(IV) Mechanical and dynamical properties

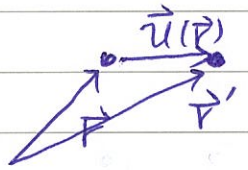
Elasticity & sound wave

In real crystals, positions of atoms are not fixed, and the crystals are deformed.

The simplest description is the phenomenological theory that describes deformation in the continuum limit and is called theory of elasticity.

In this theory, one ignores the microscopic atomic structure of a solid but keeps the symmetry.

To describe the deformation, one introduces the displacement vector $\vec{u}(\vec{r})$ so that



$$\vec{u}(\vec{r}) = \vec{r}' - \vec{r}$$

$\vec{r}'$ = position of atoms after deformation

$\vec{r}$ = " " before "

To describe the solid, one must have the following requirement (essentially, a potential energy U)

(i) $\vec{u} = 0$, the free energy is a minimum.

(ii) $\vec{u}(\vec{r}) \to \vec{u}(\vec{r}) + \vec{a}$ for all $\vec{r}$, it represents the global translation. F is not changed.

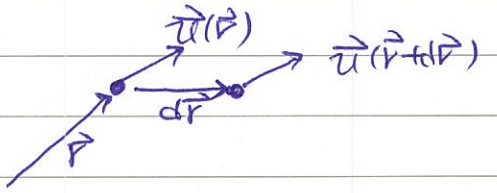
(iii) Uniform rotation of the whole solid

U is invariant.

(iii) requires that only derivatives of $\vec{u}$ matter.

For neighbouring atoms at $\vec{r}$, $\vec{r}+d\vec{r}$, one has

$\vec{u}(\vec{r})$ & $\vec{u}(\vec{r}+d\vec{r})$ $\Rightarrow$ the deformation difference is



$$\therefore d\vec{u}(\vec{r}) = \vec{u}(\vec{r}+d\vec{r}) - \vec{u}(\vec{r})$$

$$= \sum_k \frac{\partial \vec{u}(\vec{r})}{\partial x_k} dx_k$$

i.e. $$du_\alpha = \sum_k \frac{\partial u_\alpha}{\partial x_k} dx_k$$

Hence $\frac{\partial u_\alpha}{\partial x_k}$ seems to be the right quantity to describe the deformation.

Now, $$\frac{\partial u_\alpha}{\partial x_\beta} = \underbrace{\frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}\right)}_{e_{\alpha\beta}} + \underbrace{\frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x_\beta} - \frac{\partial u_\beta}{\partial x_\alpha}\right)}_{\omega_{\alpha\beta}}$$

$e_{\alpha\beta} = e_{\beta\alpha}$ Symmetric

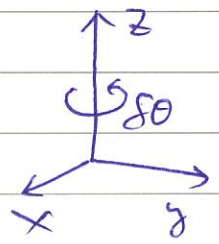
$\omega_{\alpha\beta} = -\omega_{\beta\alpha}$ antisymmetric.

Under rotatim of the whole solid, $e_{\alpha\beta} = 0$

$\omega_{\alpha\beta} \neq 0$, therefore, the gratity that describes the deformation is the strain tensor

$$e_{\alpha\beta} \equiv \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}\right)$$

example:



$$\vec{u} = \delta\vec{r} = \delta\vec{\theta}\times\vec{r} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ 0 & 0 & \delta\theta \\ x & y & z \end{vmatrix}$$

$$= (-y\delta\theta,\ x\delta\theta,\ 0)$$

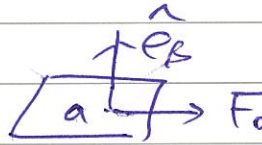
$$u_x = -y\delta\theta,\quad u_y = x\delta\theta,\quad u_z = 0 \quad \therefore \frac{\partial u_x}{\partial y} = -\delta\theta,\ \frac{\partial u_y}{\partial x} = \delta\theta$$

$$\frac{1}{2}\left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}\right) = 0 \quad \text{but} \quad \frac{1}{2}\left(\frac{\partial u_x}{\partial y} - \frac{\partial u_y}{\partial x}\right) = -\delta\theta \neq 0.$$

