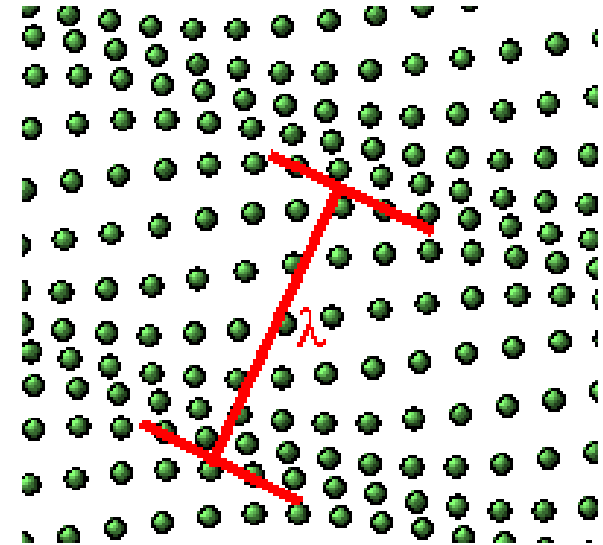


Phonons I: Crystal vibrations



classical

- one dimensional vibration
- one dimensional vibration for crystals with basis
- three dimensional vibration
- quantum theory of vibration

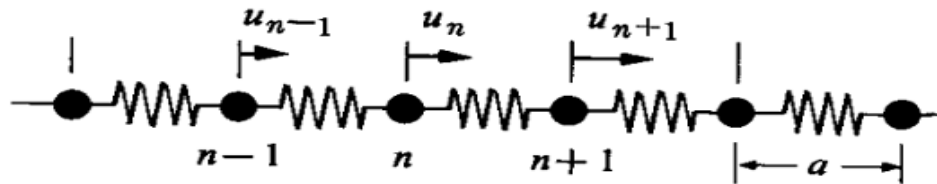
Dept of Phys



M.C. Chang

One dimensional vibration (classical analysis)

- consider only the *longitudinal* motion
- consider only the NN coupling



u_n : displacement

α : elastic constant

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

Assume $u_n = A e^{i(kX_n - \omega t)}$, where $X_n = na$,

then we'll get

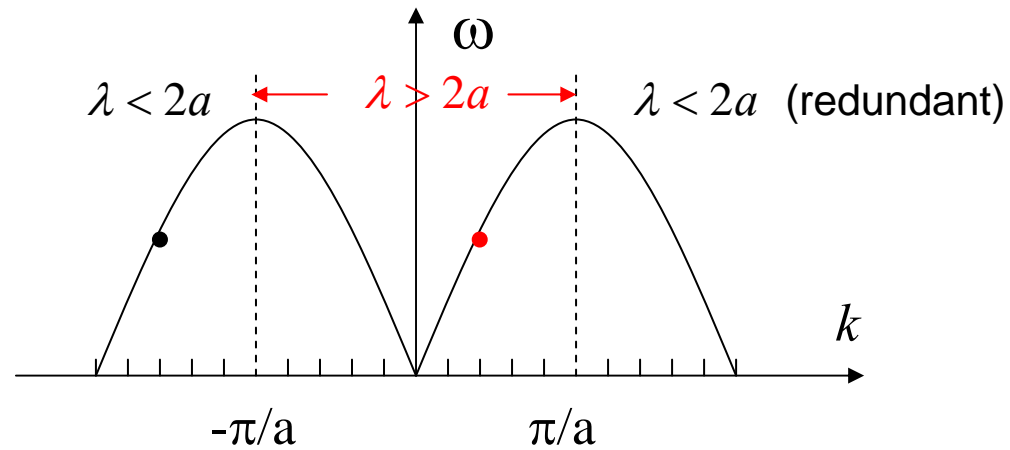
$$M(-\omega^2) e^{ikna} = -\alpha \left[2e^{ikna} - e^{ik(n+1)a} - e^{ik(n-1)a} \right],$$

which leads to

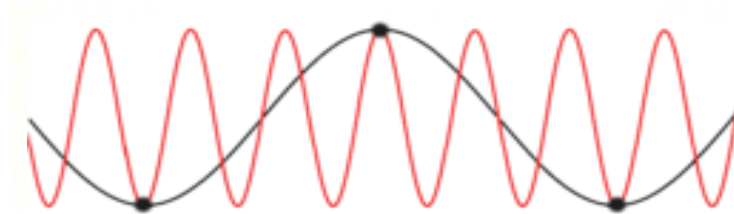
$$\omega(k) = \omega_M |\sin(ka/2)|, \quad \omega_M = 2\sqrt{\alpha/M}$$

