Dulong-Petit Law

Classical harmonic crystal $u = \frac{U^{eq}}{V} + \frac{3N}{V} k_B T$

$U = U^{eq} + 3nk_BT$; at $T = 0$ $U = U^{eq}$. (No sp motion)

$C_V = \frac{\partial U}{\partial T} = 3nk_B \rightarrow$ specific heat due to lattice vibrations (Total sp. heat ~~due~~ from an insulator)

M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford, 1954; p. 44.

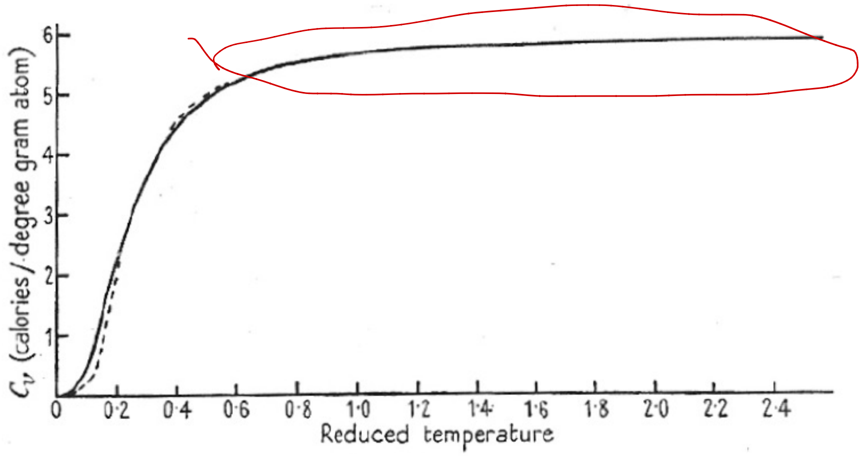


FIG. 5. Comparison of the Debye (——) and Einstein (- - - -) models.

$\omega = \sqrt{\frac{K}{M}}$

TABLE 13

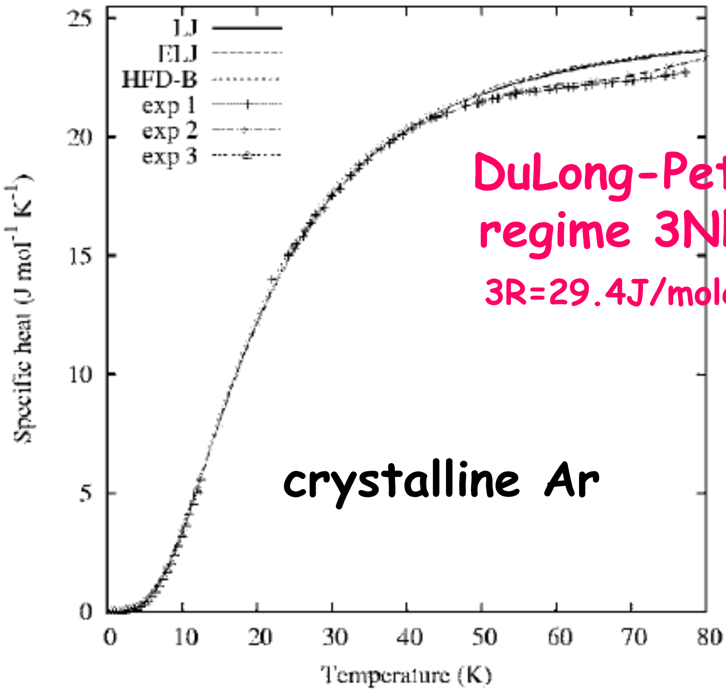
Debye Temperatures

Substance	Pb	Tl	Hg	I	Cd	Na	KBr	Ag	Ca
	88	96	97	106	168	172	177	215	226

Substance	KCl	Zn	NaCl	Cu	Al	Fe	CaF	FeS	C
	230	235	281	315	398	453	474	645	1860

Lattice specific heat (Einstein, 1907) generalized

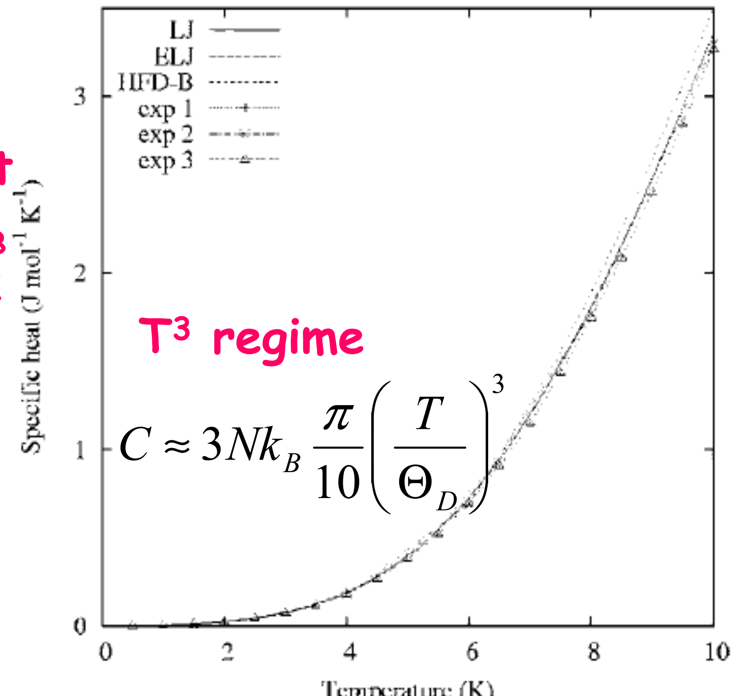
$$C(T)=\frac{d}{dT}\sum_Q \hbar\omega_Q\left(n_Q+\tfrac{1}{2}\right)=k_B\sum_Q\left[\frac{\hbar\omega_Q/2k_BT}{\sinh\left(\hbar\omega_Q/2k_BT\right)}\right]^2=\sum_Q C_E\left(\hbar\omega_Q/2k_BT\right)=\int_0^\infty d\Omega D(\Omega)C_E\left(\hbar\Omega/2k_BT\right)$$



DuLong-Petit regime $3Nk_B$

3R=29.4J/moleK

crystalline Ar



T^3 regime

$$C\approx 3Nk_B\frac{\pi}{10}\left(\frac{T}{\Theta_D}\right)^3$$

G. E. Moyano, P. Schwerdtfeger, and K. Rosciszewski
"Lattice dynamics for fcc rare gas solids Ne, Ar, and Kr from *ab initio* potentials"
Phys. Rev. B 75, 024101 (2007).

S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi,
Rev. Mod. Phys. **73**, 515-62 (2001) – review of "*ab initio*" theory

[32] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Phys. Rev. **150**, 703 (1966).

[33] L. Finegold and N. E. Phillips, Phys. Rev. **177**, 1383 (1969).

[34] D. L. Losee and R. O. Simmons, Phys. Rev. **172**, 944 (1968).

Intermediate Temperature: Debye and Einstein models

Debye

- All branches are replaced by just 3, acoustic-like branches ($\omega = cq$). If there are more than 3 branches we change the volume of integration.

→ The integral in $\vec{q}$ over the 1st BZ is changed over the Debye sphere.