Stress tensor

Whenever there is strain, it means that solids are not in static equilibrium. There must be unbalanced force which either accelerate atoms or is provided by external force. This is described by the stress tensor $\sigma_{\alpha\beta}$:

Consider a small area a with normal $\hat{e}_\beta$



the force acting on this area is $\vec{F}$

then $\sigma_{\alpha\beta} = \lim_{a\to 0} \frac{F_\alpha}{a}$

Generalized Hook's law

For small $e_{\alpha\beta}$, one expects a generalized Hook's relation holds:

$$\sigma_{ik} = \sum_{em} C_{ikem}\, e_{em} \quad \text{---} \quad (1)$$

(Note that some books adopt the notation λ_{ikem} instead!)

Here C_{ikem} are "generalized spring constants".

This generalized Hook's law implies

$$U = U_0 + \int dF = \sum_{\alpha\beta\gamma\delta} \frac{1}{2} e_{\alpha\beta} C_{\alpha\beta\gamma\delta} e_{\gamma\delta} \quad \text{--} \quad (2)$$

Eq. (1) can be then written as $\sigma_{ik} = \frac{\partial F}{\partial e_{ik}}$ --- (3)

Note that in old notations, (1) is written as

$$\sigma_{xx} = C_{11} e_{xx} + C_{12} e_{yy} + C_{13} e_{zz} + C_{14} e_{yz} + C_{15} e_{zx} + C_{16} e_{xy}$$

$$\sigma_{yy} = C_{21} e_{xx} + C_{22} e_{yy} + C_{23} \,''\, + C_{24} \,''\, + C_{25} \,''\, + C_{26} \,''$$

$$\sigma_{zz} = C_{31} \,''\, + C_{32} \,''\, + C_{33} \,''\, + \cdots + C_{36} \,''$$

$$\sigma_{yz} = C_{41} \,''\, + C_{42} \,''\, + C_{43} \,''\, + \cdots + C_{46} \,''$$

$$\sigma_{zx} = C_{51} \,''\, + C_{52} \,''\, + \cdots + C_{56} \,''$$

$$\sigma_{xy} = C_{61} \,''\, + C_{62} \,''\, + C_{63} \,''\, + \cdots + C_{66} \,''$$

There appears to have 36 constants to be specified! --- (4)

Symmetries of $C_{\alpha\beta\gamma\delta}$

In reality, symmetries of crystals will reduce the total #.

in old notations $C_{ij} = C_{ji}$

First, from eq. ②, $C_{\alpha\beta\gamma\delta} = C_{\gamma\delta\alpha\beta}$ (symmetric)

$\because e_{\alpha\beta} = e_{\beta\alpha}$, $e_{\gamma\delta} = e_{\delta\gamma}$ $\therefore C_{\alpha\beta\gamma\delta} = C_{\beta\alpha\gamma\delta}$

$= C_{\alpha\beta\delta\gamma} = C_{\beta\alpha\delta\gamma}$

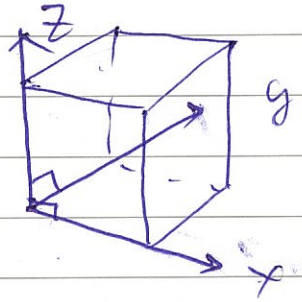
Hence in eq. ③, one doesn't need e_{xz} & σ_{xz} and using e_{zx} & σ_{zx} is sufficient.

$\therefore$ Total # of $C_{ij} = 6+5+4+3+2+1 = 21$

This is the situation no other symmetry further imposed by point group. (Triclinic)

Depending on the crystal system, one can further reduce # of C_{ij}.