↑
dispersion relation (色散關係)

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



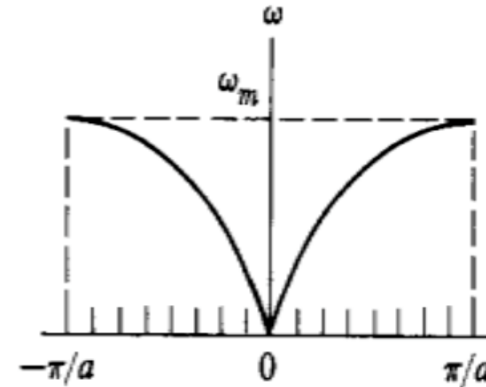
- The waves with wave numbers k and $k + 2\pi/a$ describe the same atomic displacement



- 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.

Velocities of wave (phase velocity, group velocity):

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

Linear dispersion, phase velocity = group velocity

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

$$\boxed{v_p = \frac{\omega}{k}}$$

$$\boxed{v_g = \frac{d\omega}{dk}}$$

Number of “normal modes” 簡正模

For travelling waves, use **periodic boundary condition**

$$\text{PBC: } u_0(t) = u_N(t)$$

For example, consider a 1-dim lattice with N atoms

$$u_n = A \exp[i(kX_n - \omega t)],$$

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

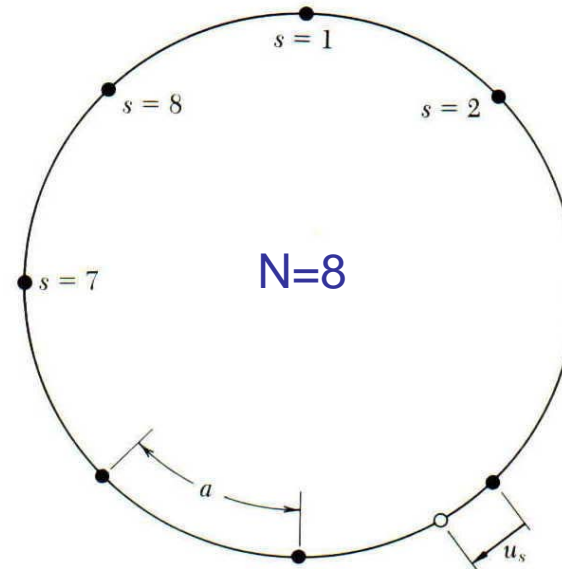
$$\therefore k = \frac{m}{N} \frac{2\pi}{a}, m = 1, 2, \dots, N$$

$$\text{or } m = -\frac{N}{2} + 1, \dots, \frac{N}{2}$$

The value of k is discrete

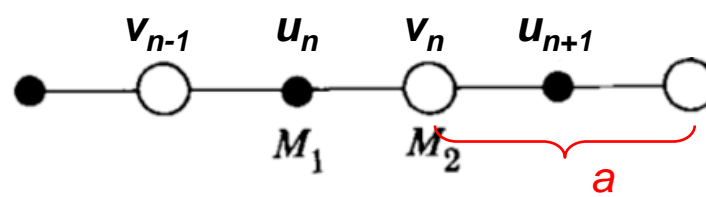
$$\Delta k = 2\pi / Na$$

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



- one dimensional vibration
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Vibration of a crystal with 2 atoms in a unit cell



$$M_1 \frac{d^2 u_n}{dt^2} = \alpha (v_n + v_{n-1} - 2u_n),$$

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

$$\text{Assume } \begin{pmatrix} u_n \\ v_n \end{pmatrix} = \begin{pmatrix} A_1 e^{ikna} \\ A_2 e^{ik(n+1/2)a} \end{pmatrix} e^{-i\omega t}$$

