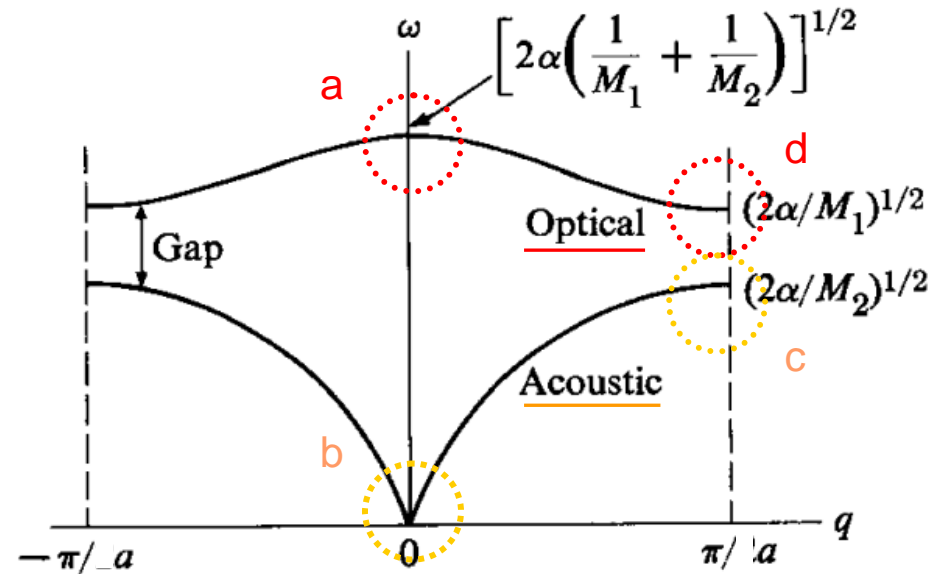
$$\text{Assume } \begin{pmatrix} u_{2n+1} \\ u_{2n+2} \end{pmatrix} = \begin{pmatrix} A_1 e^{ikX_{2n+1}} \\ A_2 e^{ikX_{2n+2}} \end{pmatrix} e^{-i\omega t}, \quad \begin{aligned} X_{2n+1} &= (2n+1)a/2 \\ X_{2n+2} &= (n+1)a \end{aligned}$$

$$\Rightarrow \begin{pmatrix} 2\alpha - M_2 \omega^2 & -2\alpha \cos(ka/2) \\ -2\alpha \cos(ka/2) & 2\alpha - M_1 \omega^2 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = 0,$$

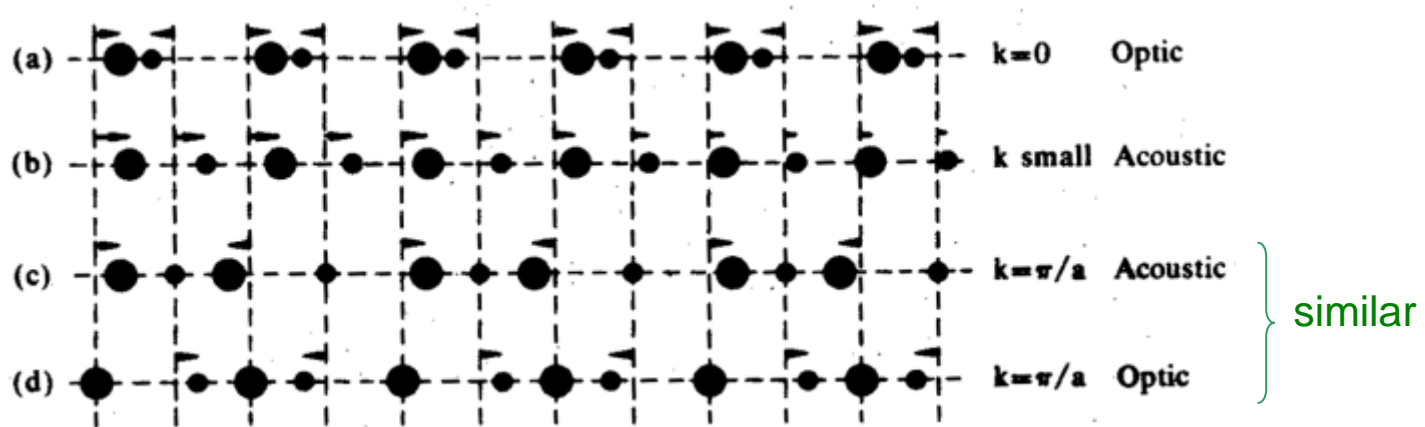
$$\Rightarrow \det \begin{pmatrix} 2\alpha - M_2 \omega^2 & -2\alpha \cos(ka/2) \\ -2\alpha \cos(ka/2) & 2\alpha - M_1 \omega^2 \end{pmatrix} = 0.$$

$$\Rightarrow \omega_{\pm}^2 = \alpha \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \pm \alpha \sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4 \sin^2(ka/2)}{M_1 M_2}}.$$

Two branches of dispersion curves (assume $M_2 > M_1$)



Patterns of vibration



See a nice demo at <http://dept.kent.edu/projects/ksuviz/leeviz/phonon/phonon.html>

Three dimensional vibration

Along a given direction of propagation, there are

1 longitudinal wave and 2 transverse waves,

each may have different velocities

Sodium
(bcc)

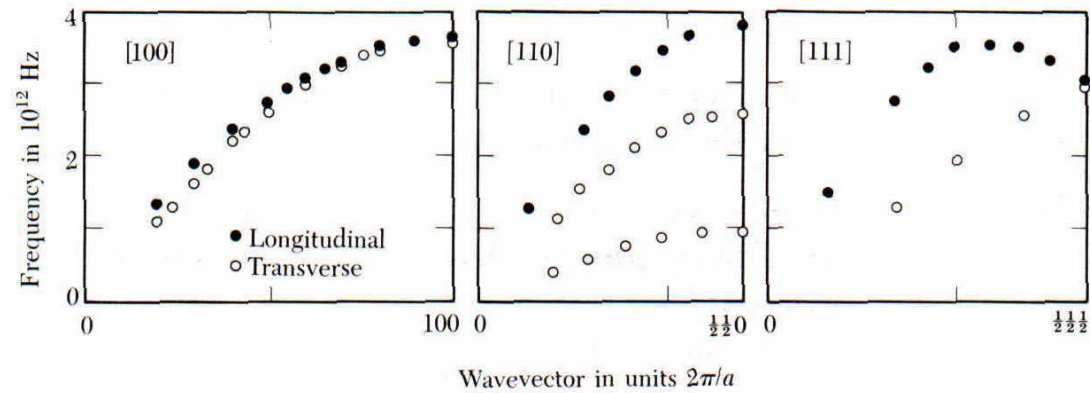
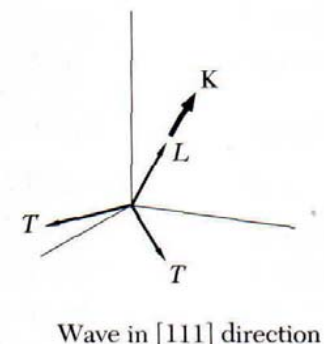
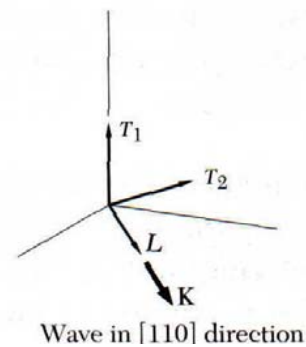
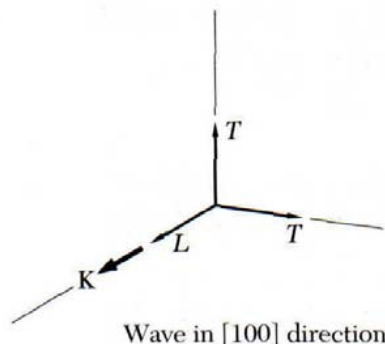