For instance, for monoclinic crystals,



one requires reflection symmetry under $z \to -z$

$\because e_{zx} \to -e_{zx}$ $\therefore$ (with odd # of z) vanish

$e_{zy} \to -e_{zy}$

Hence, eq. ④ becomes

$$\sigma_{xx} = C_{11}\varepsilon_{xx} + C_{12}\varepsilon_{yy} + C_{13}\varepsilon_{zz} + 0 + 0 + C_{16}\varepsilon_{xy}$$

$$\sigma_{yy} = \cdots + C_{22}\varepsilon_{yy} + C_{23}\varepsilon_{zz} + 0 + 0 + C_{26}\varepsilon_{xy}$$

$$\sigma_{zz} = \cdots + C_{33}\varepsilon_{zz} + 0 + 0 + C_{36}\varepsilon_{xy}$$

$$\sigma_{yz} = \cdots + C_{44}\varepsilon_{yz} + C_{45}\varepsilon_{zx} + 0$$

$$\sigma_{zx} = \cdots + C_{45}\varepsilon_{zx} + 0$$

$$\sigma_{xy} = \cdots + C_{66}\varepsilon_{xy}$$

$\therefore$ # of $C = 13$.

For cubic systems, one requires reflection symmetries

for $x \to -x$, $y \to -y$, $z \to -z$

$\therefore$ C with odd # of x, y, or z vanish

Furthermore, $C_{xxxx} = C_{yyyy} = C_{zzzz}$

i.e. C must be symmetric under $x \to y \to z$.

One finds # of $C = 3$

$$C_{11} = C_{22} = C_{33}, \quad C_{12} = C_{13} = C_{21} = C_{23} = C_{31} = C_{32} = \lambda$$

$$C_{44} = C_{55} = C_{66} = \mu$$

$$U = U_0 + \int d\vec{r}\, \frac{1}{2}\left[C_{11}(\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2) + 2\lambda(\varepsilon_{xx}\varepsilon_{yy} + \varepsilon_{yy}\varepsilon_{zz} + \varepsilon_{zz}\varepsilon_{xx}) + 4\mu(\varepsilon_{xy}^2 + \varepsilon_{yz}^2 + \varepsilon_{zx}^2)\right]$$

Isotropic solids

Many solids are effectively isotropic. Such as glass, polycrystallines (ceramics) and etc.

In this case, one only needs 2 C's!

To see this, consider an infinitesimal rotation $R = \begin{pmatrix} 1 & \theta & 0 \\ -\theta & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ in xy plane.

$C_{\alpha\beta\gamma\delta}$ is a tensor. Hence

$$C'_{xyyy} = R_{x\alpha} R_{y\beta} R_{y\gamma} R_{y\delta} C_{\alpha\beta\gamma\delta}$$

$$= (\delta_{x\alpha} + \theta\delta_{y\alpha})(\delta_{y\beta} - \theta\delta_{x\beta})(\delta_{y\gamma} - \theta\delta_{x\gamma})(\delta_{y\delta} - \theta\delta_{x\delta}) C_{\alpha\beta\gamma\delta}$$

$$= C_{xyyy} + \theta[\underbrace{C_{yyyy}}_{=C_{22}} - \underbrace{C_{xxyy}}_{=C_{12}} - C_{xyxy} - C_{xyyx}] + O(\theta^2)$$

$\therefore$ C with odd # of x $= 0$ $\qquad$ $2C_{xyxy} = 2C_{44} = 2\mu$

$\therefore C'_{xyyy} = 0 = C_{xyyy}$

$\therefore C_{yyyy} = \lambda + 2\mu$

$C_{22} = C_{11}$

$$\therefore U = U_0 + \frac{1}{2}\int d\vec{r}\, \lambda \left(\sum_\alpha e_{\alpha\alpha}\right)^2 + 2\mu \sum_{\alpha\beta} (e_{\alpha\beta})^2$$

$\lambda = C_{xxyy}$, $\mu = C_{xyxy}$

are so-called Lamé coefficients.

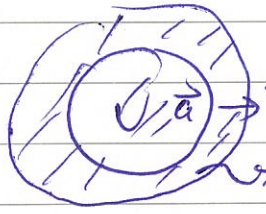
In this case, one finds

$$\sigma_{\alpha\beta} = \lambda \delta_{\alpha\beta} \sum_\ell e_{\ell\ell} + 2\mu e_{\alpha\beta} \quad \text{---} (1)$$

$$= \left(\lambda + \frac{2}{3}\mu\right) \delta_{\alpha\beta} \sum_\ell e_{\ell\ell} + 2\mu \underbrace{\left(e_{\alpha\beta} - \frac{1}{3}\delta_{\alpha\beta} \sum_\ell e_{\ell\ell}\right)}_{e'_{\alpha\beta}}$$