Debye sphere contains N wave vectors

$$\sum_{q} f(q) \longrightarrow \frac{V}{(2\pi)^3}\int_0^{q_D} d\vec{q} = N \Rightarrow \frac{V}{(2\pi)^3}\frac{4\pi}{3}\pi q_D^3 = N$$

$$\frac{N}{V} = \frac{q_D^3}{6\pi^2} \longrightarrow \boxed{q_D = \left(\frac{6\pi^2}{v_c}\right)^{1/3}} \; ; \; v_c = \frac{4}{3}\pi r_s^3$$

$$q_D = \left(\frac{9\pi}{2}\right)^{1/3}\frac{1}{r_s}$$

$$\lambda_D = \frac{2\pi}{q_D} \sim 6 r_s$$

$\lambda_D \sim$ a bit more than the lenght of a unit cell

→ lattice won't propagate waves of shorter wavelength

$$C_V = \frac{\partial}{\partial T}\frac{3\hbar^3 c^3}{2\pi^2}\int_0^{q_D}\frac{q^3}{e^{\beta\hbar c q}-1}\,dq$$

$$C_V = \frac{\partial}{\partial T}\sum_{j=1}^{3}\int_0^{q_D}\frac{d\vec{q}}{(2\pi)^3}\frac{\hbar\omega_j(q)}{e^{\hbar\omega_j(q)\beta}-1}$$

$\omega_j = cq$

$\omega_D = q_D c \quad ; \quad K_\beta \Theta_D = \boxed{\hbar \omega_D} = \hbar c q_D$

Debye Temperature.

$\boxed{\Theta_D} \rightarrow$ Measure of The Temperature at which all modes begin To be excited, bellow Θ_D They begin To be "frozen" out, therefore measures The stiffness of The crystal.

$$\frac{\hbar c q}{K_\beta T} = x \quad ; \quad C_V = 9 n k_\beta \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} \, dx$$

$$T/\Theta_D \gg 1 \rightarrow \int_0^{\Theta_D/T} \frac{x^4}{x^2} \, dx = \frac{1}{3}\left(\frac{\Theta}{T}\right)^3 \Longrightarrow C_V = 3 N k_\beta$$

How To choose Θ_D? Not unique!

We can choose iT so as $C_{V_c} = C_V$ at low T (experimental)

for $T \ll \Theta_D \quad \Theta_D / T \longrightarrow \infty$ (The integral Tends To a constant $\left(\frac{4\pi^4}{15}\right)$)

$$C_V(T \to 0) = \frac{2\pi^4}{5} n k_\beta \left(\frac{T}{\Theta_D}\right)^3$$

Θ_D plays The role of T_F ($\epsilon_F = k_\beta T_F$) in e^-. Above Θ_D separates low T region (quantum statistics) from high T (classical statistics).

Einstein Model

→ Apply only to the optical branches and describe acoustic with einstein model.

$$\omega_j(q)\ (\text{optical}) \to \omega_j \text{, independent of } q.$$

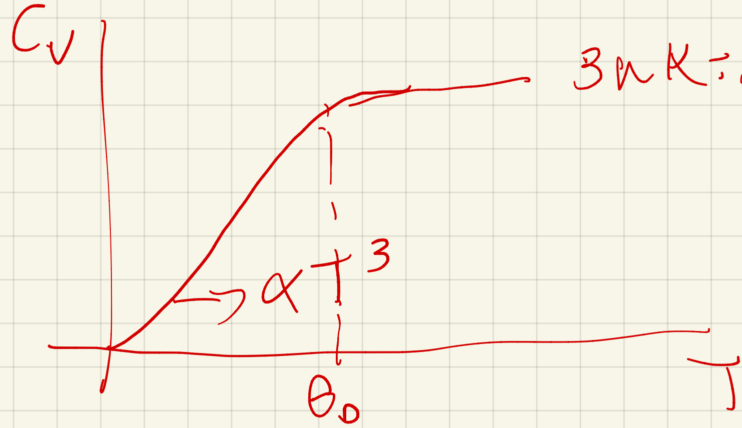
→ einstein model.

$$\frac{E}{V}\ (\text{per branch}) = \frac{n\hbar\omega_E}{e^{\hbar\omega_E/k_\beta T}-1} + \frac{n\hbar\omega_E}{2}$$

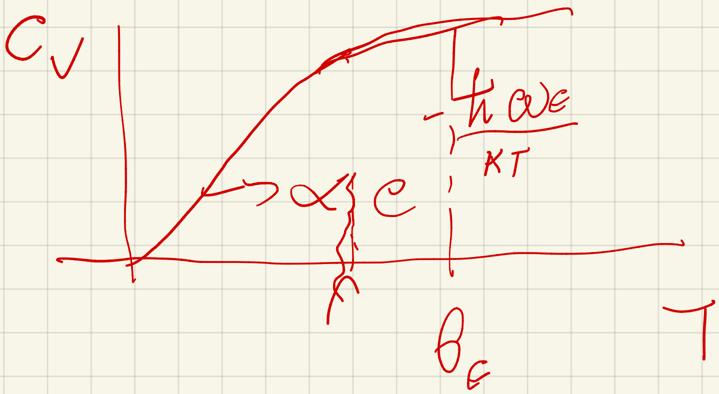
$$C_V = p\,n\,k_\beta \frac{\left(\hbar\omega_E/k_\beta T\right)^2 e^{\hbar\omega_E/k_\beta T}}{\left(e^{\hbar\omega_E/k_\beta T}-1\right)^2}$$

Einstein ⇒ Good at high T (approaches D-P).

at low T shows that optical modes decay exponentially but says nothing about acoustic modes



$3nk = 3\frac{N}{V}k_B C_V$ acoustic



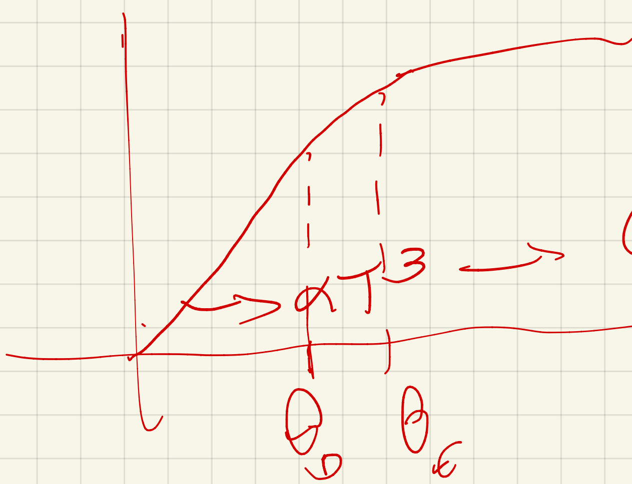
Metals: $C_V = \boxed{\alpha} T + \beta T^3$

$\underbrace{\alpha T}_{\text{electronic}} \quad \underbrace{\beta T^3}_{\text{ph.}}$

$\alpha = \frac{\pi^2}{2}\left(\frac{k_B}{E_F}\right) n k_B \qquad n = \frac{NZ}{V}$