Figure 11 The dispersion curves of sodium for phonons propagating in the [001], [110], and [111] directions at 90 K, as determined by inelastic scattering of neutrons, by Woods, Brockhouse, March and Bowers. *Na*



3D crystal with atom basis

Rules of thumb

- For a 3-dim crystal, if each unit cell has p atoms, then there are

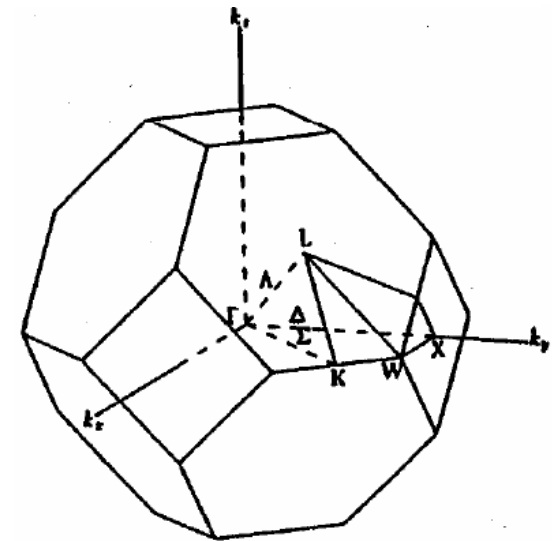
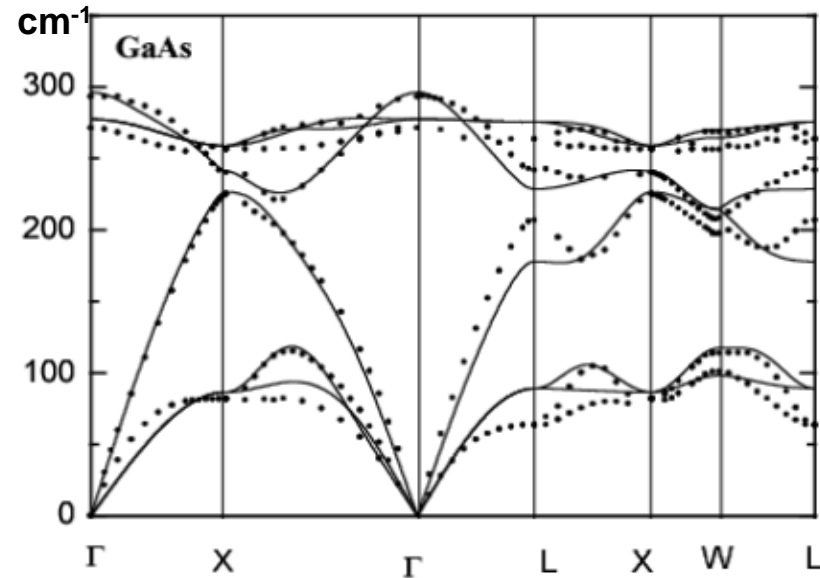
3 acoustic branches,

$3(p-1)$ optical branches

- If a crystal has N unit cells, then each branch has N normal modes ◦

- As a result, the total number of normal modes are $3pN$ (= total DOF of this system)

FCC lattice with 2-atom basis

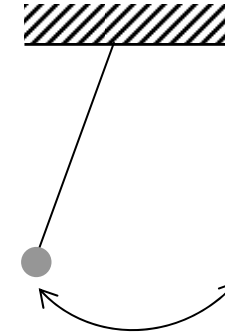


Quantum theory of vibration

Review: 1D simple harmonic oscillator (DOF=1)

$$H = \frac{p^2}{2m} + \frac{\alpha}{2} x^2$$

- Classically, it oscillates with a single freq $\omega = (\alpha/m)^{1/2}$
- The energy ε can be continuously changed.



Quantization: $[x, p] = i\hbar$

define $a = \frac{1}{\sqrt{2\hbar}} \left(\sqrt{m\omega} x + \frac{i}{\sqrt{m\omega}} p \right)$

then $[a, a^\dagger] = 1$

$$H = \left(a^\dagger a + \frac{1}{2} \right) \hbar\omega$$

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

Note:

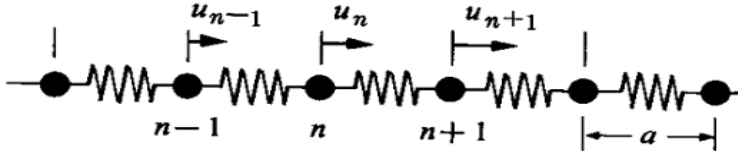
$$a|n\rangle = \sqrt{n}|n-1\rangle$$

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$$

$$a^\dagger a|n\rangle = n|n\rangle$$

- After quantization, the energy becomes discrete $\varepsilon_n = \left(n + \frac{1}{2} \right) \hbar\omega$
- The number n of energy quanta depends on the amplitude of the oscillator.

Quantization of a 1-dim vibrating lattice (DOF=N)

$$H = \sum_{\ell=1}^N \left[\frac{p_{\ell}^2}{2m} + \frac{\alpha}{2} (u_{\ell+1} - u_{\ell})^2 \right]$$


- Classically, for a given k , it vibrates with a single frequency $\omega(k)$.
The amplitude (and hence energy ε) can be continuously changed.

Quantization: $[u_{\ell}, p_{\ell'}] = i\hbar\delta_{\ell\ell'}$

Fourier transf. $\left\{ \begin{array}{l} u_{\ell} = \frac{1}{\sqrt{N}} \sum_k e^{ik\ell a} u_k \\ p_{\ell} = \frac{1}{\sqrt{N}} \sum_k e^{ik\ell a} p_k \end{array} \right.$

then $[u_k, p_{k'}^{\dagger}] = i\hbar\delta_{kk'}$

$$\Rightarrow H = \sum_k \left(\frac{1}{2m} p_k^{\dagger} p_k + \frac{m\omega_k^2}{2} u_k^{\dagger} u_k \right)$$

Note:

$$\begin{aligned} u_{\ell}^{\dagger} &= u_{\ell}; & p_{\ell}^{\dagger} &= p_{\ell} \\ \rightarrow u_k^{\dagger} &= u_{-k}; & p_k^{\dagger} &= p_{-k} \end{aligned}$$

$$k=2\pi m/L, \quad L=Na.$$

A collection of N
independent oscillators !