$\sum_\alpha e'_{\alpha\alpha} = 0$ $\therefore e'_{\alpha\beta}$ doesn't induce change of volume (see below)

$$\sum_\ell e_{\ell\ell} = \sum_\ell \frac{\partial u_\ell}{\partial x_\ell} = \vec{\nabla} \cdot \vec{u}$$



$$\delta V = \oint \vec{u} \cdot d\vec{\sigma} = \int \nabla \cdot \vec{u} \, dV = (\nabla \cdot \vec{u}) V \quad (V \text{ small})$$

$$\therefore \frac{\Delta V}{V} = \nabla \cdot \vec{u}$$

$\therefore \lambda + \frac{2}{3}\mu \equiv K =$ bulk modulus

$\mu =$ shear modulus

Equation of motion & sound waves

Given an area a with normal $\hat{n}$, the force f_α acting on this area from surrounding is

$$f_\alpha = \sum_\beta \sigma_{\alpha\beta} \hat{n}_\beta \times a$$

Hence, the total force of α component that acts on the volume (see below) is

$$\oint_S \vec{\sigma}_\alpha \cdot \hat{n}\, da$$

$$\vec{\sigma}_\alpha \equiv (\sigma_{\alpha 1}, \sigma_{\alpha 2}, \sigma_{\alpha 3})$$

$$\therefore \oint_S \vec{\sigma}_\alpha \cdot \hat{n}\, da = \int_V \nabla \cdot \vec{\sigma}_\alpha \, d^3\vec{r}$$

$$= \int_V \frac{\partial}{\partial x_\beta} \sigma_{\alpha\beta} \, d^3\vec{r}$$

If ρ = mass density of atoms, Newton's law implies

$$\int \rho \frac{\partial^2 u_\alpha}{\partial t^2} d^3\vec{r} = \int_V \frac{\partial \sigma_{\alpha\beta}}{\partial x_\beta} d^3\vec{r}$$

$$\therefore \rho \ddot{u}_\alpha(\vec{r}) = \frac{\partial \sigma_{\alpha\beta}}{\partial x_\beta} \quad \text{-- (6)}$$

By using eq. (5), one gets $\frac{\partial \sigma_{\alpha\beta}}{\partial x_\beta} = \lambda \frac{\partial}{\partial x_\alpha}(\nabla \cdot \vec{u})$

$$+ 2\mu \underbrace{\frac{\partial}{\partial x_\beta} e_{\alpha\beta}}.$$

$$\mu \frac{\partial}{\partial x_\beta}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}\right).$$

$$(6) \Rightarrow \rho \frac{\partial^2 \vec{u}}{\partial t^2} = (\lambda + \mu)\vec{\nabla}(\vec{\nabla}\cdot\vec{u}) + \mu \nabla^2 \vec{u} \quad \text{-- (7)}$$

By taking $\vec{\nabla}\cdot$ & $\vec{\nabla}\times$ on eq (1), we get

$$\rho \frac{\partial^2 \Delta}{\partial t^2} = (\lambda + 2\mu)\nabla^2 \Delta \qquad \Delta \equiv \nabla \cdot \vec{u}$$

$$\rho \frac{\partial^2 \vec{\omega}}{\partial t^2} = \mu \nabla^2 \vec{\omega} \qquad \omega \equiv \vec{\nabla} \times \vec{u}$$

These are wave equations that describe the sound waves in the continuum limit.

Clearly, if $\vec{u} = \vec{u}_0 e^{i(\vec{k}\cdot\vec{r} - \omega t)}$, one gets

$$\frac{\omega}{k} = c = \sqrt{\frac{\lambda + 2\mu}{\rho}} \quad \text{for } \Delta \ (\vec{k} \parallel \vec{u}_0)$$

longitudinal ⇓ one mode

$$= \sqrt{\frac{\mu}{\rho}} \quad \text{for } \vec{\omega} \ (\vec{k} \perp \vec{u}_0)$$

transverse : two modes

Sound waves in liquids & gases.