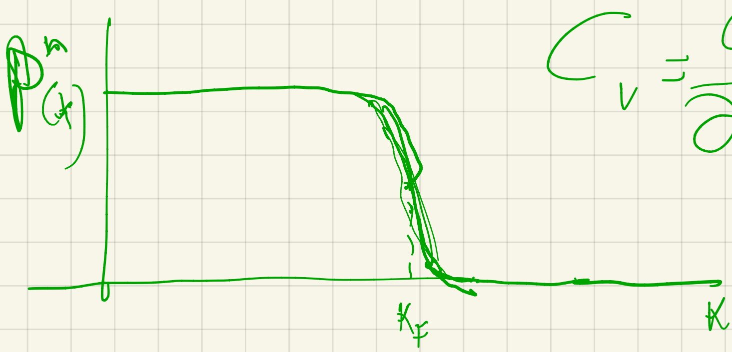
$\beta = \frac{12\pi^4}{5} n k_B \left(\frac{T}{\Theta_D}\right)^3 \qquad n = \frac{N}{V}$

$C_V^{el} / C_V^{ion} = \frac{5}{24\pi^2} Z \, \Theta_D^3 / T^2 T_F$



$\longrightarrow \quad C_V = \frac{2\pi^4}{5}\left(\frac{N}{V}\right) k_B \left(\frac{T}{\Theta_D}\right)^3$

$E_F = \frac{\hbar^2 k_F^2}{2m} \sim T^2$



$C_V = \frac{\partial}{\partial T} U(\text{electronic})$.

$E \propto T^2 \to C_V \propto T$

Phonon density of states

$$\frac{1}{V}\sum_{q,j} f(q_j) = \sum_j \int \frac{d\vec{q}}{(2\pi)^3} f(\omega_j(q))$$

$\Rightarrow$ It is more convinient to transform the integral into a frequency integral

$g(\omega) \to$ density of normal modes in frequency per unit volume.

$g(\omega)d\omega \to$ # of normal modes with ω in the ω-$\omega+d\omega$ range

$$\frac{1}{(2\pi)^3}\int d\vec{q}\, f(q_j(\omega)) \longrightarrow \int g(\omega)d\omega\, f(\omega)$$

In perfect analogy with the electronic density of states

$$g(\omega) = \sum_j \int \frac{d\vec{q}}{(2\pi)^3}\,\delta(\omega-\omega(q)) \to g(\omega) = \sum_j \int \frac{dS}{(2\pi)^3}\frac{1}{|\vec{\nabla}\omega(q)|}$$

The integral is over a surface in the 1st BZ where $\omega_j(q) = \omega = \text{constant}$

Because $\omega_j(q)$ is periodic, there will be points where $\frac{\partial \omega_j(q)}{\partial q} = 0$ (group velocity $= 0$). These points will induce singularities in the DOS => Van Hove singularities

Debye Model

. All branches in the vibrational spectrum are replaced by 3 acoustic branches $\Longrightarrow \omega = c\underline{q}$

\# degrees of freedom $= 3 r \underline{N}$

all the modes $\underline{q}$ inside a sphere of radius q_D

$$g_D(\omega) = 3 \int_{\underline{q} < q_D} \frac{d\vec{\underline{q}}}{(2\pi)^3}\, \delta(\omega - c\underline{q}) = \frac{3}{2\pi^2} \int_0^{q_D} \underbrace{\underline{q}^2\, \delta(\omega - c\underline{q})\, d\underline{q}}$$

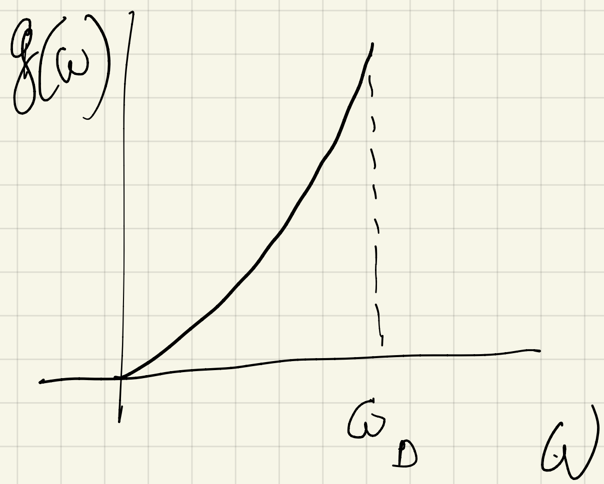
$$c\underline{q} = t \quad ; \quad d\underline{q} = \frac{1}{c}\, dt$$

$$\underline{q}^2 = t^2/c^2 \quad ; \quad c\underline{q}_D = \omega_D$$

$$\int_0^{\omega_D} \frac{t^2}{c^3}\, \delta(\omega - t) = \frac{\omega_D^2}{c^3}$$

$$g_D = \begin{cases} \dfrac{3}{2\pi^2} \dfrac{\omega^2}{c^3} & \omega < \omega_D \\ 0 & \omega > \omega_D \end{cases}$$

$$g_D \propto \omega^2$$



Ziman, chapter 2

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:

$$\mathscr{D}(\nu) = \frac{1}{8\pi^3 N}\int \frac{dS_\nu}{v_{\mathbf{q}}}$$

$$D(\omega) = \frac{1}{N}\sum_{\vec{Q}}^{BZ}\delta\left(\omega-\omega_{\vec{Q}}\right) = \frac{V_c}{(2\pi)^3}\int_{BZ} d^3Q\,\delta\left(\omega-\omega_{\vec{Q}}\right)$$

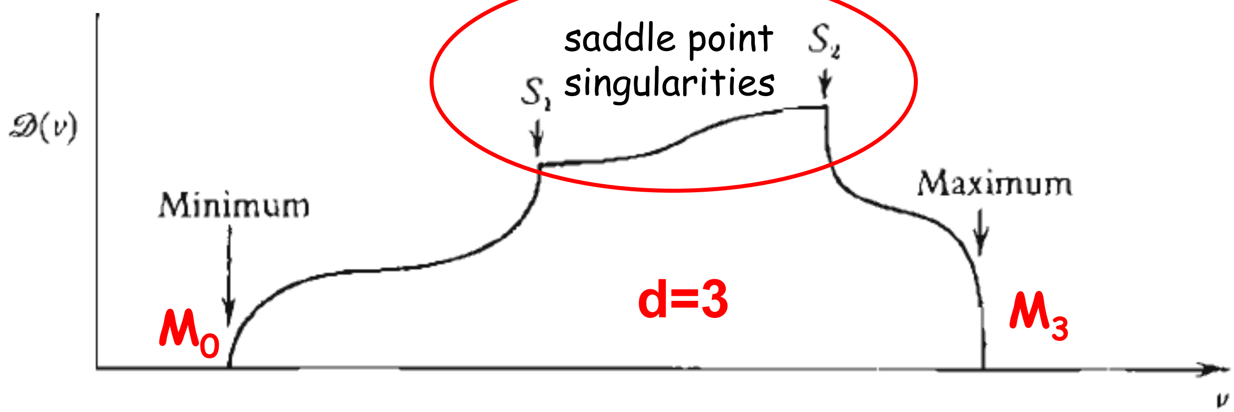


Fig. 27. Different types of van Hove singularity.

$$D_E(\omega) = 3\delta(\omega-\omega_E)$$
$$D_D(\omega) = 9(\omega^2/\omega_D^3)\theta(\omega_D-\omega)$$