Similarly, define
$$a_k = \frac{1}{\sqrt{2\hbar}} \left(\sqrt{m\omega_k} u_k + \frac{i}{\sqrt{m\omega_k}} p_k \right)$$

$$\rightarrow [a_k, a_{k'}^\dagger] = \delta_{kk'}$$

$$\rightarrow H = \sum_k \left(a_k^\dagger a_k + \frac{1}{2} \right) \hbar \omega_k$$

eigenstate $|n_1, n_2 \dots n_k, \dots\rangle$

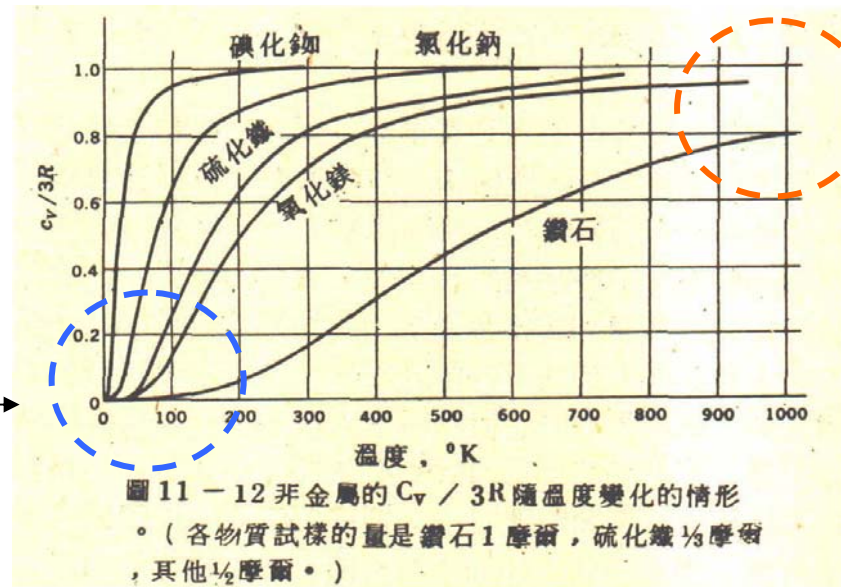
$$H |n_1, n_2 \dots n_k, \dots\rangle = \sum_k \left(n_k + \frac{1}{2} \right) \hbar \omega_k |n_1, n_2 \dots n_k, \dots\rangle$$

- The number of energy quanta (called **phonons**) for the k-mode is n_k .
- There are no interaction between phonons \rightarrow “free” phonon gas.
- If there are p -atoms in a unit cell (p branches), then the total vibrational energy of the lattice is

$$U = \sum_k \sum_{s=1}^p \left(n_{k,s} + \frac{1}{2} \right) \hbar \omega_{k,s}$$

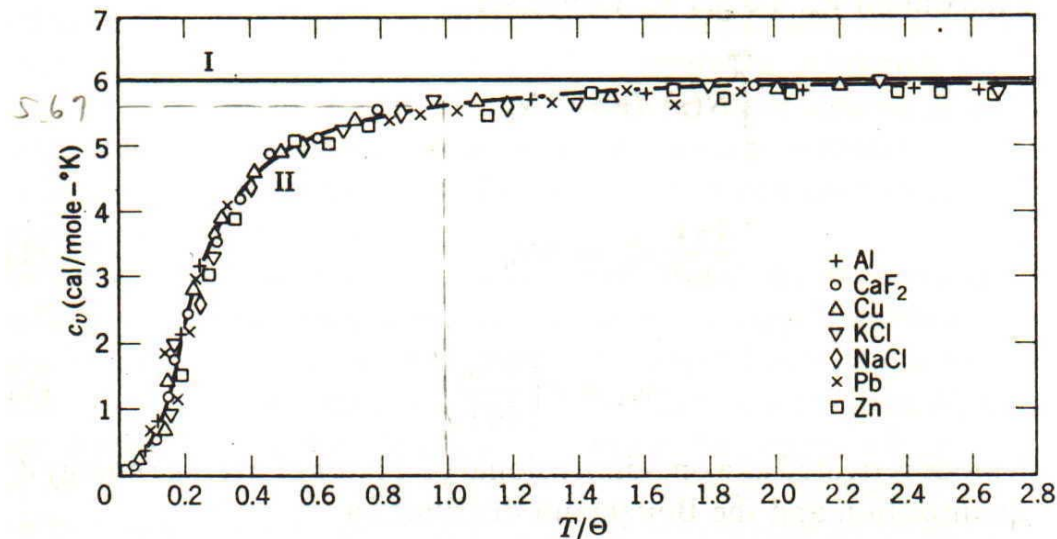
Specific heat: experimental fact

Specific heat drops to zero at low temperature



Specific heat approaches $3R$ (per mole) at high temperature (Dulong-Petit law)

After rescaling the temperature by θ (Debye temperature), which differs from material to material, a universal behavior emerges:



Debye temperature

Table 1 Debye temperature and thermal conductivity^a

Li	Be											B	C	N	O	F	Ne		
344	1440												2230					75	
0.85	2.00											0.27	1.29						
Na	Mg											Al	Si	P	S	Cl	Ar		
158	400	Low temperature limit of θ , in Kelvin										428	645					92	
1.41	1.56	Thermal conductivity at 300 K, in $W\ cm^{-1}K^{-1}$										2.37	1.48						
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
91	230	360	420	380	630	410	470	445	450	343	327	320	374	282	90		72		
1.02		0.16	0.22	0.31	0.94	0.08	0.80	1.00	0.91	4.01	1.16	0.41	0.60	0.50	0.02				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn _w	Sb	Te	I	Xe		
56	147	280	291	275	450		600	480	274	225	209	108	200	211	153		64		
0.58		0.17	0.23	0.54	1.38	0.51	1.17	1.50	0.72	4.29	0.97	0.82	0.67	0.24	0.02				
Cs	Ba	La _{β}	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
38	110	142	252	240	400	430	500	420	240	165	71.9	78.5	105	119					
0.36		0.14	0.23	0.58	1.74	0.48	0.88	1.47	0.72	3.17		0.46	0.35	0.08					
Fr	Ra	Ac																	
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
			0.11	0.12	0.16		0.13		200		210					120	210		
								0.11	0.11	0.11	0.16	0.14	0.17	0.35	0.16				
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			
			163		207														
			0.54		0.28	0.06	0.07												

In general, a harder material has a higher Debye temperature

Specific heat: theoretical framework

- **Internal energy U** of a crystal is the summation of vibrational energies (consider an insulator so there's no electronic energies)

$$U(T) = \sum_{k,s} (n_{k,s} + 1/2) \hbar \omega_{k,s}, \quad s=L/T, A/O\dots$$

- For a crystal in thermal equilibrium, the average phonon number is

$$\langle n_{k,s} \rangle = \frac{1}{e^{\hbar \omega_{k,s}/kT} - 1} \quad \text{Bose-Einstein distribution}$$

- Therefore,

$$U(T) = \sum_{k,s} \left(\frac{1}{e^{\hbar \omega_{k,s}/kT} - 1} + \frac{1}{2} \right) \hbar \omega_{k,s}$$

- **Specific heat**

$$C_V = \left(\partial U / \partial T \right)_V$$

- Density of states (similar to electron energy band)

$$\sum_k f_k = V \int \frac{d^3k}{(2\pi)^3} f_k = \int d\omega D(\omega) f_\omega$$

$$D(\omega) = \left(\frac{L}{2\pi} \right)^3 \int \frac{dS_\omega}{|\nabla_{\vec{k}} \omega|}$$

Ex: In 3D

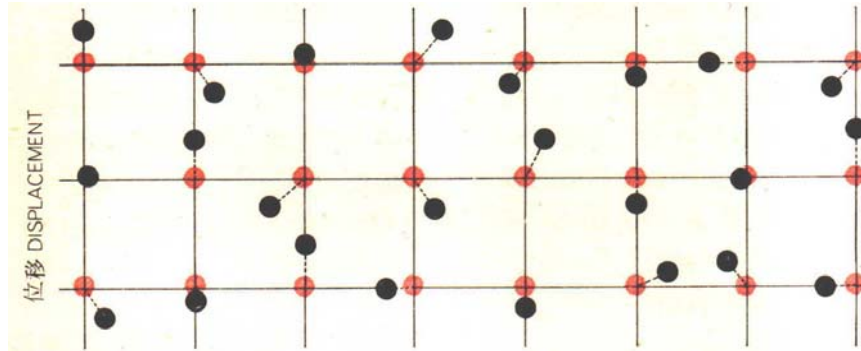
if $\omega = vk$, then $D(\omega) = V \omega^2 / 2\pi^2 v^3$