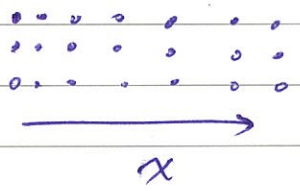
Sound waves can also propagate in liquids & gases. In that case, it appears as a density wave, and it is no longer valid to use the displacement vector $\vec{u}(\vec{r})$ to describe the sound waves!

This is the crucial difference between solid & liquids/gases.

To describe the propagation of density variation in liquids, we need:

(i) conservation of mass: $\frac{\partial \rho}{\partial t} + \frac{\partial \rho v}{\partial x} = 0$ ---(8)

($\nabla \cdot (\rho \vec{v})$ in general)



(ii) Newton's law $\rho \frac{\partial v}{\partial t} = -\frac{\partial p}{\partial x}$ p=Pressure ---(9)

(iii) Constitution relation $\rho = \rho(p)$

for density perturbation, $\rho = \rho_0 + \delta\rho$

$p = p_0 + \delta p$

$v = \delta v$

$\therefore \rho = \rho(p) = \rho(p_0) + \frac{\partial \rho}{\partial p}\delta p$

$\therefore \delta\rho = \frac{\partial \rho}{\partial p}\delta p \equiv \frac{1}{c^2}\delta p$ ---(10)

(8) & (9) to linear terms in $\delta\rho$, δp & δv

$$\rho_0 \frac{\partial \delta v}{\partial t} = -\frac{\partial \delta p}{\partial x}$$

$$\frac{\partial \delta\rho}{\partial t} + \rho_0 \frac{\partial \delta v}{\partial x} = 0$$

By taking $\frac{\partial}{\partial t} \Rightarrow c^2 \frac{\partial^2 \delta\rho}{\partial x^2} - \frac{\partial^2 \delta\rho}{\partial t^2} = 0$ Hence $\delta\rho$ satisfies a wave equation with $\omega = ck$, $c = \sqrt{\frac{\partial p}{\partial \rho}}$

Reasoning leads $\left(\frac{\partial p}{\partial \rho}\right) \rightarrow \left(\frac{\partial p}{\partial \rho}\right)_s$ (adiabatic)

Clearly, liquids & gases don't have shear modulus, i.e. "$\sigma_{\alpha\beta} = K \delta_{\alpha\beta} \sum_\varepsilon e_{\varepsilon\varepsilon}$", that is why there is only one speed for sound waves.

In fact, for liquids/gases, $\sigma_{\alpha\beta} = \Delta P \delta_{\alpha\beta}$

$\therefore \Delta P = K \underbrace{\sum_\varepsilon e_{\varepsilon\varepsilon}}_{\vec{\nabla}\cdot\vec{u}} = K \frac{\Delta V}{V}$, $K = V \frac{\Delta P}{\Delta V} = -\rho \frac{dP}{d\rho}$

$\therefore c = \sqrt{\frac{K}{\rho}}$

Effects of thermal fluctuations and "impossible" realization of 2D crystals

Once the lattice is not ideal & rigid, at finite temperatures, there will be fluctuations of positions for lattice points. This gives rise to non-vanishing heat capacity of lattice. We will discuss the heat capacity later. ↳ focus on effects on scatterings and

Cumulant expansion theorem:

In the presence of deformation, we need to evaluate $\frac{I}{NI_0} = \frac{1}{N} \left\langle \left| \sum_i e^{i\vec{q}\cdot(\vec{r}_i + \vec{u}(\vec{r}_i))} \right|^2 \right\rangle =$

$= \langle \sum_i e^{i\vec{q}\cdot\vec{R}_i} e^{i\vec{q}\cdot(\vec{u}(R_i)-\vec{u}(0))} \rangle$ Date 4-13

Hence one needs to evaluate $\langle e^{i\vec{q}(\vec{u}(R_i)-\vec{u}(0))} \rangle$.

In general, one needs to evaluate $\langle e^A \rangle$.

According to Quantum statistical mechanics, one has

$$\langle e^A \rangle = \frac{Tr\, e^{-\beta H} e^A}{Tr\, e^{-\beta H}} \equiv \frac{\sum_n \langle n| e^{-\beta H} e^A |n\rangle}{\sum_n \langle n| e^{-\beta H} |n\rangle}$$

$\beta = \frac{1}{K_B T}$

$|n\rangle$ = some complete set.