Einstein model:

$$\omega_{\vec{Q}} \approx \omega_E$$

Debye model:

$$\omega_{\vec{Q}} \approx v_s\left|\vec{Q}\right|$$

BZ=sphere of volume

$$V_{BZ} = \frac{(2\pi)^3}{V_{cell}} = \frac{4\pi}{3}Q_D^3$$

$$\omega_{\max} = \omega_D = v_s Q_D$$

$$\hbar\omega_D = k_B\Theta_D$$

Ziman pp 47-49
Van Hove singularities

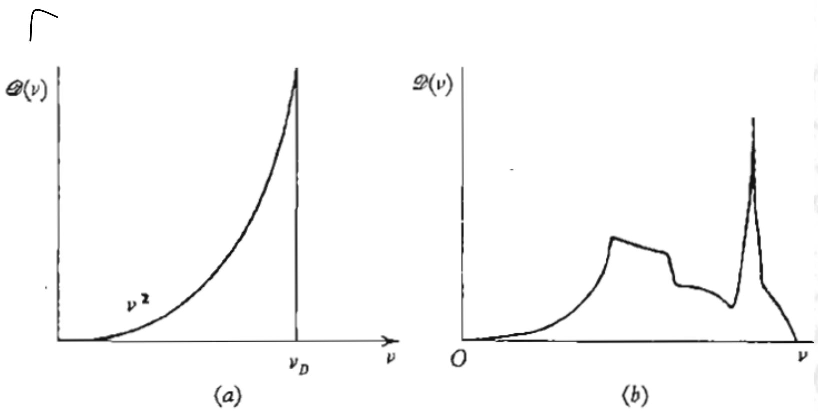


Fig. 25. (a) The Debye spectrum. (b) A true lattice spectrum.

$$\mathscr{D}(\nu) = \frac{1}{8\pi^3 N}\int \frac{dS_\nu}{v_\mathbf{q}}$$

Let us suppose that $\mathbf{q}_c$ is a critical point. Since $\nu_\mathbf{q}$ is a continuous function of $\mathbf{q}$, it can be expanded as a Taylor series around that point. The linear terms vanish, because $\mathbf{v}_\mathbf{q} = 0$, and the quadratic terms can be reduced to a sum of squares by a principal axes transformation. Thus, we can write

$$\nu_\mathbf{q} = \nu_c + \alpha_1 \xi_1^2 + \alpha_2 \xi_2^2 + \alpha_3 \xi_3^2 + \dots, \tag{2.70}$$

where $\boldsymbol{\xi} = \mathbf{q} - \mathbf{q}_c$ is the vector distance from the critical point, referred to the local principal axes, and the coefficients $\alpha_1, \alpha_2, \alpha_3$ depend on local second derivatives of $\nu_\mathbf{q}$ with respect to $\mathbf{q}$.

For example, suppose that $\alpha_1, \alpha_2, \alpha_3$ are all negative. Then ν is near a local maximum. The constant frequency surfaces (2.70) are ellipsoids; by elementary analytical geometry, the volume enclosed by the surface ν, around $\mathbf{q}_c$, is given by

$$\tfrac{4}{3}\pi \frac{(\nu_c - \nu)^{\frac{3}{2}}}{|\alpha_1 \alpha_2 \alpha_3|^{\frac{1}{2}}}, \tag{2.71}$$

whence we find, from (2.65), after a differentiation with respect to ν,

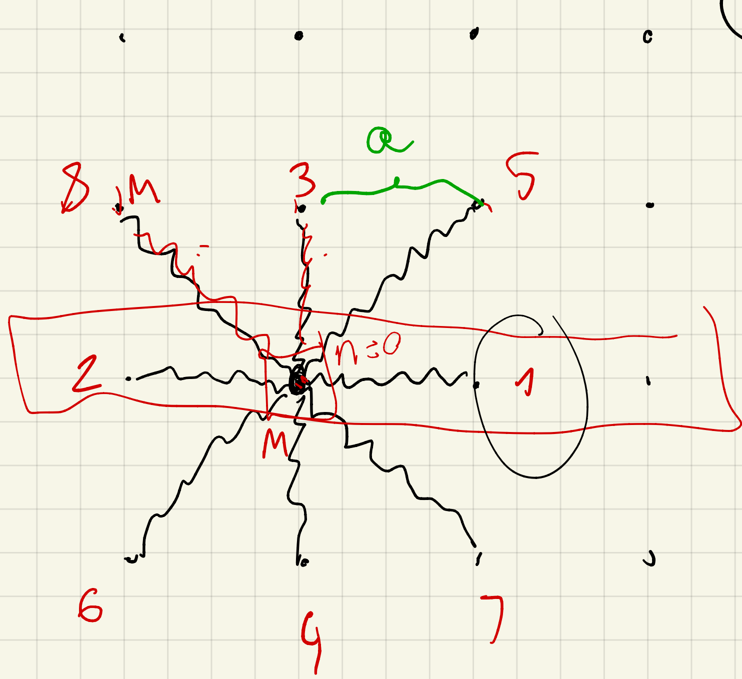
$$\mathscr{D}(\nu) = \frac{1}{4\pi^2 N\,|\alpha_1 \alpha_2 \alpha_3|^{\frac{1}{2}}}(\nu_c - \nu)^{\frac{1}{2}}. \tag{2.72}$$

This holds for $\nu < \nu_c$; when $\nu > \nu_c$, there is no contribution to $\mathscr{D}(\nu)$ from the neighbourhood of q_c. Thus, this singularity does not spoil the continuity of $\mathscr{D}(\nu)$, but its slope, $\partial\mathscr{D}(\nu)/\partial\nu$, is discontinuous and tends to $-\infty$ as $\nu \to \nu_c$ from below.

There are other possibilities for the coefficients α_1, α_2, α_3. Thus, if one is positive and the other two negative, we have a *saddle-point of index* 1. In that case the form of the spectrum in the neighbourhood of ν_c becomes, by exactly the same sort of analytical geometry,

$$\mathscr{D}(\nu) = \begin{cases} C + O(\nu - \nu_c) & (\nu < \nu_c), \\ C - \dfrac{1}{4\pi^2 N\,|\alpha_1 \alpha_2 \alpha_3|^{\frac{1}{2}}}(\nu - \nu_c)^{\frac{1}{2}} + O(\nu - \nu_c) & (\nu > \nu_c), \end{cases} \tag{2.73}$$

Phonons for a SC in 2D



(1) Size of $D(q)$?

$2\times 2 \qquad \alpha = 1,1 \quad i = 1,2$

$$D_{\alpha i}^{\alpha' i'}(q) = \frac{1}{\sqrt{M_\alpha M_{\alpha'}}} \sum_{n\alpha i} \phi_{nn'}^{n'\alpha' i'} e^{i q(\vec{R}_n - \vec{R}_{n'})}$$

ϕ = force constant $\rightarrow \vec{F}_{n'\to 0} = \overset{\text{force constant}}{a_n} \vec{e}_{n'} (\vec{e}_{n'} \cdot \vec{S}_{n'})$

$\vec{S}_{n'}$ = displacement vector.