Einstein model (1907)

Assume that each atom vibrates independently of each other, and every atom has the same vibration frequency ω_0

DOS

$$D(\omega) = 3N\delta(\omega - \omega_0)$$



3 dim \times number of atoms

$$U = 3N \left(\langle n \rangle + \frac{1}{2} \right) \hbar\omega_0 = 3N \frac{\hbar\omega_0}{\exp(\hbar\omega_0/kT) - 1} + 3N \frac{\hbar\omega_0}{2}$$

$$C_V = (\partial U / \partial T)_V = 3Nk \left(\frac{\hbar\omega_0}{kT} \right)^2 \frac{e^{\hbar\omega_0/kT}}{(e^{\hbar\omega_0/kT} - 1)^2}$$

$$\approx e^{-\hbar\omega_0/kT} \text{ as } T \rightarrow 0K$$

(Activation behavior)

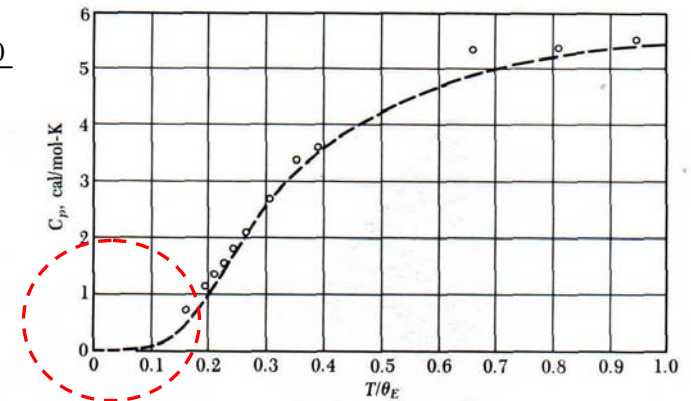


Figure 11 Comparison of experimental values of the heat capacity of diamond with values calculated on the earliest quantum (Einstein) model, using the characteristic temperature $\theta_E = \hbar\omega/k_B = 1320$ K. To convert to J/mol-deg, multiply by 4.186.

Debye model (1912)

Atoms vibrate collectively in a wave-like fashion.

$$U(T) = \sum_{k,s} \langle n_{k,s} \rangle \hbar \omega_{k,s} \quad (\hbar \omega_{k,s}/2 \text{ neglected})$$

$$= \sum_s \int d\omega D_s(\omega) \frac{\hbar \omega}{e^{\hbar \omega/kT} - 1}$$

- Debye assumed a simple dispersion relation:

$$\omega = v_s k. \text{ Therefore, } D_s(\omega) = V \omega^2 / 2\pi^2 v_s^3$$

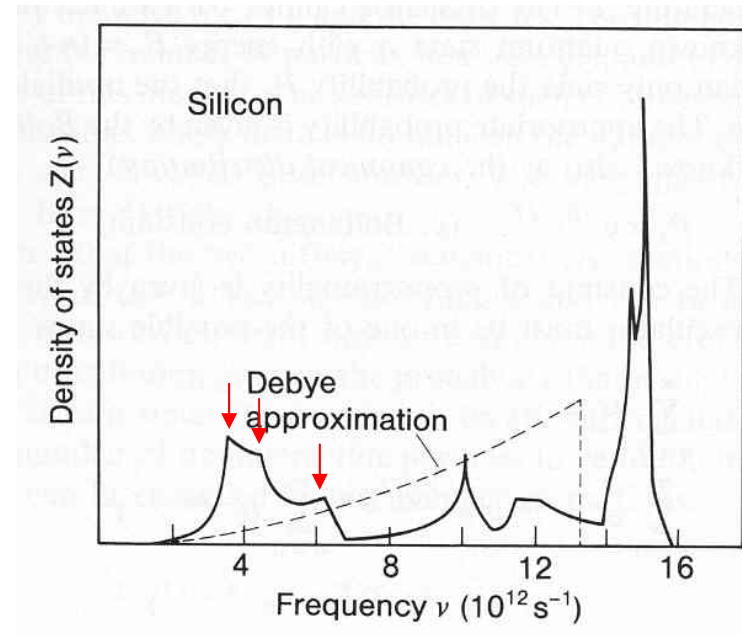
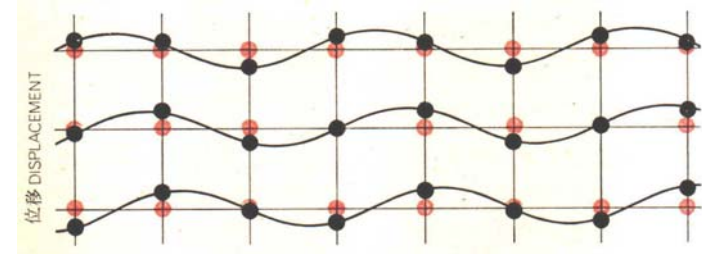
Also, the 1st BZ is approximated by a sphere with the same volume

$$\sum_{s=1}^3 \int d\omega D_s(\omega) = 3N$$

$$\rightarrow \sum_{s=1}^3 \frac{V \omega_D^3}{6\pi^2 v_s^3} = 3N$$

$$\frac{3}{v^3} \equiv \sum_{s=1}^3 \frac{1}{v_s^3}$$

$$\rightarrow \omega_D = v(6\pi^2 n)^{1/3}, n = N/V$$



If $v_g = |\nabla_{\vec{k}} \omega| = 0$, then there is
"van Hove singularity".

$$\begin{aligned}
 U(T) &= \sum_{s=1}^3 \frac{V}{2\pi^2 v_s^3} \int_0^{\omega_D} d\omega \omega^2 \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \\
 &= \frac{3V}{2\pi^2 v^3} \hbar \left(\frac{kT}{\hbar} \right)^4 \int_0^{x_D} dx \frac{x^3}{e^x - 1}, \quad x_D = \frac{\hbar\omega_D}{kT} = \frac{\theta}{T}, \quad k\theta \equiv \hbar\omega_D \\
 &= 9NkT \left(\frac{T}{\theta} \right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1} = \pi^4/15 \text{ as } T \rightarrow 0 \\
 \therefore C_V &= \frac{12\pi^4}{5} Nk \left(\frac{T}{\theta} \right)^3 \propto T^3 \text{ as } T \rightarrow 0
 \end{aligned}$$

