What is special about eigenvectors |i> of D?

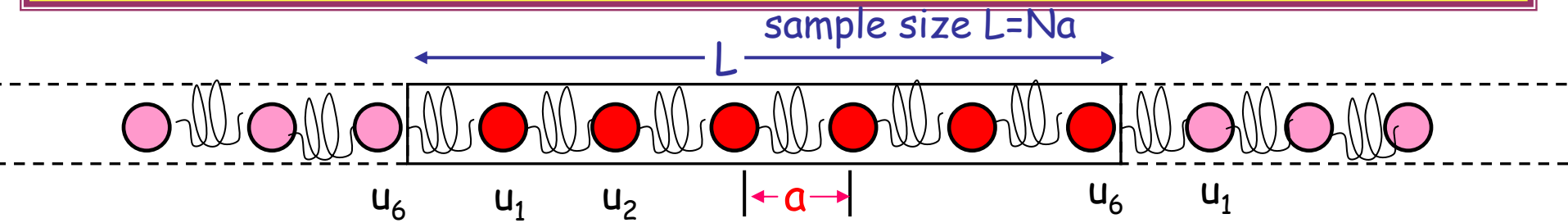
$|s\rangle = A\cos(\omega t+\varphi)|i\rangle$ is a solution of Newton's laws provided ω is chosen as the eigenvalue ω_i. It is a "stationary solution" or "normal mode." The "pattern" of oscillation is fixed in time.

The normal modes are "complete." All solutions of Newton's laws can be built from them. They also generate corresponding quantum results, *i.e.* solutions of the Schrödinger equation.

A simple way to designate a complete set of stationary (many body) quantum states is $|n_1, n_2, \ldots, n_i, \ldots\rangle$. This specifies, for each normal mode, the integer level n_i of excitation of the i^{th} mode. **Reinterpretation**: Instead of the excitation level of a normal mode, we regard $\mathbf{n_i}$ as its "occupancy." That is, we ask how many quanta of vibration are "in the i^{th} mode."

The different normal modes are "independent" (in Harmonic approximation.) All extensive thermodynamic functions are sums over the thermodynamics of the independent normal modes. **There are 3N normal modes for a bound system of N atoms in d=3** (actually 3N-6 when we separate uniform translations and rotations.)

4: Periodic systems and Bloch's theorem



lattice constant a

A finite system can't be truly periodic. Solution –**Born-von Karman** (periodic) boundary conditions. Attach periodic replicas which copy the N-atom finite system.

$$V = \tfrac{1}{2}k(u_1-u_2)^2 + \tfrac{1}{2}k(u_2-u_3)^2 + \ldots + \tfrac{1}{2}k(u_N-u_1)^2$$

Finite and periodic

$$-m\frac{d^2}{dt^2}\begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{pmatrix} = \begin{pmatrix} 2k & -k & 0 & 0 & 0 & -k \\ -k & 2k & -k & 0 & 0 & 0 \\ 0 & -k & 2k & -k & 0 & 0 \\ 0 & 0 & -k & 2k & -k & 0 \\ 0 & 0 & 0 & -k & 2k & -k \\ -k & 0 & 0 & 0 & -k & 2k \end{pmatrix}\begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{pmatrix}$$

Unequal masses are treated as in CO_2 – Homework!

Translation operators $\hat{T}_n$

$$\hat{T}_1 \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{pmatrix} = \begin{pmatrix} u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \\ u_1 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{pmatrix}$$

Multiplication rules: T_i form an Abelian group

$T_1^2 = T_2$, $T_1^N = T_N = T_0 = 1$

$T_1^{-1} = T_{-1}$, $T_m T_n = T_{m+n}$

$T_m T_n = T_n T_m$

Newton equation of motion in matrix form using translation matrices

$$-\frac{d^2}{dt^2}|u> = \frac{k}{m}\left(2\hat{T}_0 - \hat{T}_1 - \hat{T}_{-1}\right)|u> = \hat{D}\,|u>$$

Dynamical matrix D is built from translation matrices T, and commutes with them. Therefore, we can build eigenstates of the dynamical matrix using eigenstates of translations. These are traveling waves.

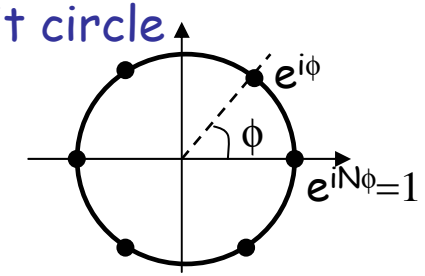
Look for eigenstates of T_1

$$|\phi\rangle = \begin{pmatrix} e^{i\phi} \\ e^{i2\phi} \\ e^{i3\phi} \\ e^{i4\phi} \\ e^{i5\phi} \\ e^{i6\phi} \end{pmatrix} \qquad \hat{T}_1|\phi\rangle = \begin{pmatrix} e^{i2\phi} \\ e^{i3\phi} \\ e^{i4\phi} \\ e^{i5\phi} \\ e^{i6\phi} \\ e^{i\phi} \end{pmatrix} = e^{i\phi}|\phi\rangle$$

If $|\phi\rangle$ is an eigenstate of T_1 with eigenvalue $e^{i\phi}$, then it is an eigenstate of T_2 with eigenvalue $e^{i2\phi}$, etc.