Classically, A is a function of $\vec{r}_i, \vec{p}_i$, $H = \sum_i \frac{p_i^2}{2m} + U(r_1, r_N)$

$$\langle e^A \rangle = \frac{\int d^3\vec{r}_1 \int d^3\vec{p}_1 \cdots \int d^3\vec{r}_N \int d^3\vec{p}_N\, e^{-\beta\left(\sum_i \frac{p_i^2}{2m_i} + U(r_1 \cdots r_N)\right)} e^A}{\int d^3\vec{r}_1 \cdots \int d^3\vec{p}_N\, e^{-\beta H}}$$

Obviously, by expansion of $e^{\alpha A}$, we get

$\langle e^{\alpha A} \rangle = \sum_{n=0}^{\infty} \frac{\alpha^n}{n!} \langle A^n \rangle$. Here α is a parameter introduced for convenience.

Therefore, one needs to evaluate $\langle A^n \rangle$.

In practice, we have experience in evaluating $\langle A^n \rangle$.

This can be done by using <u>generating functions</u>:

example: to evaluate $\int_{-\infty}^{\infty} x^2 e^{-x^2} dx$

we first consider $I(\alpha) = \int_{-\infty}^{\infty} e^{-x^2 + \alpha x^2} dx$

then $\int_{-\infty}^{\infty} x^2 e^{-x^2} dx = \left.\frac{d^2 I(\alpha)}{d\alpha}\right|_{\alpha=0}$

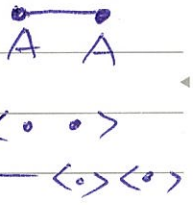
$\because I(\alpha) = \sqrt{\frac{\pi}{1-\alpha}} \quad \therefore \int_{-\infty}^{\infty} x^2 e^{-x^2} dx = \frac{\sqrt{\pi}}{2}$

Hence we introduce $\beta\bar{H} = \beta H + \alpha A$

$Z(\alpha) = \mathrm{Tr}\, e^{-\beta\bar{H}}$, $\langle A^n \rangle = \frac{\left.\frac{d^n Z}{d\alpha^n}\right|_{\alpha=0}}{Z(0)}$, $\langle e^{\alpha A} \rangle = \frac{Z(\alpha)}{Z(0)}$

On the other hand, $\left.\frac{d \ln Z}{d\alpha}\right|_{\alpha=0} = \left.\frac{1}{Z}\frac{dZ}{d\alpha}\right|_{\alpha=0} = \langle A \rangle$

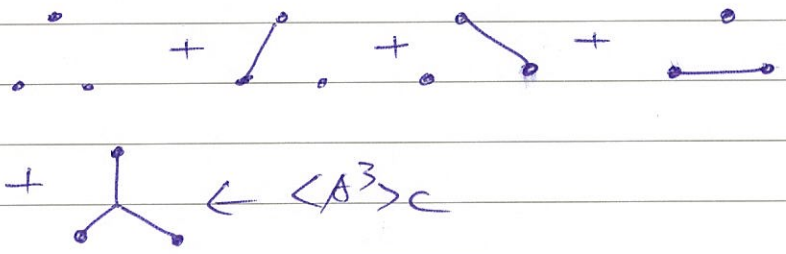
$$\left.\frac{d^2 \ln Z}{d\alpha^2}\right|_0 = \left.\frac{1}{Z}\frac{d^2 Z}{d\alpha^2} - \left(\frac{1}{Z}\frac{dZ}{d\alpha}\right)^2\right|_0 = \langle A^2 \rangle - \langle A \rangle^2 \equiv \langle A^2 \rangle_c$$



$$\left.\frac{d^3 \ln Z}{d\alpha^3}\right|_0 = \left.\frac{1}{Z}\frac{d^3 Z}{d\alpha^3} - \left(\frac{1}{Z}\frac{d^2 Z}{d\alpha^2}\right)\left(\frac{1}{Z}\frac{dZ}{d\alpha}\right) - 2\frac{1}{Z}\frac{d^2 Z}{d\alpha^2}\frac{1}{Z}\frac{dZ}{d\alpha} + \left(\frac{1}{Z}\frac{dZ}{d\alpha}\right)^2 \frac{1}{Z}\frac{dZ}{d\alpha}\right|_0$$

$$= \langle A^3 \rangle - 3\langle A^2 \rangle \langle A \rangle + \langle A \rangle^3 \equiv \langle A^3 \rangle_c$$

pictorial: $\langle A^3 \rangle =$



$\therefore$ generally, $\left.\frac{d^n \ln Z}{d\alpha^n}\right|_{\alpha=0} = \langle A^n \rangle_c$