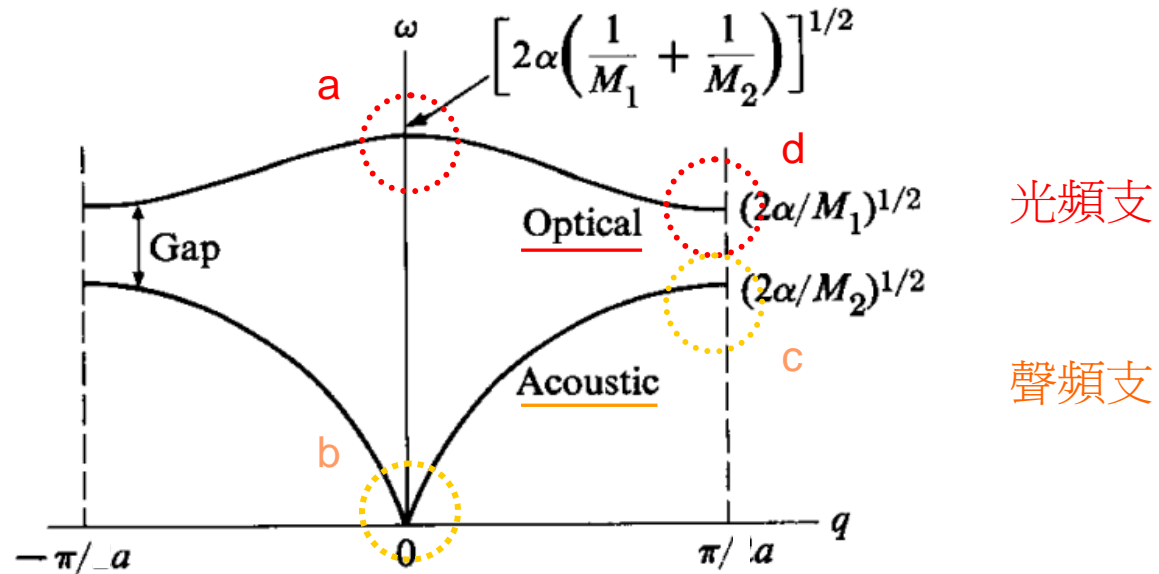
$$\Rightarrow \begin{pmatrix} 2\alpha - M_2 \omega^2 & -2\alpha \cos(ka/2) \\ -2\alpha \cos(ka/2) & 2\alpha - M_1 \omega^2 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = 0,$$

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

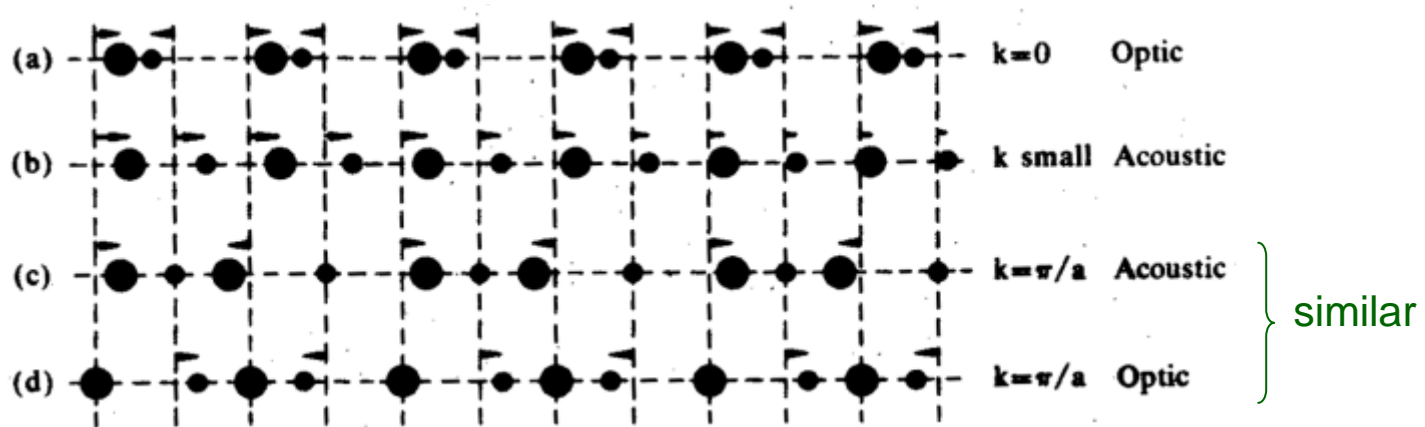
$$\Rightarrow \omega_{\pm}^2 = \alpha \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \pm \alpha \sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4 \sin^2(ka/2)}{M_1 M_2}}.$$

important

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



Patterns of vibration: (Prob.3)