Debye temperature

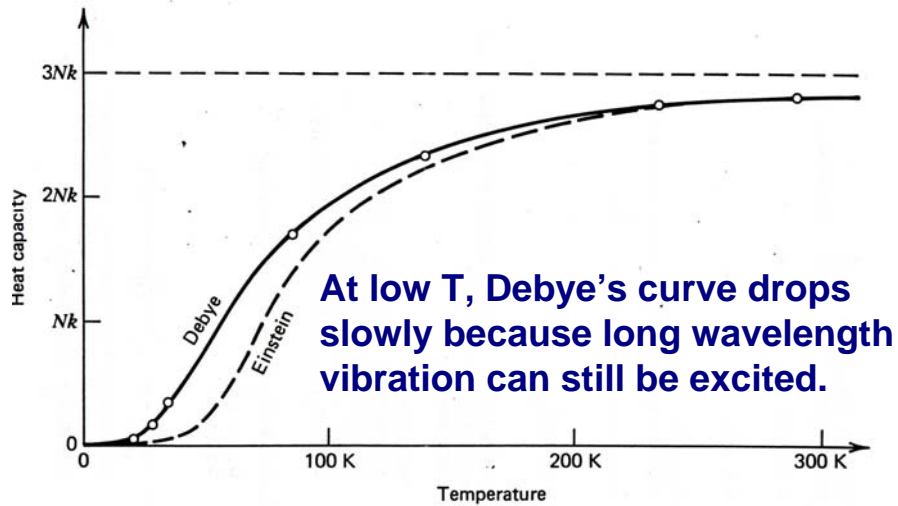
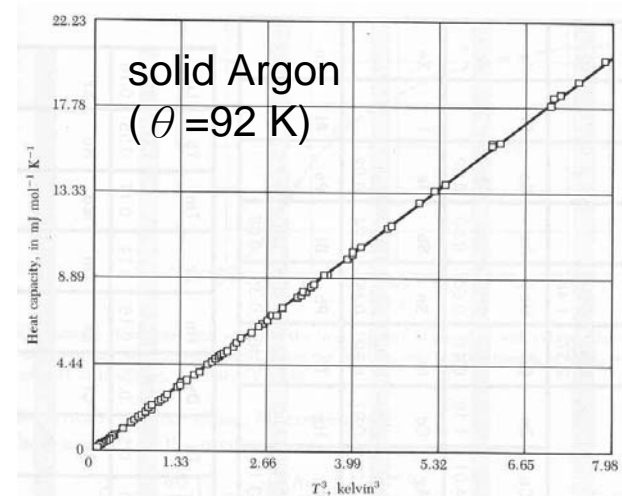


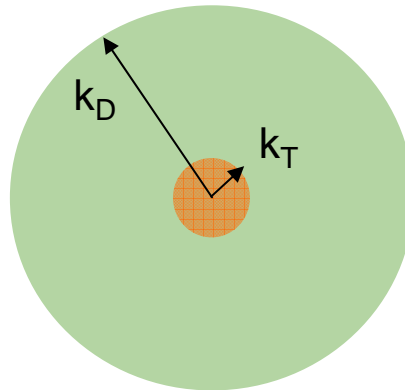
Figure 27.12 Comparison of Einstein and Debye model predictions with data for the heat capacity of copper.



A simple explanation of the T^3 behavior:

Suppose that

1. All the phonons with wave vector $k < k_T$ are excited with thermal energy kT .
2. All the modes between k_T and k_D are not excited.



Then the fraction of excited modes

$$= (k_T/k_D)^3 = (T/\theta)^3.$$

energy $U \sim kT \cdot 3N(T/\theta)^3$, and the heat capacity

$$C \sim 12Nk(T/\theta)^3$$

Thermal expansion

Coeff. Of volume expansion: $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$,

Bulk modulus: $B = -V \left(\frac{\partial P}{\partial V} \right)_T$
 $\rightarrow \beta = \frac{1}{B} \left(\frac{\partial P}{\partial T} \right)_V$

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

Free energy: $F = E_{elastic} + F_{phonon}$, $E_{elastic} = \frac{B}{2} \left(\frac{\Delta V}{V} \right)^2$

use

$$\left(\frac{\partial x}{\partial y} \right)_z = \frac{1}{\left(\frac{\partial y}{\partial x} \right)_z} \quad \text{and}$$

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1$$



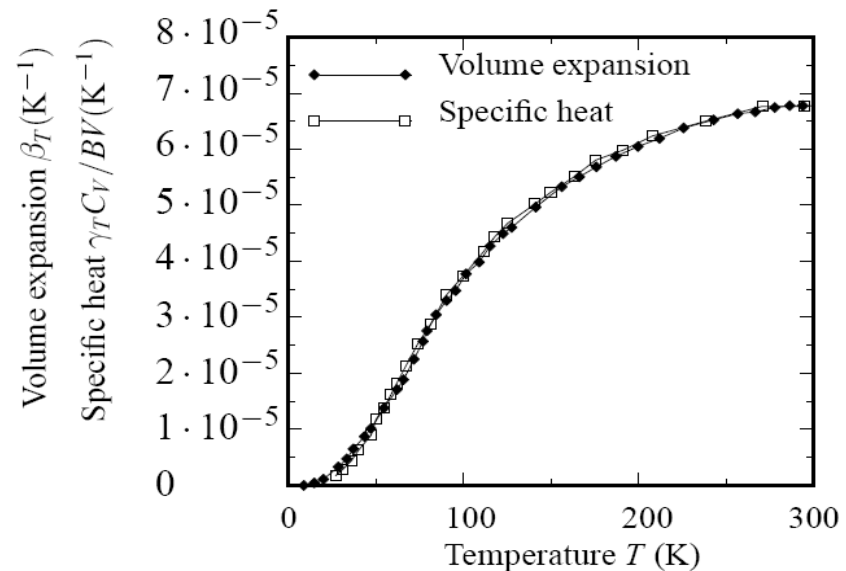
Next page we'll show that,

$$P = - \left(\frac{\partial E_{els}}{\partial V} \right)_T + \gamma \frac{U(T)}{V}$$

Indep of T

$$\Rightarrow \frac{1}{B} \left(\frac{\partial P}{\partial T} \right)_V = \beta = \frac{\gamma}{B} c_v \quad (c_v = C_v / V)$$

$\propto T^3$ at low T



Partition function:

$$Z_{ph} = \sum_i e^{-E_i/kT} \quad (E_i \text{ are the macroscopic eigen-energies})$$

$$= \sum_{\{n_{ks}\}} \exp \left[-\frac{1}{kT} \sum_{ks} \left(n_{ks} + \frac{1}{2} \right) \hbar \omega_{ks} \right]$$

$$= \prod_{ks} \sum_{n_{ks}=0}^{\infty} \exp \left[-\frac{1}{kT} \left(n_{ks} + \frac{1}{2} \right) \hbar \omega_{ks} \right]$$



$$F_{ph} = -kT \ln Z_{ph}$$

$$= kT \sum_{ks} \ln \left(e^{\hbar \omega_{ks}/2kT} - e^{-\hbar \omega_{ks}/2kT} \right)$$

$$P' \equiv - \left(\frac{\partial F_{ph}}{\partial V} \right)_T = -\frac{1}{2} \sum_{ks} \left(\frac{\partial \hbar \omega_{ks}}{\partial V} \right)_T \frac{e^{\hbar \omega_{ks}/kT} + 1}{e^{\hbar \omega_{ks}/kT} - 1}$$

$$\frac{\hbar \omega_{ks}}{V} \frac{d\omega_{ks}}{\omega_{ks}} \frac{V}{dV} \equiv -\gamma_{ks} \frac{\hbar \omega_{ks}}{V}$$

$$\therefore P' = \frac{1}{V} \sum_{ks} \gamma_{ks} U_{ks}(T),$$

$$\text{where } U_{ks}(T) \equiv \hbar \omega_{ks} \left(\frac{1}{e^{\hbar \omega_{ks}/kT} - 1} + \frac{1}{2} \right)$$

Grüneisen parameter

$$\frac{d\omega_{ks}}{\omega_{ks}} = -\gamma_{ks} \frac{dV}{V}$$

$$\Rightarrow \beta = \frac{1}{B} \left(\frac{\partial P'}{\partial T} \right)_V$$

$$= \frac{1}{B} \frac{1}{V} \sum_{ks} \gamma_{ks} C_{V,ks} = \frac{\gamma}{B} \frac{C_V}{V}$$

$$\text{where } \gamma \equiv \frac{\sum_{ks} \gamma_{ks} C_{V,ks}}{\sum_{ks} C_{V,ks}}$$

$$C_V = \sum_{ks} C_{V,ks}$$

($\gamma \sim 1-2$ for most materials)

Neutron scattering

$$E_n = \frac{(\hbar k)^2}{2m_n} = 2.07k^2 \text{ meV}\text{\AA}^2$$

Why neutron?