$n=0 \to n=1 \quad \vec{R}_1 = (0\ 1)\cdot a$

$\vec{R}_{n'} = \vec{e}_{n'} |R_{n'}|$

unit vector along the $n \to n'$ direction.

$$\phi_{0i}^{n'i'} = -a_n e_{n'i} e_{n'i'}$$

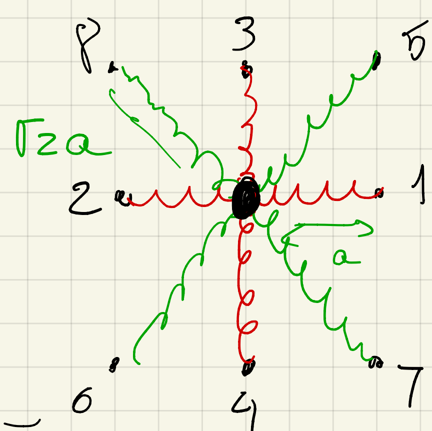
Component in the direction i' of vector $\vec{e}_{n'}$

F sum rule:

The force constant $\Phi^{0i'}_{0i}$ describes the force on atom of cell 0 after displacing this atom by vector $\vec{S}_0$ = Sum of all the forces that result after displacing all the NN by vector $-\vec{S}_0$

$$\Phi^{0i'}_{0i} = \sum_{n'\neq 0}^{NN} \Phi^{n'i'}_{0i} = \sum_{n'\neq 0} a_n e_{n'i} e_{n'i'}$$

$\vec{R}_8 = \left(\frac{-a}{\sqrt{2}}, \frac{a}{\sqrt{2}}\right) = (-a, a)$; $|R_8| = \sqrt{2}a$



→ force constant G

→ force constant K

● → cell n=0

$$\Phi^{11}_{01} = \Phi^{21}_{01} = \Phi^{32}_{02} = \Phi^{42}_{02} = -K$$

Longitudinal

$\vec{e} \parallel \vec{q}$

Transversal

$\vec{e} \perp \vec{q}$

$$\left\{\begin{array}{l} \Phi^{5i'}_{0i} = \Phi^{6i'}_{0i} = -\frac{G}{2} \quad (i, i' = 1, 2) \\ \Phi^{7i}_{0i} = \Phi^{8i}_{0i} = -\frac{G}{2} \quad (i = 1, 2) \\ \Phi^{7j}_{0i} = \Phi^{8j}_{0i} = +G/2 \quad (i \neq j = 1, 2) \\ \Phi^{01}_{01} = \Phi^{02}_{02} = 2(K + G) \end{array}\right.$$

$$\vec{e}_1 = (1, 0) \quad \vec{e}_5 = \left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}\right)$$

$$\vec{e}_2 = (-1, 0) \quad \vec{e}_6 = \left(-\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}\right)$$

$$\vec{e}_3 (0, 1) \quad \vec{e}_7 = \left(\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}\right)$$

$$\vec{e}_4 = (0, -1) \quad \vec{e}_8 = \left(-1/\sqrt{2}, 1/\sqrt{2}\right)$$

$$D^{\alpha' i'}_{\alpha i} = D^{i'}_{i} \quad (1 \text{ atom in the basis})$$

2×2 matrix. $\quad \vec{q} \to (q_x, q_y) \quad \vec{R}_n = a \vec{e}_n$ (a: lattice constant)

$$D^1_1(q) = \underbrace{-K e^{i q_x a}}_{n'=1} \underbrace{- K e^{-i q_x a}}_{n'=2} \underbrace{- \frac{G}{2} e^{ia(q_x + q_y)}}_{n=5}$$

$$\underbrace{- \frac{G}{2} e^{ia(-q_x - q_y)}}_{n=6} \underbrace{- \frac{G}{2} e^{ia(q_x - q_y)}}_{n=7} \underbrace{- \frac{G}{2} e^{ia(q_y - q_x)}}_{n=8} \underbrace{+ 2(K + G)}_{n=0}$$

$$= 2K(1 - \cos q_x a) + 2G(1 - \cos q_x a \cos q_y a)$$

$$D^2_2(q) = 2K(1 - \cos q_y a) + 2G(1 - \cos(q_y a) \cos(q_x a))$$

$$D_2^1(q) = \phi_{02}^{51} e^{i\vec{q}\vec{e}_5} + \phi_{02}^{81} e^{i\vec{q}\vec{e}_8} + \phi_{02}^{71} e^{i\vec{q}\vec{e}_7} + \phi_{02}^{61} e^{i\vec{q}\vec{e}_6}$$

$$-\frac{G}{2} e^{iq_x a} e^{iq_y a} \qquad +\frac{G}{2} e^{-iq_x a} e^{iq_y a}$$

$$+\frac{G}{2} e^{iq_x a} e^{-iq_y a} - \frac{G}{2} e^{-iq_x a} e^{-iq_y a}$$

$$= \frac{G}{2}\left[e^{iq_x \frac{a}{\sqrt{2}}} \underbrace{\left(e^{-iq_y a} - e^{iq_y a} \right)}_{-2i\sin(q_y a)} + e^{-iq_x a} \underbrace{\left(e^{iq_y a} - e^{-iq_y a} \right)}_{2i\sin(q_y a)} \right]$$

$$= \frac{G}{2}\left(2i\sin\left(q_y a\right)\right)\left[\underbrace{e^{-iq_x a} - e^{iq_x a}}_{-2i\sin(q_x a)}\right] =$$

$$D_2^1 = \underbrace{+2G\sin(q_x a)}\cos(q_y a) = D_1^2$$

To find the dispersion curves:

$$\left|\begin{vmatrix} D^1_1 \cdot M - \omega^2 & D^1_2 \\ D^2_1 & M D^2_2 - \omega^2 \end{vmatrix}\right| = 0$$

$$\omega^{\pm}(q)$$

Phonons → From classical To quantum;

(in Dirac Notation)

The harmonic energy of any collection of particles is:

$$H = \frac{1}{2}\langle \dot{U}|\hat{M}|\dot{U}\rangle + \frac{1}{2}\langle U|\hat{K}|U\rangle = \frac{1}{2}\langle \dot{S}|\dot{S}\rangle + \frac{1}{2}\langle S|\hat{D}|S\rangle$$

Force constant matrix

where $|U\rangle$ is the displacement and

$|S\rangle = \hat{M}^{1/2}|U\rangle$ is the mass weighted displacement.

$|S(x,y,z)\rangle$

- Now Diagonalize the dynamical matrix

$$\hat{D} = \hat{M}^{-1/2}\hat{K}\hat{M}^{-1/2}$$

$\vec{q} \rightarrow \vec{Q}_j$

$$\hat{D}|\vec{Q}j\rangle = \omega(\vec{Q}_j)^2|\vec{Q}_j\rangle$$

in This notation, $\vec{Q}$ is The wave vector and j is the branch index for The $3r$ branches, with $r = \#$atoms in The unit cell.

· These eigenstates are complete, and we can use them in the original hamiltonian (change of basis).

$$\sum_{\vec{Q}_j} |\vec{Q}_j\rangle\langle\vec{Q}_j| = \mathbb{I}$$

$$s(\vec{Q}_j) = \langle\vec{Q}_j|s\rangle \qquad \dot{s}(\vec{Q}_j) = \langle\vec{Q}_j|\dot{s}\rangle = \Pi(\vec{Q}_j)$$

The result is:

$$H = \frac{1}{2}\sum_{\vec{Q}_j}\left[\Pi^*(\vec{Q}_j)\,\Pi(\vec{Q}_j) + \omega^2(\vec{Q}_j)\,s^*(\vec{Q}_j)\,s(\vec{Q}_j)\right]$$

This has the form of uncoupled oscillators, but has the unfortunate aspect of introducing the dynamical variables $s(\vec{Q}_j)$ and $(\dot{s}(\vec{Q}_j))$, which are complex.