Provided $e^{iN\phi}=1$ (here N=6)

$e^{i\phi}$ must be one of the N roots of unity. There are N such roots, on the unit circle



$$\phi = \frac{2\pi m}{N} = \frac{2\pi m a}{Na = L} \equiv ka \qquad k \equiv \frac{2\pi m}{L} = \frac{2\pi}{\lambda}$$

$$|\phi\rangle = |k\rangle = \begin{pmatrix} e^{ika} \\ e^{i2ka} \\ e^{3ika} \\ e^{i4ka} \\ e^{i5ka} \\ e^{i6ka} \end{pmatrix}$$

Mathematical meaning of the **wave vector k** - the eigenvalue of $T_1 = T(a)$ is e^{ika} Therefore, k and $k+2\pi/a$ have exactly the same meaning.

Warning – notation!
k is used for wave vector and for spring constant!

Bloch's Theorem

Operators like $\mathcal{H}$ and D for a periodic system commute with the translations. Therefore, we can choose eigenstates of $\mathcal{H}$ and D to be simultaneously eigenstates of all T_i. These eigenstates are labeled by their wavevector $\vec{k}$.

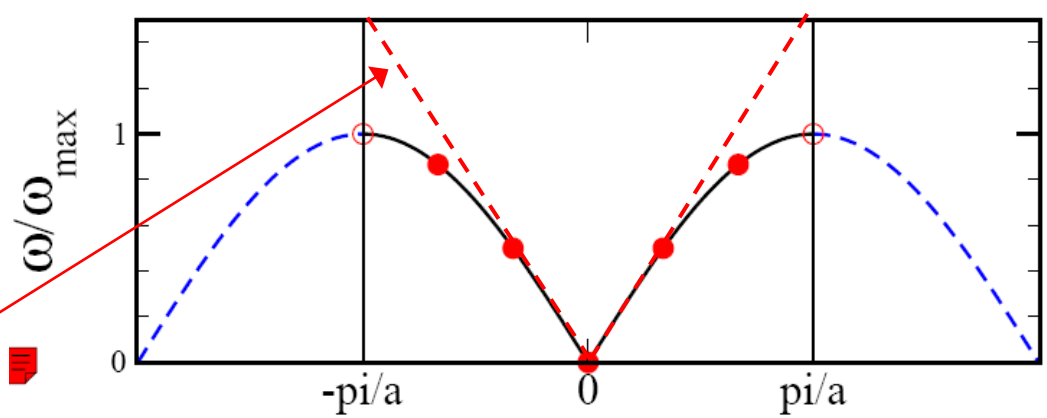
$$\hat{T}_1 \,|\, k >= e^{ika} \,|\, k > \qquad \hat{D} = \frac{k}{m}\left(2\hat{T}_0 - \hat{T}_1 - \hat{T}_{-1}\right) \rightarrow \frac{k}{m}\left(2 - e^{ika} - e^{-ika}\right)$$

$\omega^2(k)$ = eigenvalue of D = $\frac{k}{m}\left(2 - 2\cos(ka)\right) = 4\frac{k}{m}\sin^2(ka/2)$

$$\omega(k) = \omega_{\max}\left|\sin(ka/2)\right|$$

$$\omega_{\max} = 2\sqrt{\frac{k}{m}}$$

Continuum ("Debye") limit: propagating sound waves $\omega = v|k|$



Counting rules in k-space.

1. There are exactly N k-vectors $\vec{k}$ which label the inequivalent eigenvectors |k> of T. These N k-vectors lie in the Brillouin zone.
2. Bloch states |k> with inequivalent $\vec{k}$'s are orthogonal.
   Norm = 1. Thus $\langle k'|k\rangle=(1/N)\sum_R e^{i(k-k')R} = \delta(k,k')$ ***modulo G***
3. The states |k> are complete in the N-dimensional space:
   $\sum_k |k\rangle\langle k| = (1/N)\sum_k e^{ik(R-R')} = \delta(R-R')$ [R runs over the discrete lattice points.]
4. Sums become integrals: $\sum_k f(k) = \left(\frac{L}{2\pi}\right)^d \int_{BZ} d^d k \; f(k)$

Ziman's notation

I will use ω instead of ν.

Same linear chain, lattice constant a, spring constant α, alternating masses M_1 and M_2.