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

How many **normal modes** (k points) in each branch?

$$\text{Imposing PBC on } \begin{pmatrix} u_n \\ v_n \end{pmatrix} = \begin{pmatrix} A_1 e^{ikna} \\ A_2 e^{ik(n+1/2)a} \end{pmatrix} e^{-i\omega t}$$

$$\begin{pmatrix} u_N \\ v_N \end{pmatrix} = \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} \Rightarrow \exp(ikNa) = 1$$

$$\therefore k = \frac{m}{N} \frac{2\pi}{a}, m = 1, 2, \dots, N$$

or $m = -\frac{N}{2} + 1, \dots, \frac{N}{2}$ Same as before (a lattice with no basis)

- The total number of k points is $2N$, same as the total DOF of the atoms (this remains true for complex crystals in higher dimensions)

Q: what happens if the two atoms in a basis are of the same type?

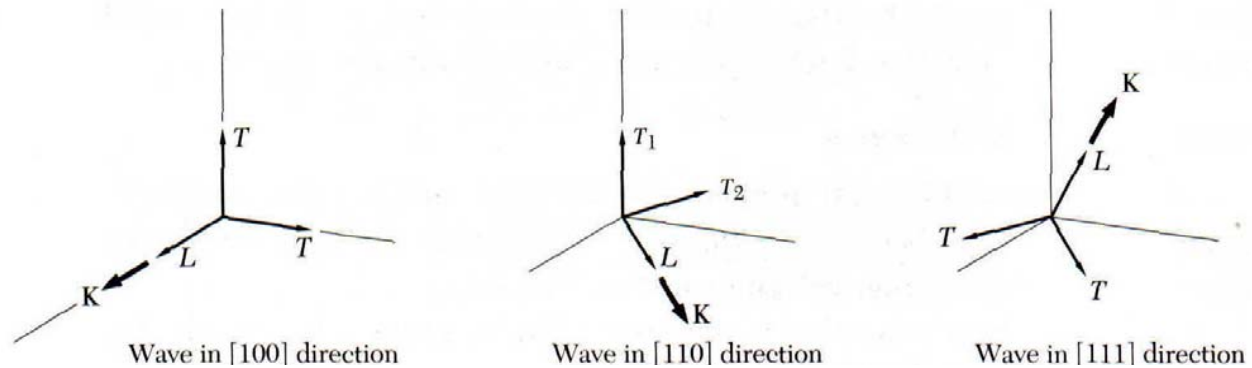
- one dimensional vibration
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Three dimensional vibration

Along a given direction of propagation, there are

1 longitudinal wave and 2 transverse waves,

each may have different velocities



Sodium
(BCC)

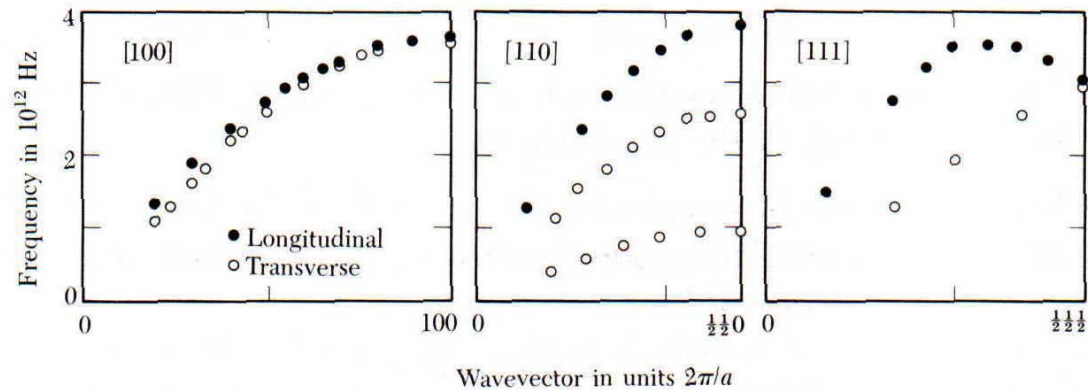


Figure 11 The dispersion curves of sodium for phonons propagating in the [001], [110], and [111] directions at 90 K, as determined by inelastic scattering of neutrons, by Woods, Brockhouse, March and Bowers. *Na*