Since each variable has both real and imaginary parts, there are twice as many variables than we need.

There is no avoiding of complex variables, but the problem of apparent excess variables is solved by carefull analysis.

Note that $\hat{D}$ is a real, symmetric matrix, while the eigenstates $|\vec{Q}_j\rangle$ are necessarily complex because Bloch Th. If a complex eigenvector is found for a real matrix, it is guaranteed that it's complex conjugate vector is also an eigenstate (an has the same eigenvalue).

$|\vec{Q}_j\rangle^* = |-\vec{Q}_j\rangle$

The complex conjugate of $|\vec{Q}_j\rangle$ has wavevector $-\vec{Q}_j$.

This is a new eigenvector that we can label $|-\vec{Q}_j\rangle$.

This is equivalent to say that we choose a phase convention, that the phases of $|Q_j\rangle$ and $|-Q_j\rangle$ are forced to be such that these states are complex conjugates of each other.

The frequencies $\omega(\vec{Q}_j)$ are square roots of the eigenvalues, and therfore $\omega(\vec{Q}_j) = \omega(-\vec{Q}_j)$.

It also follows that $s(-\vec{Q}_j) = \langle -Q_j|s\rangle = \langle Q_j|s\rangle^* = s^*(\vec{Q}_j)$

This shows that there are only half as many independent dynamical variables as appeared at first sight.

Classical Treatment

So far, the algebra did not depend on any distinction between classical and quantum mechanics.
In the classical treatment, the primitive variables:

$$s(\vec{\ell}\alpha) = M_\alpha^{1/2} u(\vec{\ell}_\alpha) = \langle \vec{\ell}\alpha | s \rangle$$ are real numbers,

cell index

whereas the new variables $s(\vec{Q}_j)$ are complex.

The notation is that $s(\vec{\ell}\alpha)$ is the mass weighted displacement $u(\vec{\ell}\alpha)$ of the atom whose cell is denoted by $\vec{\ell}$. The additional $3r$ choices (r atoms in the cell and 3 cartesian directions) are all summarized by the index α.

The general solution of Newton's law for the primitive variables is:

$$u(\vec{\ell}\alpha, t) = M_\alpha^{-1/2} s(\vec{\ell}\alpha, t) = M_\alpha^{-1/2} \langle \vec{\ell}\alpha | s(t) \rangle =$$

$$= \sum_{Q_j} M_\alpha^{-1/2} \langle \vec{\ell}\alpha | \vec{Q}_j \rangle \langle \vec{Q}_j | s(t) \rangle$$

$$v(\vec{l}\alpha, t) = \mathrm{Re} \sum_{\vec{Q}_j} M_\alpha^{-1/2} \langle \vec{l}\alpha | \vec{Q}_j \rangle A(\vec{Q}_j) e^{i\phi(\vec{Q}_j)} e^{-i\omega(\vec{Q}_j)t}$$

where the amplitude $s(\vec{Q}_j, t) = \langle \vec{Q}_j | s(t) \rangle$ of the $\vec{Q}_j$ normal mode has been written as a positive amplitude $A(\vec{Q}_j)$ times a time dependent phase factor $e^{i\phi(Q_j) - i\omega(Q_j)t}$

The eigenvectors $|\vec{Q}_j\rangle$ of the dynamical matrix have the spatial representation: $\langle l\alpha | \vec{Q}_j \rangle = \varepsilon_\alpha(\vec{Q}_j) e^{i\vec{Q}\vec{l}} \cdot \frac{1}{\sqrt{N}}$

where $\varepsilon_\alpha(\vec{Q}_j)$ is called the "polarization vector".

It is normalized by the equation $\sum_\alpha \varepsilon_\alpha(\vec{Q}_j)^* \varepsilon_\alpha(\vec{Q}_{j'})$

$$= \delta(\vec{Q}, \vec{Q}')\delta(j, j')$$

It cannot in general be forced to be real, but it is forced to obey the relation $\varepsilon_\alpha(\vec{Q}_j)^* = \varepsilon_\alpha(-\vec{Q}_j)$

It can be written as a real vector times a phase factor

$$\varepsilon_\alpha(\vec{Q}_j) = \hat{\varepsilon}_\alpha(\vec{Q}_j) \exp[i\gamma_\alpha(\vec{Q}_j)]$$

With this, we can write the general solution of Newton's Law as

$$u(\vec{l}\alpha, t) = \left(\frac{1}{M_\alpha N}\right)^{1/2} \sum_{\vec{Q}_j} A(\vec{Q}_j)\,\hat{\varepsilon}_\alpha(\vec{Q}_j)\,\cdot$$

$$\cdot \cos\left[\vec{Q}\cdot\vec{l} + \gamma_\alpha(\vec{Q}_j) - \omega(\vec{Q}_j)t + \phi(\vec{Q}_j)\right]$$

. Let's say we want to calculate an average quantity like $\langle u(\vec{l}\alpha, t)\,u(\vec{l}'\alpha', t')\rangle$ (correlation function).

In thermal equilibrium the amplitudes $A(\vec{Q}_j)$ are gaussian random numbers with probability $P(A(\vec{Q}_j)) \propto \exp\left[-\frac{\omega(\vec{Q}_j)^2 A(\vec{Q}_j)^2}{4k_B T}\right]$ while the phases $\phi(\vec{Q}_j)$ are randomly distributed between $0 - 2\pi$.

Some Trigonometrical relations that are needed:

$$\cos(x)\cos(y) = \frac{1}{2}\left[\cos(x+y) + \cos(x-y)\right]$$

$\langle \cos(x+\phi)\rangle = 0$ if ϕ is random

Then: $\left\langle \cos[X+\phi(\vec{Q}_j)] \cos(Y+\phi(\vec{Q}',j')) \right\rangle =$

$$= \frac{1}{2}\cos(X-Y)\cdot \delta(\vec{Q},\vec{Q}')\,\delta(j,j')$$

$$\left\langle u(\vec{l}\alpha,t)\, u(\vec{l}'\alpha',t') \right\rangle =$$

$$\frac{1}{N}\sum_{\vec{Q}_j} \frac{k_B T}{M_\alpha \omega(\vec{Q}_j)^2}\, \hat{\varepsilon}_\alpha(\vec{Q}_j)^2 \cos\left[\vec{Q}\cdot(\vec{l}-\vec{l}') - \omega(\vec{Q}_j)(t-t')\right]\delta_{\alpha\alpha'}$$

For example the Debye-Waller factor (see neutron scattering cross section later) is

$$\left\langle u(\vec{l}\alpha,t)^2 \right\rangle = \frac{1}{N}\sum_{\vec{Q}_j} \frac{k_B T}{M_\alpha \omega(\vec{Q}_j)}\, \hat{\varepsilon}_\alpha^2(Q_j)$$

3rN terms in the sum, N cancels 1/N and 3r balances the squared ε-vector

Quantum Treatment

· Start from the separated (diagonalized) hamiltonian

$$H = \frac{1}{2} \sum_{\vec{Q}_j} \left[\Pi(-\vec{Q}_j) \Pi(\vec{Q}_j) + \omega(\vec{Q}_j)^2 S(-\vec{Q}_j) S(\vec{Q}_j) \right]$$