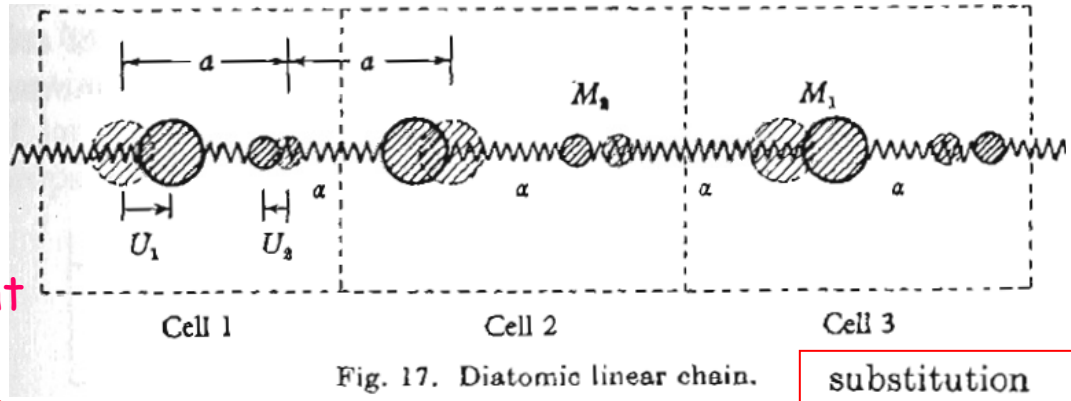


Fig. 17. Diatomic linear chain.

spring constant
$K \rightarrow \alpha$

$$\left.\begin{aligned} M_1 \ddot{U}_1 &= -2\alpha U_1 + 2\alpha \cos qa \,.\, U_2, \\ M_2 \ddot{U}_2 &= -2\alpha U_2 + 2\alpha \cos qa \,.\, U_1. \end{aligned}\right\} \qquad (2.22)$$

substitution

$$u_l = U_q e^{iql}$$

has been generalized:
$u_{n1}=U_1(t)\exp(iq(2n)a)$
$u_{n2}=U_2(t)\exp(iq(2n+1)a)$

To find the frequency ν, we must solve the determinantal equation

$$\begin{vmatrix} 2\alpha - M_1\nu^2 & -2\alpha\cos qa \\ -2\alpha\cos qa & 2\alpha - M_2\nu^2 \end{vmatrix} = 0, \qquad (2.23)$$

which has the two roots

$$\nu_\pm^2 = \alpha\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm \alpha\sqrt{\left\{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4\sin^2 qa}{M_1 M_2}\right\}}. \qquad (2.24)$$

using mass-scaled variables:

$$\begin{pmatrix} 2\alpha/M_1 & -2\alpha\cos(qa)/\sqrt{M_1M_2} \\ -2\alpha\cos(qa)/\sqrt{M_1M_2} & 2\alpha/M_2 \end{pmatrix}\begin{pmatrix} U_1 \\ U_2 \end{pmatrix} = \omega^2\begin{pmatrix} U_1 \\ U_2 \end{pmatrix}$$

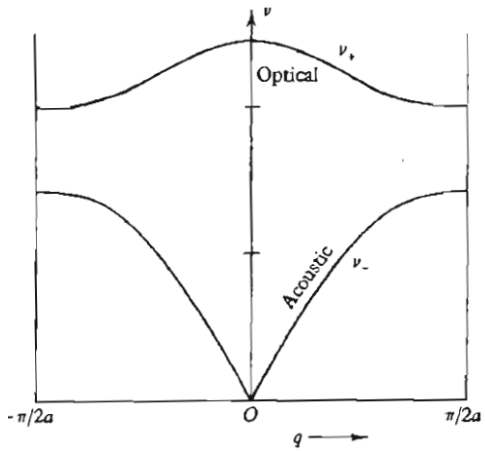


Fig. 18. Vibration frequencies of diatomic chain.

end of recycled lecture!

$$\mathscr{V} = \mathscr{V}_0 + \sum_{slj} u^j_{sl} \left[\frac{\partial \mathscr{V}}{\partial u^j_{sl}}\right]_0 + \frac{1}{2} \sum_{ss',ll',jj'} u^j_{sl} u^{j'}_{s'l'} \left[\frac{\partial^2 \mathscr{V}}{\partial u^j_{sl} \partial u^{j'}_{s'l'}}\right]_0 + \ldots \quad (2.2)$$

$$M_s \ddot{u}^j_{sl} = -\sum_{s'l'j'} \left[\frac{\partial^2 \mathscr{V}}{\partial u^j_{sl} \partial u^{j'}_{s'l'}}\right]_0 u^{j'}_{s'l'}$$

counting: N values of ℓ, n values of s, 3 values of j

N = # cells in crystal; n = # atoms in unit cell, 3 = # dimensions of space.

3nN x 3nN matrix eigen problem ("generalized Hermitean eigenvalue problem; convert to ordinary Hermitean eigenvalue problem using mass-weighted coordinates.