3D crystal *with atom basis*

Rules of thumb:

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

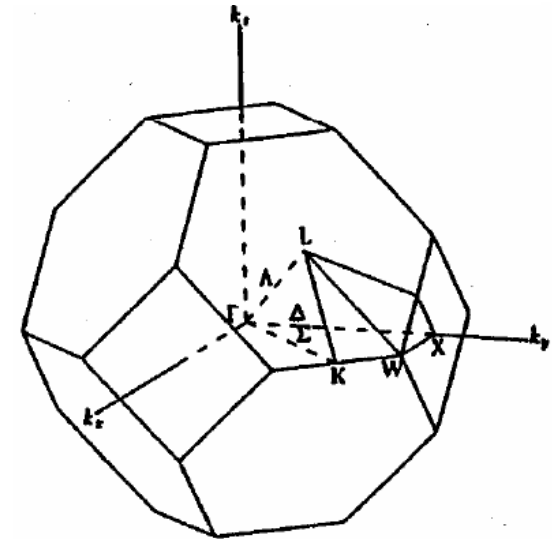
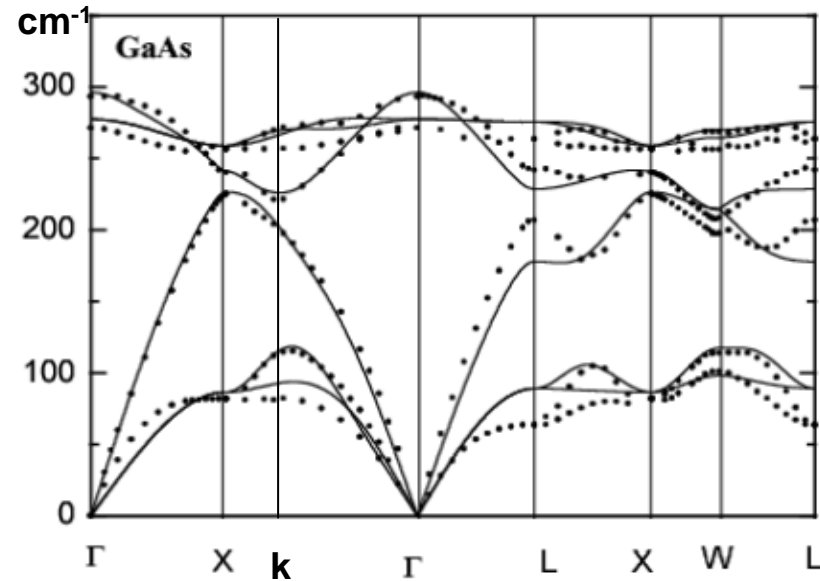
3 acoustic branches,

$3(p-1)$ optical branches

- If a crystal has N unit cells, then each branch has N normal modes (number of k-points for each dispersion curve).

- As a result, the total number of normal modes of the whole crystal is $3pN$ (= total DOF of this crystal).

FCC lattice with 2-atom basis



- one dimensional vibration
- one dimensional vibration for crystals with basis
- three dimensional vibration
- *quantum* theory of vibration

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 $\omega = (\alpha/m)^{1/2}$

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

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

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

Creation and annihilation operators:

if $|n\rangle$ is an energy eigenstate, then

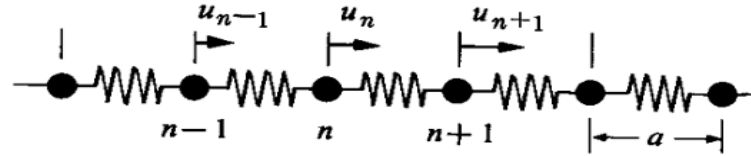
$$a |n\rangle = \sqrt{n} |n-1\rangle$$

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

- After quantization, the energy becomes discrete
$$\varepsilon_n = \left(n + \frac{1}{2} \right) \hbar\omega$$
$$n = 0, 1, 2, \dots$$

Quantization of a 1-dim vibrating lattice (see App. C for details)