→ Let's introduce the new variables (second quantization)

commutation relations

$$** \; a(\vec{Q}_j) = \frac{1}{\sqrt{2\hbar\omega(\vec{Q}_j)}} \left[\Pi(-\vec{Q}_j) - i\omega(\vec{Q}_j) S(\vec{Q}_j) \right]$$

$$** \; a^+(\vec{Q}_j) = \frac{1}{\sqrt{2\hbar\omega(\vec{Q}_j)}} \left[\Pi(\vec{Q}_j) + i\omega(\vec{Q}_j) S(-\vec{Q}_j) \right]$$

In terms of these variables, the energy:

$$H = \frac{1}{2} \sum_{\vec{Q}_j} \hbar\omega(\vec{Q}_j) \left[a(\vec{Q}_j) a^+(\vec{Q}_j) + a^+(-\vec{Q}_j) a(-\vec{Q}_j) \right]$$

$$\left[a(\vec{Q}_j), a^+(\vec{Q}_j) \right] = \frac{1}{2\hbar\omega(\vec{Q}_j)} \left[\Pi(-\vec{Q}_j) - i\omega(\vec{Q}_j) S(\vec{Q}_j), \Pi(\vec{Q}_j) + i\omega(\vec{Q}_j) S(-\vec{Q}_j) \right] =$$

$$= \frac{i}{\hbar} \left[\Pi(\vec{Q}_j), S(Q_j) \right] = 1 \quad *$$

* This is because $s(\vec{Q}_j) = \langle \vec{Q}_j | s \rangle$
$\Pi(\vec{Q}_j) = \langle \vec{Q}_j | \dot{s} \rangle$ are unitary Transformations of The variables
$s(\vec{\ell}\alpha) = \langle \vec{\ell}\alpha | s \rangle$
$\dot{s}(\vec{\ell}\alpha) = \langle \vec{\ell}\alpha | \dot{s} \rangle$

and The usual quantum mecanical commutations relations

$$[\vec{p}(\vec{\ell}\alpha), s(\vec{\ell}'\alpha')] = \left(\frac{\hbar}{i}\right)\delta(\ell,\ell')\delta(\alpha,\alpha')$$

So in This new variables the Hamiltonian.

$$H = \sum_{\vec{Q}_j} \hbar\omega(\vec{Q}_j)\left[a^{\dagger}(\vec{Q}_j)\, a(\vec{Q}_j) + \frac{1}{2}\right]$$

Statistical averages are easily found by using:

$$\langle a^{\dagger}(\vec{Q}_j)\, a(\vec{Q}'_{j'})\rangle = \left[\frac{1}{e^{\frac{\hbar\omega(\vec{Q}_j)}{k_B T}} - 1}\right]\delta(\vec{Q},\vec{Q}')\,\delta(j,j')$$

For example To find The Debye-Waller factor The first step is To invert eq. **

$$s(\vec{Q}_j) = i\sqrt{\frac{\hbar}{2\omega(\vec{Q}_j)}}\left[a(\vec{Q}_j) - a^{\dagger}(-\vec{Q}_j)\right]$$

Then using:

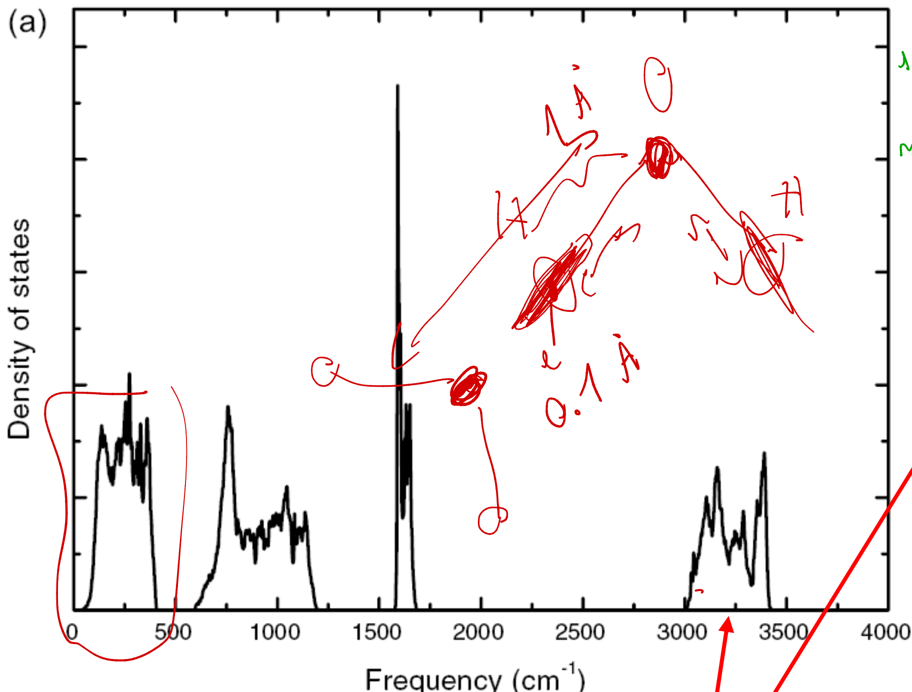
$$u(\vec{l}\alpha) = M_\alpha^{-1/2} s(\vec{l}\alpha) = M_\alpha^{-1/2} \langle \vec{l}\alpha | s \rangle = \sum_{\vec{Q}_j} M_\alpha^{-1/2} \langle \vec{l}\alpha | \vec{Q}_j \rangle * s(\vec{Q}_j)$$

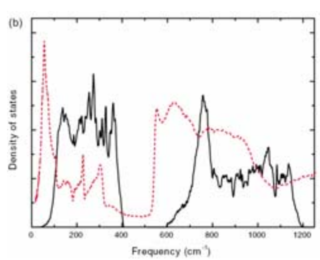
$$\langle u(\vec{l}\alpha)^2 \rangle = \frac{1}{N} \sum_{\vec{Q}_j} \frac{\hbar}{M_\alpha \omega(\vec{Q}_j)} \hat{\varepsilon}_\alpha(\vec{Q}_j)^2 \left[n(\vec{Q}_j) + \frac{1}{2} \right]$$

with $n(\vec{Q}_j)$ = ~~Bose~~-Einstein distribution function $\dfrac{1}{e^{\frac{\hbar\omega(\vec{Q}_j)}{k_B T}} - 1}$