$$\hat{M}\frac{d^2}{dt^2}|u\rangle = -\hat{K}|u\rangle \qquad |s\rangle = \hat{M}^{1/2}|u\rangle \qquad \hat{D} = \hat{M}^{-1/2}\hat{K}\hat{M}^{-1/2} \qquad \frac{d^2}{dt^2}|s\rangle = -\hat{D}|s\rangle$$

$$\hat{D}|s_\lambda\rangle = \omega_\lambda^2 |s_\lambda\rangle$$

$$|u(t)\rangle = \sum_\lambda A_\lambda \cos(\omega_\lambda t + \phi_\lambda)\hat{M}^{-1/2}|s_\lambda\rangle$$

the general solution of Newton's law

Bloch-wave transformation: 3nN-vector |s> as direct product of 3n-vector |ε> and N-vector |**Q**>

$$s_{s\ell}{}^j = \varepsilon_{sj} e^{i\vec{Q}\cdot\vec{\ell}}/\sqrt{N}$$

$$|s\rangle = |\varepsilon(\vec{Q})\rangle \otimes |\vec{Q}\rangle$$

} eigenvectors of T_{op}

$$|\varepsilon(\vec{Q})\rangle = \begin{pmatrix} \varepsilon_{1x} \\ \varepsilon_{1y} \\ \vdots \\ \varepsilon_{nz} \end{pmatrix} \qquad |\vec{Q}\rangle = \frac{1}{\sqrt{N}} \begin{pmatrix} \exp(i\vec{Q}\cdot\ell_1) \\ \exp(i\vec{Q}\cdot\ell_2) \\ \vdots \\ \exp(i\vec{Q}\cdot\ell_N) \end{pmatrix}$$

Translational invariance: $\left\langle \vec{\ell}', s'\alpha' \middle| \hat{D} \middle| \vec{\ell}, s\alpha \right\rangle = \left\langle 0, s'\alpha' \middle| \hat{D} \middle| \vec{\ell} - \vec{\ell}', s\alpha \right\rangle$

Transform from one orthonormal basis to another *via* a unitary matrix:

$$\left\langle \vec{Q} \middle| \hat{U} \middle| \vec{\ell} \right\rangle = \left\langle \vec{Q} \middle| \vec{\ell} \right\rangle = \exp(-i\vec{Q}\cdot\vec{\ell})/\sqrt{N}$$

$$\hat{U}\hat{U}^{+} = \hat{U}^{+}\hat{U} = 1$$

$$\frac{1}{N}\sum_{\vec{\ell}} e^{i(\vec{Q}-\vec{Q}')\vec{\ell}} = \delta_{\vec{Q},\vec{Q}'} \quad \text{and} \quad \frac{1}{N}\sum_{\vec{Q}} e^{i\vec{Q}\cdot(\vec{\ell}-\vec{\ell}')} = \delta_{\vec{\ell},\vec{\ell}'}$$

The dynamical matrix is "block-diagonalized":

$$\sum_{\vec{\ell},\vec{\ell}'} \left\langle \vec{Q}' \middle| \vec{\ell}' \right\rangle \left\langle \vec{\ell}', s'\alpha' \middle| \hat{D} \middle| \vec{\ell}, s\alpha \right\rangle \left\langle \vec{\ell} \middle| \vec{Q} \right\rangle = \left\langle s'\alpha' \middle| \hat{D}\left(\vec{Q}\right) \middle| s\alpha \right\rangle \delta_{\vec{Q},\vec{Q}'}$$

$$\left\langle s'\alpha' \middle| \hat{D}\left(\vec{Q}\right) \middle| s\alpha \right\rangle = \sum_{\vec{\ell},\vec{\ell}'} \left\langle \vec{\ell}', s'\alpha' \middle| \hat{D} \middle| \vec{\ell} s\alpha \right\rangle e^{i\vec{Q}\cdot(\vec{\ell}-\vec{\ell}')}/N$$

$$\sum_{\vec{\ell},\vec{\ell}'} \left\langle \vec{Q} \middle| \vec{\ell} \right\rangle \left\langle \vec{\ell}, s\alpha \middle| u \right\rangle = \varepsilon_{s\alpha}\left(\vec{Q}\right)$$

$$\hat{D}\left(\vec{Q}\right)\left| \varepsilon_{\lambda}\left(\vec{Q}\right)\right\rangle = \omega_{\lambda}^{2}\left(\vec{Q}\right)\left| \varepsilon_{\lambda}\left(\vec{Q}\right)\right\rangle$$

$\hat{D}\left(\vec{Q}\right)$ is the 3n x 3n dynamical matrix, $\varepsilon_{\lambda}\left(\vec{Q}\right)$ is the 3n-eigenvector or "polarization vector" (mass-weighted)