- Neutron has no charge (can probe bulk properties)
- Neutron wavelength comparable to interatomic spacings (1-5 Å)
- Neutron energy comparable to phonon's (5-100 meV)
- Neutron has spin (can probe magnetic structure and magnetic excitations)

Measure phonon dispersions by neutron scattering

More than one phonon mode may be excited

$$\Delta n_{q,s} = n'_{q,s} - n_{q,s}$$

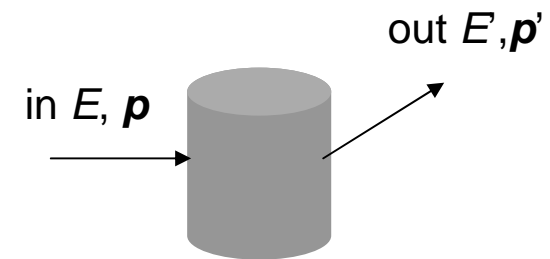
Conservation of energy

$$E_n' + \sum_{q,s} \hbar\omega_{q,s} \Delta n_{q,s} = E_n$$

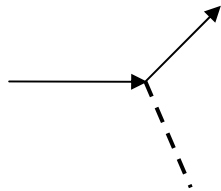
Conservation of crystal momentum (for a proof. see App. M of A+M)

$$\vec{p}' + \sum_{q,s} \hbar\vec{q} \Delta n_{q,s} = \vec{p} + \hbar\vec{G}$$

(momentum of phonon with $\lambda < a$ must be shifted by G)



One phonon scattering



$$E_n' = E_n \pm \hbar\omega_s(\vec{q})$$

$$\vec{p}' = \vec{p} \pm \hbar\vec{q} + \hbar\vec{G} \quad (\vec{p}' \equiv \hbar\vec{k}'; \vec{p} \equiv \hbar\vec{k})$$

Neutron energy:

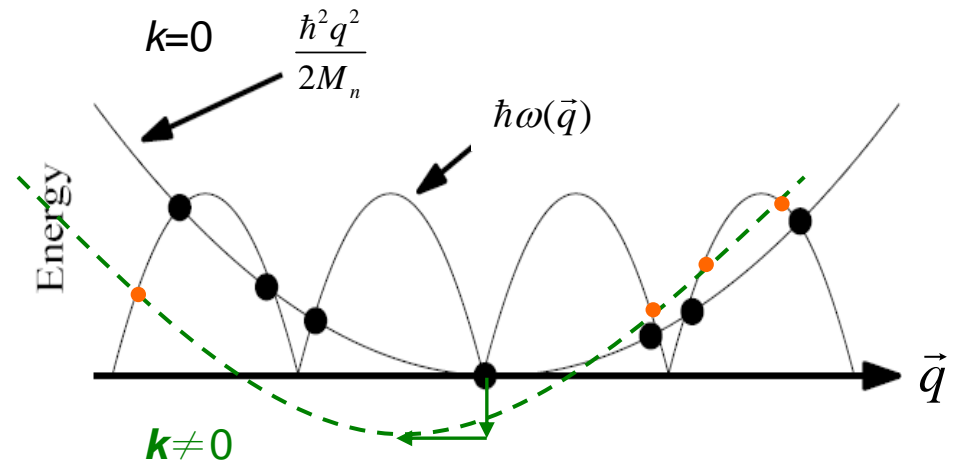
$$E_n = p^2/2m_n \quad \frac{p'^2}{2m_n} = \frac{p^2}{2m_n} \pm \hbar\omega_s(\vec{q}), \quad \vec{q} = \pm(\vec{k}' - \vec{k})$$

Consider phonon absorption

$$\frac{p'^2}{2m_n} - \frac{p^2}{2m_n} = \hbar\omega_s(\vec{k}' - \vec{k})$$

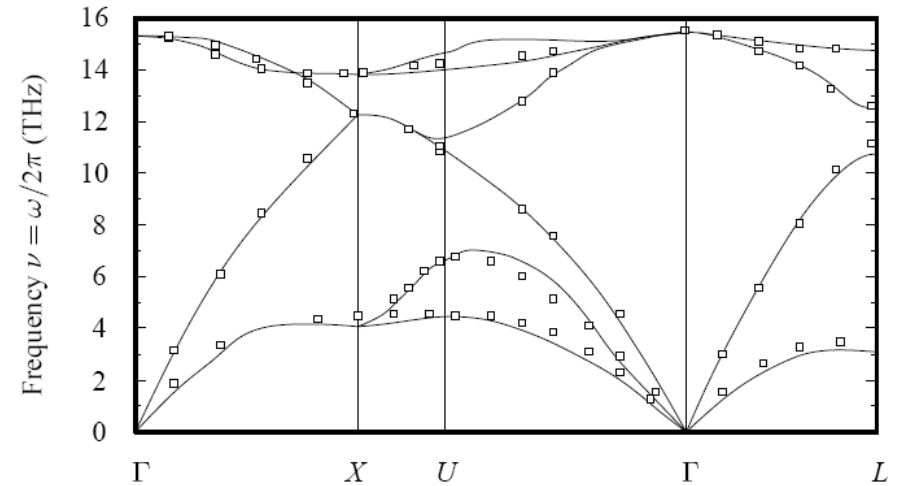
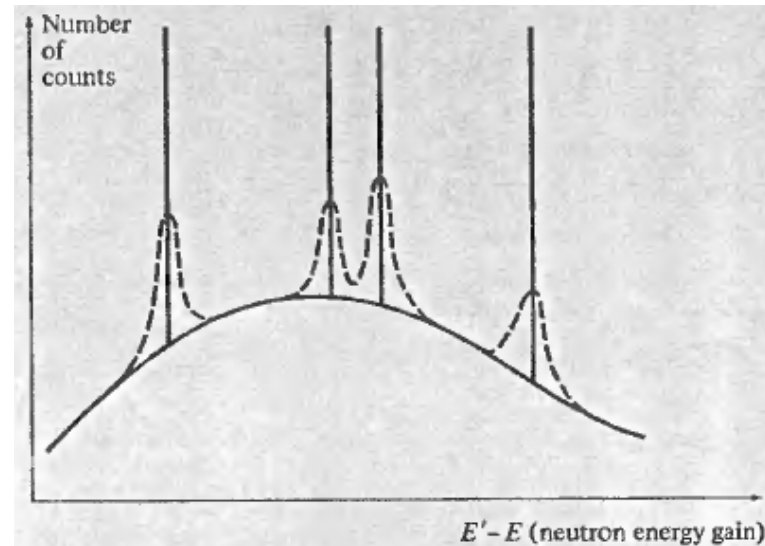
$$\Rightarrow f_k(\vec{q}) \equiv \frac{\hbar^2 |\vec{q} + \vec{k}|^2}{2m_n} - \frac{\hbar^2 k^2}{2m_n} = \hbar\omega_s(\vec{q})$$

\vec{q} and ω_s can be determined from the intersections in the figure.



several solutions at a given direction.