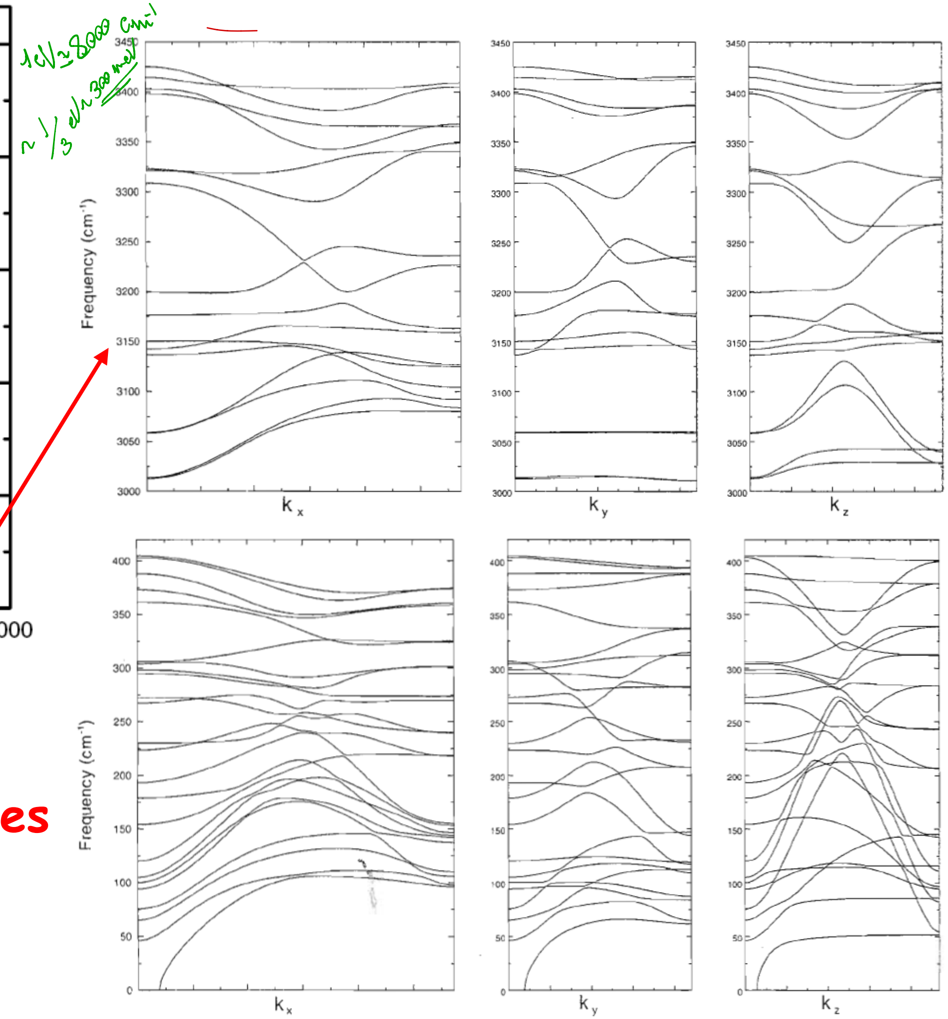
A. S. Cote, I. Morrison, X. Cui X, S. Jenkins, and D. K. Ross,
Ab-initio density-functional lattice-dynamics studies of ice
CAN. J. PHY. 81, 115 (2003).

8 molecules/cell ➔ 72 branches





"OH stretch" modes

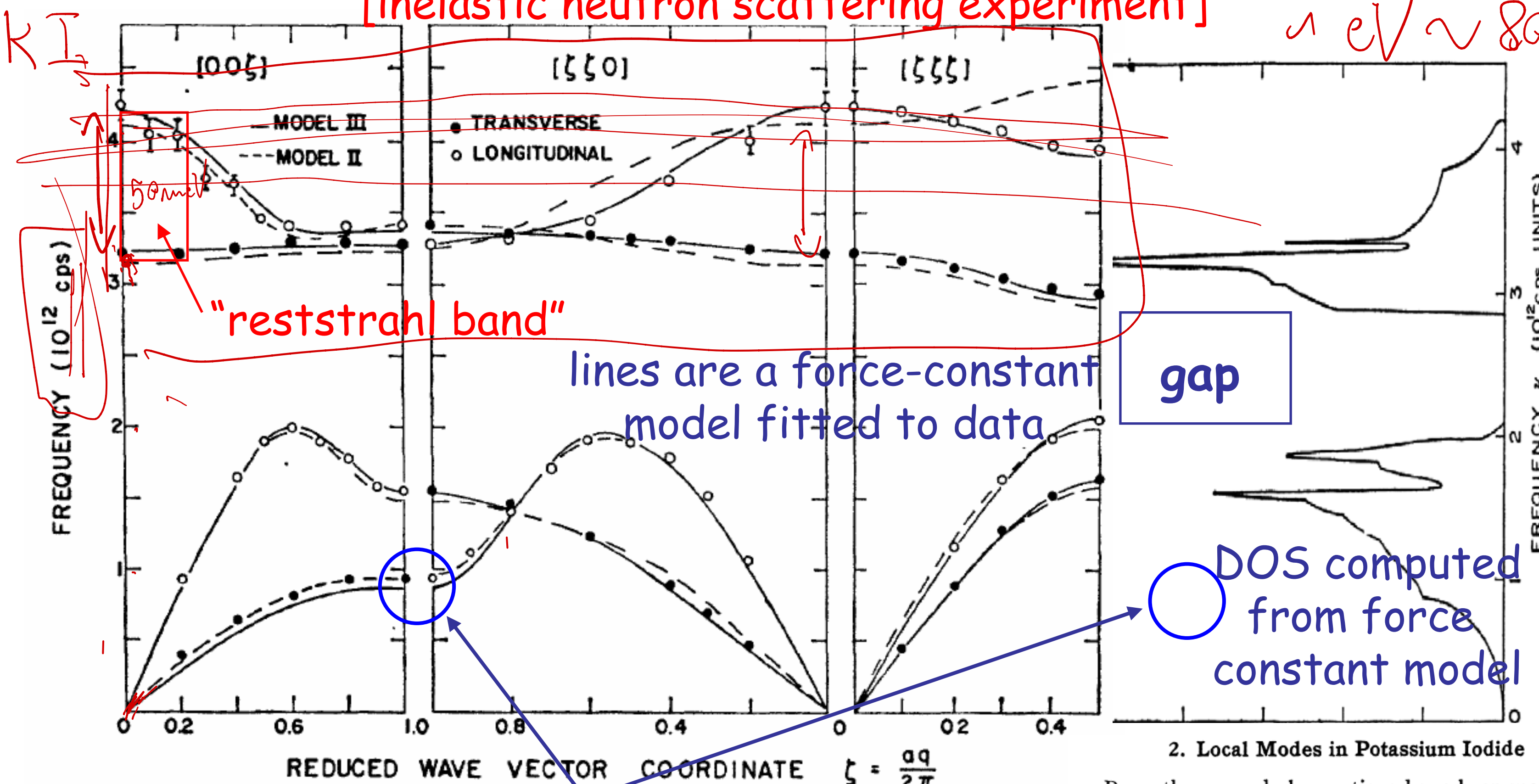


G. Dolling, R. A. Cowley, C. Schittenhelm, and I. M. Thorson, *Normal Vibrations of Potassium Iodide*, Phys. Rev. **147**, 577 (1966)

[inelastic neutron scattering experiment]

KI

1 eV ~ 8000 cm^{-1}



A nice 3-d saddle point van Hove singularity

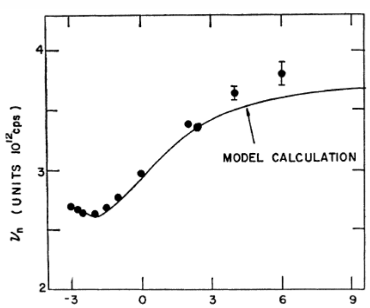


FIG. 4. Equivalent "Debye" frequencies computed from the moments of the distribution function (Fig. 2) and compared with values (filled circles) derived from heat-capacity data.[24]

Fcc (Rock salt).

1 GeV ~ 0.4 fm^{-1}

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.