Umklapp *versus* Normal

a. x-ray or neutron inelastic scattering

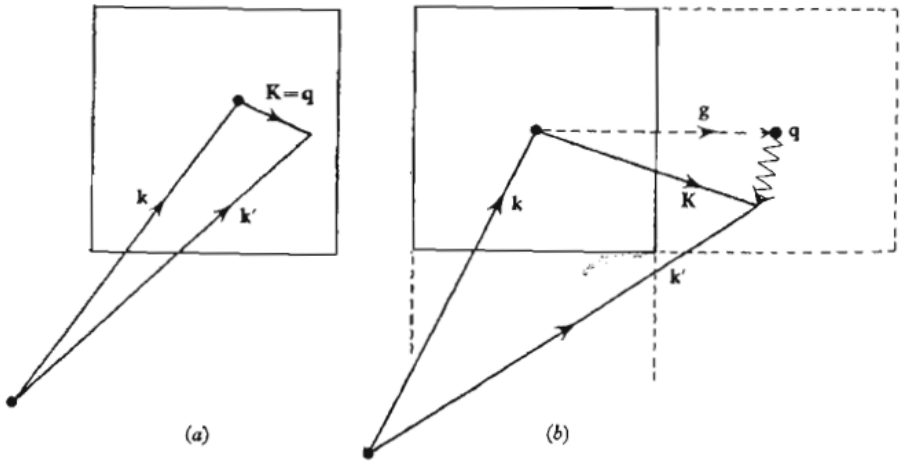
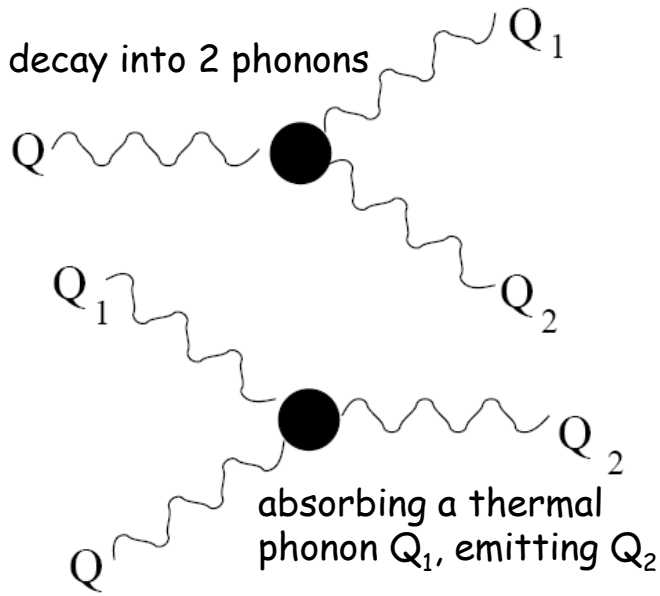
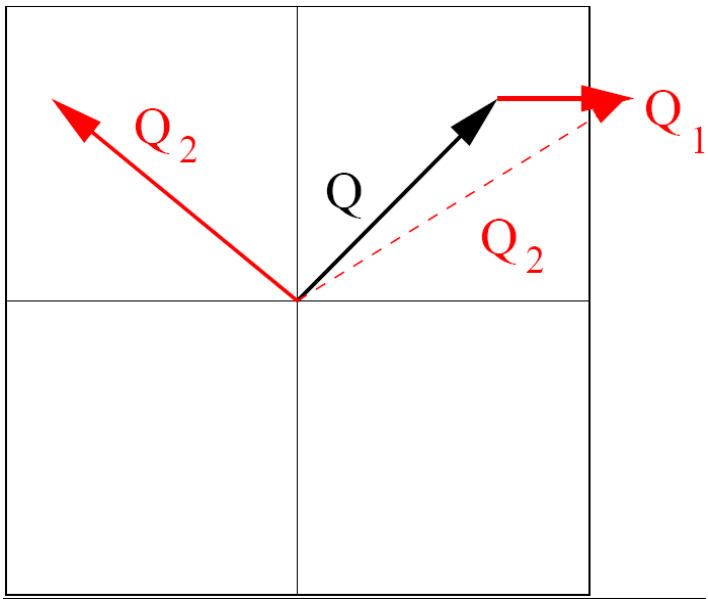


Fig. 32. (a) Normal process. (b) Umklapp process.

b. anharmonic phonon decay





When $Q+Q_1$ lies outside the zone, map it back to Q_2 inside the zone (Umklapp process) – *i.e.* subtract a reciprocal lattice vector.

Conservation of crystal momentum

$$\vec{Q}_1 + \vec{Q}_2 + \cdots = const (\mathrm{mod}\, \vec{G})$$

a consequence of discrete crystalline translational invariance, *e.g.*,

$$V_{\alpha\beta\gamma}\left(\vec{\ell}_1, \vec{\ell}_2, \vec{\ell}_3\right) = V_{\alpha\beta\gamma}\left(0, \vec{\ell}_2 - \vec{\ell}_1, \vec{\ell}_3 - \vec{\ell}_1\right)$$

just as Newtonian momentum conservation is a consequence of the translational symmetry of space.

the mathematical root of it:

$$\frac{1}{N}\sum_{\vec{\ell}} \exp\left[i\left(\vec{Q}_1 + \vec{Q}_2 + \cdots\right)\cdot\vec{\ell}\right] = \begin{cases} 1 \text{ if } \vec{Q}_1 + \vec{Q}_2 + \cdots = 0 (\mathrm{mod}\, \vec{G}) \\ 0 \text{ otherwise} \end{cases}$$

a typical example—anharmonic coupling

$$\sum_{\vec{\ell}_1,\vec{\ell}_2,\vec{\ell}_3} V_{\alpha\beta\gamma}\left(\vec{\ell}_1, \vec{\ell}_2, \vec{\ell}_3\right) u_{\vec{\ell}_1\alpha} u_{\vec{\ell}_2\beta} u_{\vec{\ell}_3\gamma} =$$