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



N atoms

DOF=N

- For a given k , it vibrates with a single frequency $\omega(k)$

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

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

$k=2\pi m/L$

$L=Na$

then

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

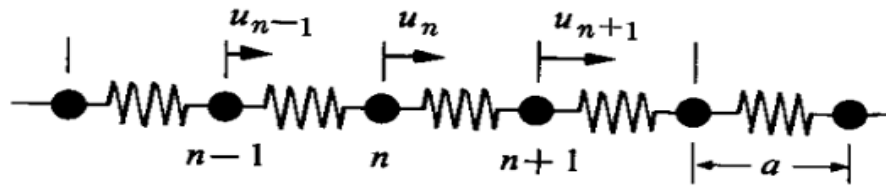
$$\Rightarrow H = \sum_k \left(\frac{1}{2m} p_k^{\dagger} p_k + \frac{m\omega_k^2}{2} u_k^{\dagger} u_k \right)$$

Note:

$$u_{\ell}^{\dagger} = u_{\ell}; \quad p_{\ell}^{\dagger} = p_{\ell}$$

$$\rightarrow u_k^{\dagger} = u_{-k}; \quad p_k^{\dagger} = p_{-k}$$

A collection of **N independent oscillators** !
(each normal mode is a SHO.)



- Total vibrational energy of a simple 1D lattice:

$$U = \sum_k \left(n_k + \frac{1}{2} \right) \hbar \omega_k$$

- Energy dispersion of a normal mode (a given k): $\hbar \omega_k$
the number of energy quanta (called **phonons**, 聲子) being excited is n_k .
- There are no interaction between phonons, so the vibrating lattice can be treated as a “free” phonon gas.
(this is no longer true if the elastic force is nonlinear.)
- In general, for a 3D crystal with atom basis

$$U = \sum_{\vec{k}, s} \left(n_{\vec{k}, s} + \frac{1}{2} \right) \hbar \omega_{\vec{k}, s}, \quad s = 1 \cdots 3p \quad (\text{L/T, A/O...})$$

Some Identities Related to Fourier Analysis of Periodic Systems

To derive Fourier inversion formulas it suffices to establish the identity

$$\boxed{\sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} = N\delta_{\mathbf{k},\mathbf{0}},} \quad (\text{F.1})$$

where \mathbf{R} runs through the N sites of the Bravais lattice

$$\mathbf{R} = \sum_{i=1}^3 n_i \mathbf{a}_i, \quad 0 \leq n_i < N_i, \quad N_1 N_2 N_3 = N, \quad (\text{F.2})$$

and \mathbf{k} is any vector in the first Brillouin zone consistent with the Born-von Karman boundary condition appropriate to the N points specified by (F.2).

The identity is most simply proved by noting that because \mathbf{k} is consistent with the Born-von Karman periodic boundary condition, the value of the sum in (F.1) is unchanged if every \mathbf{R} is displaced by the same \mathbf{R}_0 , where \mathbf{R}_0 is itself any vector of the form (F.2):

$$\sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot (\mathbf{R} + \mathbf{R}_0)} = e^{i\mathbf{k} \cdot \mathbf{R}_0} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}}. \quad (\text{F.3})$$

Consequently the sum must vanish unless $e^{i\mathbf{k} \cdot \mathbf{R}_0} = 1$, for all \mathbf{R}_0 of the form (F.2), i.e., for all vectors \mathbf{R}_0 of the Bravais lattice. This is possible only if \mathbf{k} is a reciprocal lattice vector. But $\mathbf{k} = \mathbf{0}$ is the only reciprocal lattice vector in the first Brillouin zone.¹ Hence the left side of (F.1) does indeed vanish if $\mathbf{k} \neq \mathbf{0}$, and is trivially equal to N , when $\mathbf{k} = \mathbf{0}$.

A closely related identity of similar importance is

$$\boxed{\sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}} = N\delta_{\mathbf{R},\mathbf{0}},} \quad (\text{F.4})$$

where \mathbf{R} is any vector of the form (F.2), and the sum on \mathbf{k} runs through all sites in the first Brillouin zone consistent with the Born-von Karman boundary condition. The sum in (F.4) is now unchanged if every \mathbf{k} is translated by the same vector \mathbf{k}_0 lying in the first zone and consistent with the Born-von Karman boundary condition, for the primitive cell constructed by shifting the entire first zone by \mathbf{k}_0 , can be re-assembled into the first zone by shifting appropriate pieces of it through reciprocal lattice vectors. Since no term of the form $e^{i\mathbf{k} \cdot \mathbf{R}}$ is changed when \mathbf{k} is shifted by a reciprocal lattice vector, the sum over the shifted zone is identical to the sum over the original zone. Thus:

$$\sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}} = \sum_{\mathbf{k}} e^{i(\mathbf{k} + \mathbf{k}_0) \cdot \mathbf{R}} = e^{i\mathbf{k}_0 \cdot \mathbf{R}} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}}, \quad (\text{F.5})$$

and therefore the sum on the left side of (F.4) must vanish unless $e^{i\mathbf{k}_0 \cdot \mathbf{R}}$ is unity for all \mathbf{k}_0 consistent with the Born-von Karman boundary condition. The only \mathbf{R} of the form (F.2) for which this is possible is $\mathbf{R} = \mathbf{0}$. And when $\mathbf{R} = \mathbf{0}$, the sum in (F.4) is trivially equal to N .

A \mathbf{k} -mode phonon acts as if it has momentum $\hbar\mathbf{k}$ in a scattering process (for a math proof, see Ashcroft and Mermin, App. M)

Recoil momentum of the crystal

- Elastic scattering of photon: $\hbar\mathbf{k}' = \hbar\mathbf{k} + \hbar\mathbf{G}$ (chap 2)
- Inelastic scattering of photon: $\hbar\mathbf{k}' = \hbar\mathbf{k} \pm \hbar\mathbf{k}_{\text{phonon}} + \hbar\mathbf{G}$ (Raman scattering)

However, the momentum of a vibrating crystal with wave vector \mathbf{k} is zero

$$P = M \sum_n \frac{du_n}{dt}, u_n = Ae^{i(kX_n - \omega t)}$$

$$= MA(-i\omega)e^{-i\omega t} \sum_{n=0}^{N-1} e^{ikna}$$

$$= MA(-i\omega)e^{-i\omega t} \frac{1 - e^{ikNa}}{1 - e^{ika}}$$

$$= 0 \quad \text{since } k = 2\pi m / Na \quad (\neq 0 \text{ ONLY when } k=0)$$

↑
no center-of-mass motion

uniform translation of the crystal



Therefore, we call $\hbar\mathbf{k}$ a **crystal momentum** (of the phonon), in order not to be confused with the actual momentum.

Von Laue was struck in 1912 by the intuition that X-ray might scatter off crystals in the way that ordinary light scatters off a diffraction grating.

He discussed

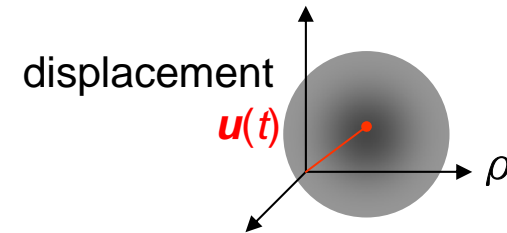
his idea with colleagues Sommerfeld, Wien and others with the result of encountering a strong disbelief in a significant outcome of any diffraction experiment based upon the regularity of the internal structure of crystals. It was argued that the inevitable temperature motion of the atoms would impair the regularity of the grating to such an extent that no pronounced diffraction maxima could be expected. —Ewald (1962), p. 42

- For example, for NaCl, the thermal fluctuation is expected to be $2 \cdot 10^{-9}$ cm ~ the wavelength of X-ray 10^{-9} cm (Marder, p.43)
- Now we know that **thermal fluctuation would only broaden the diffraction peaks, but not destroy them.**
- Laue did not actually do the experiment himself. Rather, he persuaded a couple of graduate students to do the experiment for him. Laue then set an example that has inspired PIs ever since – he was given all the credit! https://wasatch.biochem.utah.edu/chris/teaching/2011/SM_3.pdf

Debye-Waller factor due to atom vibration (Kittel. App. A)

• atomic form factor

$$\begin{aligned}\tilde{f}_a(\vec{G}) &= \int d^3\rho e^{-i\vec{G}\cdot\vec{\rho}} n(\vec{\rho}-\vec{u}) \\ &= \int d^3r e^{-i\vec{G}\cdot\vec{r}} n(\vec{r}) \cdot e^{-i\vec{G}\cdot\vec{u}}, \quad \vec{\rho} = \vec{r} + \vec{u}(t) \\ &= f_a(\vec{G}) e^{-i\vec{G}\cdot\vec{u}}\end{aligned}$$