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$$\therefore \langle e^{\alpha A} \rangle = \frac{Z(\alpha)}{Z(0)}$$

$$\therefore \ln \langle e^{\alpha A} \rangle = \ln Z(\alpha) - \ln Z(0)$$

$$= \sum_{n=1}^{\infty} \frac{\alpha^n}{n!} \frac{\partial^n \ln Z}{\partial \alpha^n} \Big|_{\alpha=0}$$

Taylor expansion

$$= \sum_{n=1}^{\infty} \frac{\alpha^n}{n!} \langle A^n \rangle_c$$

$$\therefore \langle e^{\alpha A} \rangle = e^{\sum_{n=1}^{\infty} \frac{\alpha^n}{n!} \langle A^n \rangle_c}$$

Debye - Waller factor (classical)

Therefore $$\frac{I}{N I_0} = \sum_i e^{i \vec{g} \cdot \vec{R}_i} \left\langle e^{i \vec{g} \cdot (\vec{u}(\vec{R}_i) - \vec{u}(0))} \right\rangle$$

$$= \sum_i e^{i \vec{g} \cdot \vec{R}_i} \; e^{i \langle \vec{g} \cdot (\vec{u}(\vec{R}_i) - \vec{u}(0)) \rangle - \frac{1}{2} \langle [\vec{g} \cdot (\vec{u}(\vec{R}_i) - \vec{u}(0))]^2 \rangle_c + \cdots}$$

$\because \langle \vec{u}(\vec{R}_i) \rangle = 0$ $\quad \langle [\vec{g} \cdot (\vec{u}(\vec{R}_i) - \vec{u}(0))]^2 \rangle_c$

$$= \langle [\vec{g} \cdot (\vec{u}(\vec{R}_i) - \vec{u}(0))]^2 \rangle - \cancel{\left(\langle \vec{g} \cdot (\vec{u}(\vec{R}_i) - \vec{u}(0)) \rangle \right)^2}$$

$$\therefore \frac{I}{N I_0} \simeq \sum_i e^{i \vec{g} \cdot \vec{R}_i} \; e^{-\frac{1}{2} \langle [\vec{g} \cdot (\vec{u}(\vec{R}_i) - \vec{u}(0))]^2 \rangle} \text{ to lower order in } u$$

L - (11)

this is known as Debye - Waller factor.

- Whose existence is due to fluctuations (either thermal or quantum, for quantum, care has to paid to non-commutability of $u_x, u_y \ldots$)

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Fluctuation of ρ_G & $\langle u^2 \rangle$

The order of a crystal is describe by

$$\langle n_G \rangle = \left\langle \sum_i e^{i\vec{G}\cdot(\vec{r}_i + \vec{u}(r_i))} \right\rangle$$

$$= \sum_i e^{i\vec{G}\cdot\vec{r}_i - \frac{1}{2}\langle (\vec{G}\cdot\vec{u}(r_i))^2 \rangle + \cdots}$$

For isotropic solids, one has $\langle (\vec{G}\cdot\vec{u})^2 \rangle = \langle G^2 (u_G)^2 \rangle = \frac{1}{d}\langle G^2 \vec{u}^2 \rangle$

$$\langle n_G \rangle = \sum_i e^{i\vec{G}\cdot\vec{r}_i - \frac{1}{2d}G^2\langle \vec{u}^2 \rangle + \cdots} \quad \leftarrow (12)$$

Therefore, the order $\langle \rho_G \rangle$ crucially depends on $\langle u^2 \rangle$. In early development of x-ray scattering, Sommerfeld et. al did n't believe that x-ray can exhibit atoms because they thought $\langle u^2 \rangle \sim a^2$ would destroy the signal.