$$\sum_{\vec{Q}_1,\vec{Q}_2,\vec{Q}_3} \sum_{\vec{\ell}_2,\vec{\ell}_3} \left[\sum_{\vec{\ell}_1} V_{\alpha\beta\gamma}\left(0, \vec{\ell}_2 - \vec{\ell}_1, \vec{\ell}_3 - \vec{\ell}_1\right)\right] u_{\vec{Q}_1\alpha} u_{\vec{Q}_2\beta} u_{\vec{Q}_3\gamma}$$

$$\times \exp\left(i\left[\vec{Q}_1 + \vec{Q}_2 + \vec{Q}_3\right]\cdot\vec{\ell}_1\right) \exp\left(i\vec{Q}_2\cdot\left[\vec{\ell}_2 - \vec{\ell}_1\right]\right) \exp\left(i\vec{Q}_3\cdot\left[\vec{\ell}_3 - \vec{\ell}_1\right]\right)$$

$$= \sum_{\vec{Q}_2,\vec{Q}_3} V\left(\underbrace{-\vec{Q}_2 - \vec{Q}_3, \vec{Q}_2, \vec{Q}_3}_{\text{modulo } G}\right) u_{-\vec{Q}_2-\vec{Q}_3\alpha} u_{\vec{Q}_2\beta} u_{\vec{Q}_3\gamma}$$

new variables

$$\begin{cases} \vec{\ell}_4 = \vec{\ell}_2 - \vec{\ell}_1 \\ \vec{\ell}_5 = \vec{\ell}_3 - \vec{\ell}_1 \end{cases}$$

Density of states

Let us consider, for simplicity, a single branch of the spectrum. The proportion of modes with frequency in the range $d\nu$ is equal to

$$\mathscr{D}(\nu)\,d\nu = \frac{v_c}{8\pi^3}\iiint d^3q, \qquad (2.65)$$

where the integration is through the volume of the shell in **q**-space where $\nu \leqslant \nu_{\mathbf{q}} \leqslant \nu + d\nu$.

I like to use ω instead of ν. The true mathematical meaning of Ziman's expression is correctly captured by the Dirac delta function:

$$\mathscr{D}(\nu) = \frac{1}{8\pi^3 N}\int \frac{dS_\nu}{v_{\mathbf{q}}} \qquad D(\omega) = \frac{1}{N}\sum_{\vec{Q}} \delta\left(\omega - \omega_{\vec{Q}}\right) = \frac{V_c}{(2\pi)^3}\int d^3Q\,\delta\left(\omega - \omega_{\vec{Q}}\right)$$

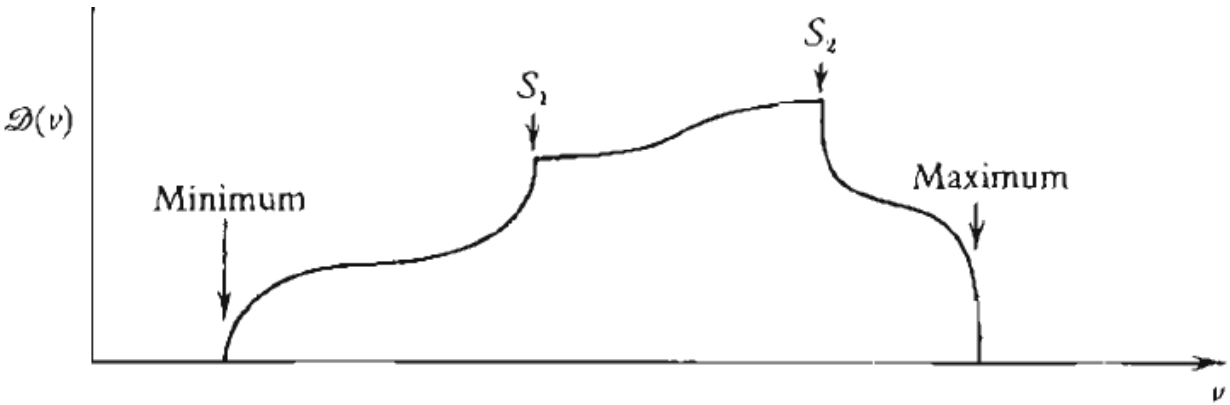
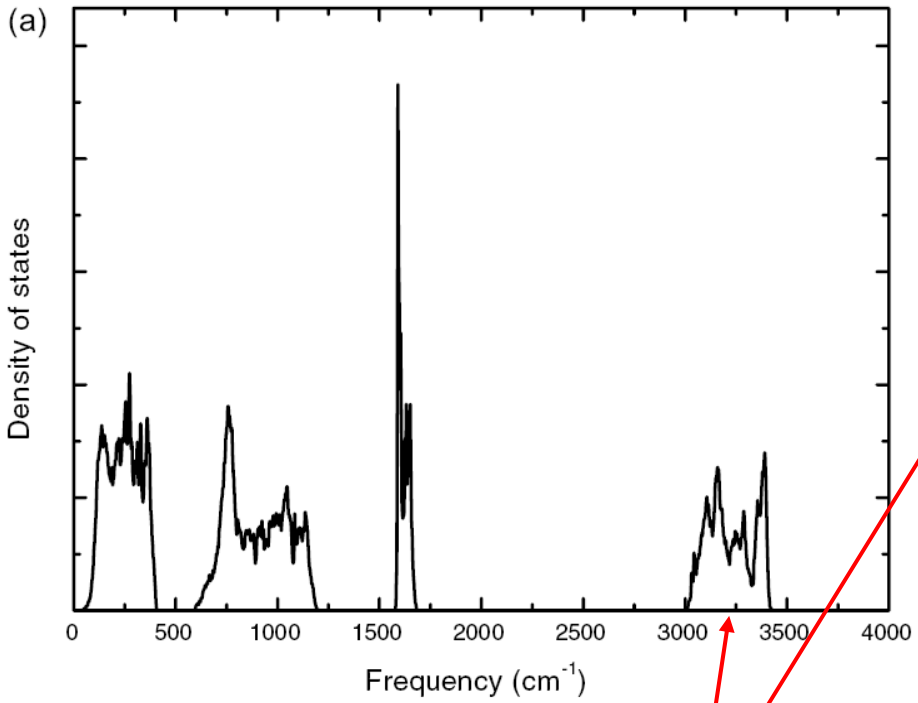
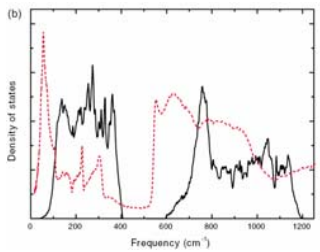