• Time (thermal) average

$$\begin{aligned}\langle e^{-i\vec{G}\cdot\vec{u}} \rangle &= 1 - i\langle \vec{G}\cdot\vec{u} \rangle - \frac{1}{2}\langle (\vec{G}\cdot\vec{u})^2 \rangle + \dots \\ &\cong e^{-\frac{1}{2}\langle (\vec{G}\cdot\vec{u})^2 \rangle}\end{aligned}$$

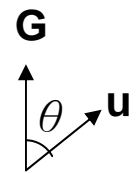
• Intensity of diffraction spot:

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

$$\text{where } W \equiv \frac{1}{2}\langle (\vec{G}\cdot\vec{u})^2 \rangle$$

• a rough estimate

$$\begin{aligned}2W &= G^2 \langle u^2 \rangle \langle \cos^2 \theta \rangle \\ &= \frac{1}{3} G^2 \langle u^2 \rangle\end{aligned}$$



$$\text{use } \frac{m_{ion}}{2} \omega^2 \langle u^2 \rangle = \frac{3}{2} k_B T$$

$$\rightarrow e^{-2W} = \exp\left(-\frac{G^2}{m_{ion}\omega^2} k_B T\right)$$

Debye-Waller factor

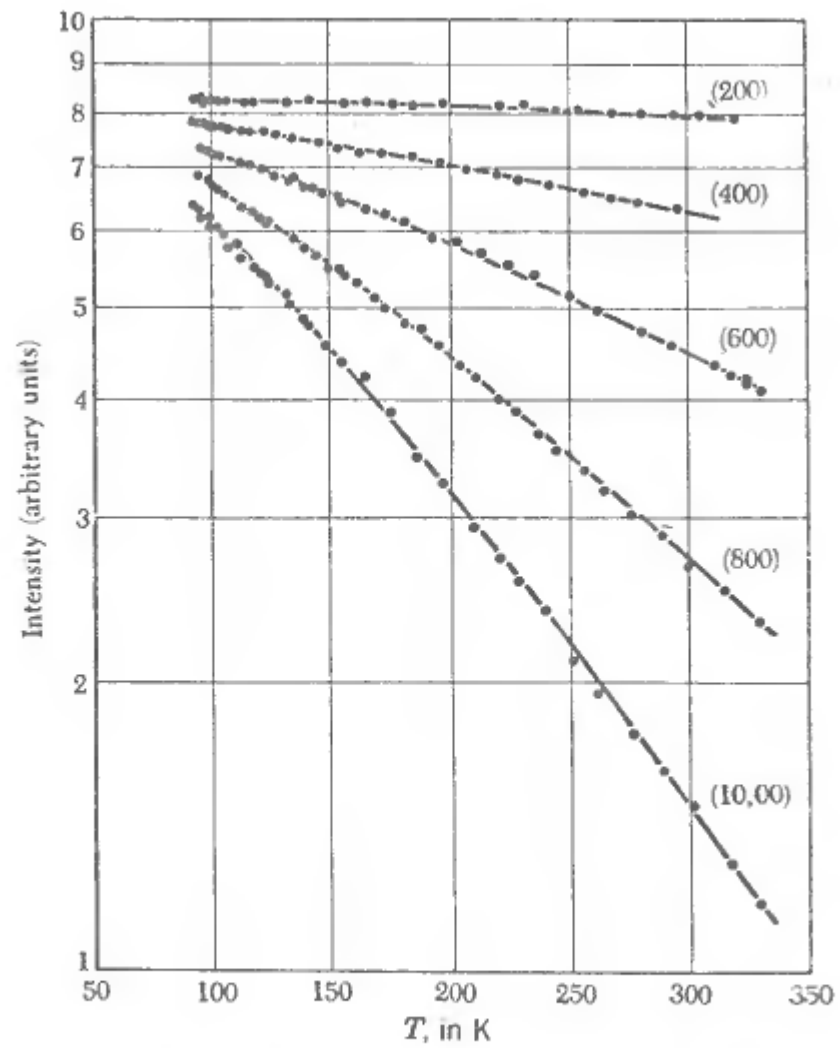


Figure 1 The dependence of intensity on temperature for the $(h00)$ x-ray reflections of aluminum. Reflections $(h00)$ with h odd are forbidden for an fcc structure. (After R. M. Nicklow and R. A. Young.)

The larger G is, the weaker the diffraction at high temperatures.