→ a series of peaks in the data



Phonon dispersion curve for Si,
comparing experimental data and
ab initio calculation (Wei and Chou 1994)

- Width of one-phonon peaks due to anharmonic effect
- Multi-phonon scatterings give a continuous background

Neutron scattering: formal theory

- Fermi golden rule
(transition rate)

$$R_{i \rightarrow [f]} = \frac{2\pi}{\hbar} \sum_f \left| \langle \Psi_f | V | \Psi_i \rangle \right|^2 \delta(E_f - E_i)$$

- Neutron states scattered to d^3k' (per unit time)

$$R_{\vec{k} \rightarrow \vec{k}'} \cdot V \frac{d^3k'}{(2\pi)^3} = R_{\vec{k} \rightarrow \vec{k}'} \cdot V \frac{m_n \hbar k' d\varepsilon d\Omega}{(2\pi\hbar)^3}$$

- Differential cross-section

$$\left(\frac{d^2\sigma}{d\Omega d\varepsilon} \right) d\Omega d\varepsilon \equiv \frac{R_{\vec{k} \rightarrow [d\Omega, d\varepsilon]}}{\text{incident particle flux}}$$

$$\vec{j} = \rho \vec{v} = |\psi_k|^2 \frac{\hbar \vec{k}}{m_n} = \frac{1}{V} \frac{\hbar \vec{k}}{m_n}$$

$$\Rightarrow \left(\frac{d^2\sigma}{d\Omega d\varepsilon} \right) = \frac{k'}{k} \frac{(Vm_n)^2}{(2\pi\hbar)^3} R_{\vec{k} \rightarrow \vec{k}'}$$

- Quantum state of “neutron + crystal”

$$\Psi = \psi_{\vec{k}}(\vec{r}) \Phi_{\text{crystal}}, \quad \psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}$$

initial: $\Psi_i = \psi_{\vec{k}}(\vec{r}) \Phi_i, \quad E_i = \frac{\hbar^2 k^2}{2m_n} + E_i$

final: $\Psi_f = \psi_{\vec{k}'}(\vec{r}) \Phi_f, \quad E_f = \frac{\hbar^2 k'^2}{2m_n} + E_f$

Neutron energy Crystal energy

- The energy **gained** by a neutron due to a phonon in crystal

$$\frac{\hbar^2 k'^2}{2m_n} - \frac{\hbar^2 k^2}{2m_n} = E_i - E_f = \hbar\omega$$

Momentum transfer

$$\vec{q} = \vec{k}' - \vec{k}$$

Neutron-ion interaction potential

$$V(\vec{r}) = \sum_{\vec{R}} v(\vec{r} - \vec{r}(\vec{R})), \quad \text{where } \vec{r}(\vec{R}) = \vec{R} + \vec{u}(\vec{R})$$

$v(r)$ is the atomic potential

Matrix element

$$\text{let } v(\vec{r} - \vec{r}(\vec{R})) = \frac{1}{V} \sum_{\vec{q}} v_q e^{i\vec{q}\cdot\vec{r}} e^{-i\vec{q}\cdot\vec{r}(\vec{R})}$$

$$\begin{aligned} \langle \Psi_f | V | \Psi_i \rangle &= \sum_{\vec{R}} \langle \psi_{k'} \Phi_f | v | \psi_k \Phi_i \rangle \\ &= \frac{1}{V} \sum_{\vec{R}, \vec{q}} v_q \underbrace{\langle \psi_{k'} | e^{i\vec{q}\cdot\vec{r}} | \psi_k \rangle}_{\delta_{\vec{k}+\vec{q}, \vec{k}'}} \langle \Phi_f | e^{-i\vec{q}\cdot\vec{r}(\vec{R})} | \Phi_i \rangle \end{aligned}$$

$$= \frac{1}{V} \sum_{\vec{R}} v_{k'-k} \langle \Phi_f | e^{-i(\vec{k}'-\vec{k})\cdot\vec{r}(\vec{R})} | \Phi_i \rangle$$

$$v_{k'-k} \sim v_0$$

since Δk for phonon $\sim 10^8 \text{ cm}^{-1}$

\ll the range of $v_q \sim 10^{13} \text{ cm}^{-1}$

$$\therefore \left(\frac{d\sigma}{d\Omega d\varepsilon} \right) = \frac{k'}{k} \left(\frac{v_0 m_n}{2\pi\hbar^2} \right)^2 \sum_f \delta(E_f - E_i) \left| \sum_{\vec{R}} \langle \Phi_f | e^{i\vec{q}\cdot\vec{r}(\vec{R})} | \Phi_i \rangle \right|^2$$

Sum over a complete set of phonon states

One can re-write $\left(\frac{d\sigma}{d\Omega d\varepsilon}\right)$ using dynamical structure factor

$$\delta(E_f - E_i) = \frac{1}{\hbar} \delta\left(\frac{E_f - E_i}{\hbar} + \omega\right) = \frac{1}{2\pi\hbar} \int dt e^{i\omega t} e^{i(E_f - E_i)t/\hbar} \quad \text{for phonon absorption}$$

(always from neutron's viewpoint)

use $e^{i(E_f - E_i)t/\hbar} \langle \Phi_f | A | \Phi_i \rangle = \langle \Phi_f | A(t) | \Phi_i \rangle$

$$\begin{aligned} \text{then } \left(\frac{d\sigma}{d\Omega d\varepsilon}\right) &= \frac{k'}{k} \frac{1}{h} \left(\frac{m_n v_0}{2\pi\hbar^2}\right)^2 \int dt e^{i\omega t} \sum_{\vec{R}, \vec{R}'} \langle \Phi_i | e^{i\vec{q}\cdot\vec{r}(\vec{R}')} e^{-i\vec{q}\cdot\vec{r}(\vec{R}, t)} | \Phi_i \rangle \\ &= \frac{k'}{k} \frac{1}{h} \left(\frac{m_n v_0}{2\pi\hbar^2}\right)^2 2\pi N S_i(\vec{q}, \omega) \end{aligned}$$

Dynamical structure factor

$$\begin{aligned} S_i(\vec{q}, \omega) &\equiv \frac{1}{N} \int \frac{dt}{2\pi} e^{i\omega t} \sum_{\vec{R}, \vec{R}'} \langle \Phi_i | e^{i\vec{q}\cdot\vec{r}(\vec{R}')} e^{-i\vec{q}\cdot\vec{r}(\vec{R}, t)} | \Phi_i \rangle \\ &= \int \frac{dt}{2\pi} e^{i\omega t} \frac{1}{N} \langle \Phi_i | \rho_{\vec{q}}(0) \rho_{-\vec{q}}(t) | \Phi_i \rangle \end{aligned}$$

Density correlation function

Density operator (for ions)

$$\begin{aligned} \rho(\vec{r}) &= \sum_{\vec{R}} \delta(\vec{r} - \vec{r}(\vec{R})) \\ \rho_{\vec{q}} &= \int d^3r e^{i\vec{q}\cdot\vec{r}} \rho(\vec{r}) = \sum_{\vec{R}} e^{i\vec{q}\cdot\vec{r}(\vec{R})} \end{aligned}$$

For a crystal at finite temperature

$$\langle \Phi_i | \rho_{\vec{q}}(0) \rho_{-\vec{q}}(t) | \Phi_i \rangle \rightarrow \langle \rho_{\vec{q}}(0) \rho_{-\vec{q}}(t) \rangle_T = \frac{\sum_i e^{-E_i/kT} \langle \Phi_i | \rho_{\vec{q}} \rho_{-\vec{q}}(t) | \Phi_i \rangle}{\sum_i e^{-E_i/kT}}$$

Evaluation of the dynamical structure factor

$$\left\langle e^{i\vec{q}\cdot\vec{r}(\vec{R}')} e^{-i\vec{q}\cdot\vec{r}(\vec{R},t)} \right\rangle_T = e^{i\vec{q}\cdot(\vec{R}'-\vec{R})} \left\langle e^{i\vec{q}\cdot\vec{u}(\vec{R}')} e^{-i\vec{q}\cdot\vec{u}(\vec{R},t)} \right\rangle_T \quad \vec{r}(\vec{R}) \equiv \vec{R} + \vec{u}(\vec{R})$$