Fig. 27. Different types of van Hove singularity.

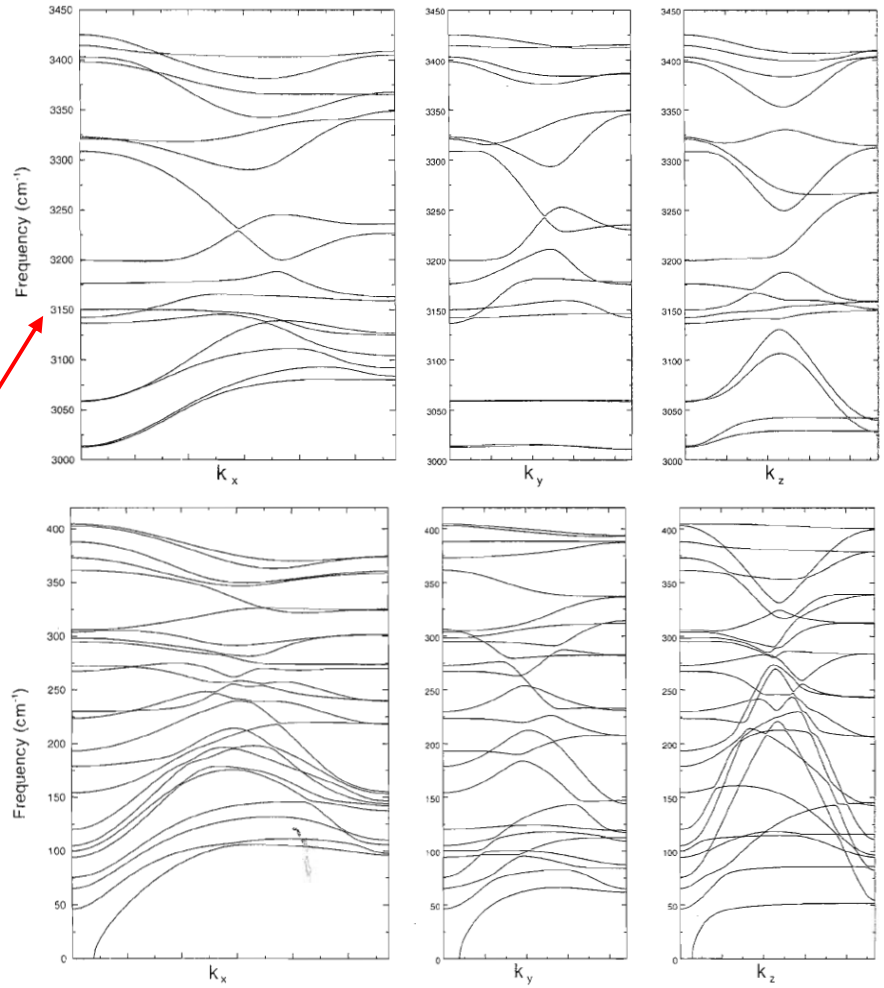
A. S. Cote, I. Morrison, X. Cui X, S. Jenkins, and D. K. Ross,
Ab-initio density-functional lattice-dynamics studies of ice
CAN. J. PHY. 81, 115 (2003).

8 molecules/cell ➔ 72 branches



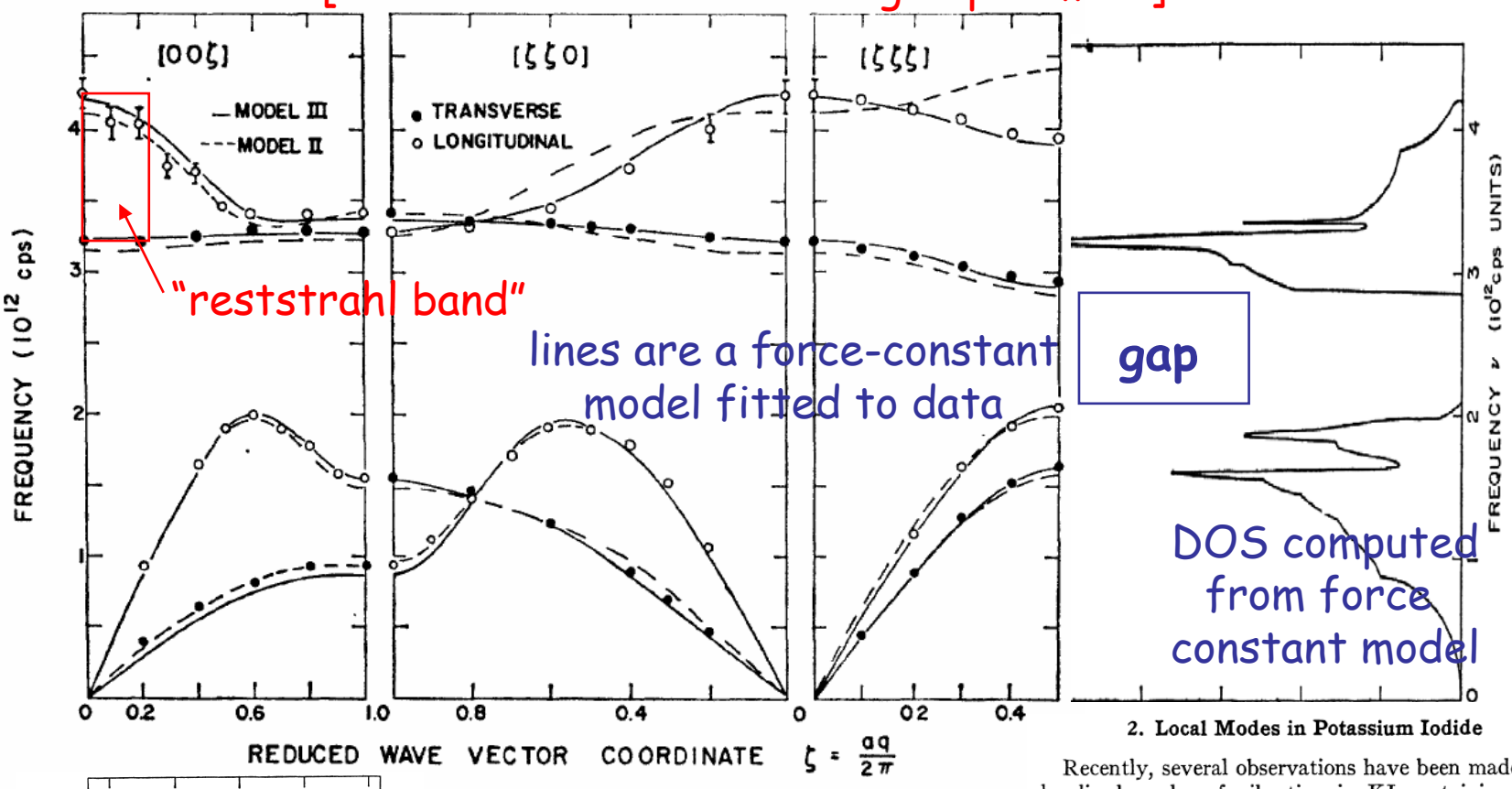


"OH stretch" modes



G. Dolling, R. A. Cowley, C. Schittenhelm, and I. M. Thorson,
Normal Vibrations of Potassium Iodide, Phys. Rev. **147**, 577 (1966)

[inelastic neutron scattering experiment]



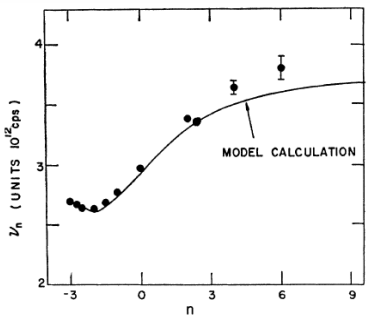


FIG. 4. Equivalent "Debye" frequencies computed from the moments of the distribution function (Fig. 2) and compared with values (filled circles) derived from heat-capacity data.[24]

2. Local Modes in Potassium Iodide

Recently, several observations have been made[7–9] of localized modes of vibration in KI containing small amounts of KNO_2. A calculation of the vibration frequency of the NO_2^- ion in the KI lattice, on the basis of simple mass-defect theories,[10] indicated that it would probably fall in the gap in the frequency distribution function of the host. In practice, a complex spectrum of localized modes is observed, which is believed[8,11] to be associated with various rotational degrees of freedom of the NO_2^- ion. The present experiments and calculations give the location of the energy gap in pure KI with a precision of 2 or 3%, and confirm that the local modes of the KI:KNO_2 system do in fact fall within that gap.