It can be shown that, for A, B linear in a, a^\dagger

$$\left\langle e^A e^B \right\rangle_T = e^{\frac{1}{2}\langle A^2 + 2AB + B^2 \rangle_T} \quad \text{D. Mermin, J Math.Phys. 7,1038 (1966)}$$

$$\text{use } \left\langle \left[\vec{q} \cdot \vec{u}(\vec{R}') \right]^2 \right\rangle_T = \left\langle \left[\vec{q} \cdot \vec{u}(\vec{R}, t) \right]^2 \right\rangle_T = \left\langle \left[\vec{q} \cdot \vec{u}(0) \right]^2 \right\rangle_T \equiv 2W$$

$$\text{and } \left\langle \left[\vec{q} \cdot \vec{u}(\vec{R}') \right] \left[\vec{q} \cdot \vec{u}(\vec{R}, t) \right] \right\rangle_T = \left\langle \left[\vec{q} \cdot \vec{u}(0) \right] \left[\vec{q} \cdot \vec{u}(\vec{R} - \vec{R}', t) \right] \right\rangle_T$$

↑
Translation symmetry
of the system

Debye-Waller factor

$$\Rightarrow S(\vec{q}, \omega) \equiv e^{-2W} \int \frac{dt}{2\pi} e^{i\omega t} \sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} e^{\langle [\vec{q}\cdot\vec{u}(0)] [\vec{q}\cdot\vec{u}(\vec{R}, t)] \rangle_T}$$

Exact so far
(for a harmonic crystal)

$$e^{\langle \rangle_T} = 1 + \langle \rangle_T + \frac{1}{2} \langle \rangle_T^2 + \dots$$

↑ ↑
0-phonon 1-phonon process ...

Zero-phonon process

$$S_0(\vec{q}, \omega) = e^{-2W} \delta(\omega) \sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}}$$

Debye-Waller factor

Elastic scattering

$N \sum_{\vec{G}} \delta_{\vec{q}, \vec{G}}$
Laue's diffraction condition

- Rough estimate (Kittel. App.A)

$$\begin{aligned} 2W &= \left\langle (\vec{G} \cdot \vec{u})^2 \right\rangle_T \\ &= G^2 \left\langle u^2 \right\rangle_T \left\langle \cos^2 \theta \right\rangle_T \\ &= \frac{1}{3} G^2 \left\langle u^2 \right\rangle_T \end{aligned}$$

$$\text{use } \frac{m_{ion}}{2} \omega^2 \left\langle u^2 \right\rangle_T = \frac{3}{2} kT$$

$$\rightarrow e^{-2W} = e^{-\frac{G^2}{m_{ion}\omega^2} kT}$$

Differential cross-section

$$\left(\frac{d\sigma}{d\Omega d\varepsilon} \right) = \frac{k'}{k} \frac{1}{h} \left(\frac{m_n v_0}{2\pi\hbar^2} \right)^2 2\pi N S(\vec{q}, \omega)$$

or $= \frac{k'}{k} a^2 \frac{N}{\hbar} S(\vec{q}, \omega)$

$$v_0 \equiv \frac{2\pi\hbar^2 a}{m_n} \quad \text{Scattering length}$$

Intensity $I = I_0 e^{-2W}$ (I_0 for a rigid lattice)

Cf: $\left(\frac{d\sigma}{d\Omega d\varepsilon} \right) = \frac{N}{\hbar} S(\vec{q}, \omega)$

For X-ray scattering
(the same S)

For more discussion,
see A+M, App. N

- A more accurate evaluation

$$a_{ks} = \frac{1}{\sqrt{2\hbar}} \left(\sqrt{m\omega_{ks}} \vec{u}_{ks} + \frac{i}{\sqrt{m\omega_{ks}}} \vec{p}_{ks} \right) \cdot \hat{e}_{ks}$$

$$a_{-ks}^\dagger = \frac{1}{\sqrt{2\hbar}} \left(\sqrt{m\omega_{ks}} \vec{u}_{ks} - \frac{i}{\sqrt{m\omega_{ks}}} \vec{p}_{ks} \right) \cdot \hat{e}_{ks}$$



$$(\hat{e}_{-ks}^* = \hat{e}_{ks})$$

$$\vec{u}_{ks} = \sqrt{\frac{\hbar}{2m_{ion}\omega_s(\vec{k})}} (a_{ks} + a_{-ks}^\dagger) \hat{e}_{ks}$$

$$\vec{p}_{ks} = -i\sqrt{\frac{2m_{ion}\omega_s(\vec{k})}{\hbar}} (a_{ks} - a_{-ks}^\dagger) \hat{e}_{ks}$$

$$\vec{u}(\vec{R}) = \frac{1}{\sqrt{N}} \sum_{k,s} \vec{u}_{ks} e^{i\vec{k}\cdot\vec{R}}$$

$$\vec{p}(\vec{R}) = \frac{1}{\sqrt{N}} \sum_{k,s} \vec{p}_{ks} e^{i\vec{k}\cdot\vec{R}}$$

$$\text{use } \langle a_{ks}^\dagger a_{ks} \rangle_T = n_{ks}$$

$$\Rightarrow \langle (\vec{G} \cdot \vec{u})^2 \rangle_T = \frac{1}{N} \sum_{ks} \frac{\hbar |\vec{G} \cdot \hat{e}_{ks}|^2}{2m_{ion}\omega_s(\vec{k})} (2n_{ks} + 1)$$

In 3D Debye model (at $T=0!$)

$$2W = \frac{3}{4} \frac{\hbar}{m_{ion} v} \frac{G^2}{k_D} \quad (\text{Prob. 7})$$

In the calculation, one has

$$\int_0^{k_D} k^{D-1} dk \frac{1}{k} = \int_0^{k_D} k^{D-2} dk$$

- In 3D, W weakens the diffraction peaks.
- In 2D, W is finite at $T=0$ but infinite at finite- T .
- In 1D, no long-range order even at $T=0$

Mermin-Wagner theo (Mermin PR1968)

There is no long-range crystalline order at finite- T in 2D.

One-phonon process

$$S_1(\vec{q}, \omega) = e^{-2W} \int \frac{dt}{2\pi} e^{i\omega t} \sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} \left\langle [\vec{q}\cdot\vec{u}(0)] [\vec{q}\cdot\vec{u}(\vec{R}, t)] \right\rangle_T$$

$$\vec{q}\cdot\vec{u}(\vec{R}, t) = \frac{1}{\sqrt{N}} \sum_{ks} \left(\frac{\hbar}{2m_{ion}\omega_{ks}} \right)^{1/2} e^{i\vec{k}\cdot\vec{R}} \left(a_{ks}(t) + a_{-ks}^\dagger(t) \right) \vec{q}\cdot\hat{e}_{ks}$$

$$a_{ks}(t) = e^{-i\omega_{ks}t} a_{ks}$$

$$\Rightarrow S_1(\vec{q}, \omega) = e^{-2W} \sum_s \frac{\hbar}{2m_{ion}\omega_{qs}} (\vec{q}\cdot\hat{e}_{qs})^2 \left[(1+n_{qs})\delta(\omega + \omega_{qs}) + n_{qs}\delta(\omega - \omega_{qs}) \right]$$

Phonon emission absorption

Delta peaks are broadened only if anharmonic effect (phonon-phonon interaction) is included.

One-phonon cross-section

$$\left(\frac{d\sigma}{d\Omega d\varepsilon} \right) = \frac{k'}{k} a^2 \frac{N}{\hbar} S_1(\vec{q}, \omega)$$