From (12), obviously, this is not the case! $\langle u^2 \rangle$ appears in the exponential. If $\langle u^2 \rangle \sim a^2$

$\langle n_G \rangle \sim e^{-\frac{1}{2d}G^2a^2} \sum_i e^{i\vec{G}\vec{r}_i}$ is still a dela function peak!

Physically, for how large of $\langle u^2 \rangle$, $\langle n_G \rangle$ can be destroyed?

For this purpose, we need to calculate $\langle u^2 \rangle$.

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We first note that $U = \frac{1}{2}\int d\vec{r}\,\lambda\left(\sum_\alpha e_{\alpha\alpha}\right)^2 + 2\mu\sum_{\alpha\beta}(e_{\alpha\beta})^2$

$= \frac{1}{2}\int d\vec{r}\,\lambda(\vec{\nabla}\cdot\vec{u})^2 + \frac{1}{2}\mu\sum_{\alpha\beta}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}\right)^2$. Using

Fourier transformation, $u_\alpha(\vec{r}) = \sum_k u_\alpha(\vec{k})\, e^{i\vec{k}\cdot\vec{r}}$.

We can rewrite $(u_\alpha(k) = u_\alpha^*(k))$

$$\langle u^2\rangle = \left\langle \int \frac{d^3\vec{r}}{V} \sum_\alpha u_\alpha(r)\, u_\alpha(r)\right\rangle$$

↑ Volume

$$= \sum_{\alpha k}\langle u_\alpha(k)\, u_\alpha(-k)\rangle \quad \left(\int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}\, e^{i\vec{k}'\cdot\vec{r}} = V\delta_{k,-k'}\right)$$

$$= \sum_{\alpha,k}\langle |u_\alpha(k)|^2\rangle$$

$$\int d\vec{r}\,\lambda(\vec{\nabla}\cdot\vec{u})^2 = \sum_{k,k'}\int d\vec{r}\,\lambda\, i^2 k_\alpha u_\alpha(k) k'_\beta u_\beta(k') \times e^{i\vec{k}\cdot\vec{r}}\, e^{i\vec{k}'\cdot\vec{r}}$$

$$= \sum_k V\lambda\, k_\alpha u_\alpha(k)\, k_\beta u_\beta(-k)$$

Similarly, $\int \mu \sum_{\alpha\beta}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}\right)^2$

$$= V\mu\sum_{k,\alpha} 2k^2 u_\alpha(k) u_\alpha(-k) + 2 k_\alpha k_\beta u_\alpha(k) u_\beta(-k)$$

$$\therefore U = \frac{V}{2}\sum_{k\alpha\beta} u_\alpha(k)\,\Phi_{\alpha\beta}(k)\, u_\beta(-k)$$

$$\Phi_{\alpha\beta}(k) = \frac{\lambda}{2}k_\alpha k_\beta + \frac{1}{2}\mu k^2\delta_{\alpha\beta} + \frac{1}{2}\mu k_\alpha k_\beta$$

$$= \frac{1}{2}(\lambda+\mu)k_\alpha k_\beta + \frac{1}{2}\mu k^2\delta_{\alpha\beta}$$

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Therefore, ($k, -k$ included $\downarrow$ $1/2 \to 1$)

$$\langle \vec{u}^2 \rangle = \sum_{\alpha,k} \frac{\prod_{\beta q} \int du_{q\beta} du^*_{\beta q}\; u_\alpha(k)\, u^*_\alpha(k)\; e^{-V\beta \sum_{q\alpha\beta} u_\alpha(q)\, \Phi_{\alpha\beta}(q)\, u^*_\beta(q)}}{\prod_{\beta q} \int du_{\beta q} du^*_{\beta q}\; e^{-1/\beta \sum_{q\alpha\beta} u_\alpha(q)\, \Phi_{\alpha\beta}(q)\, u^*_\beta(q)}}$$

(Note that integrals over momentum are independent from that of integrals over $\vec{u}$. They can be factored out & dropped!)

Furthermore, since integrals over u_q for different qs are independent from each other, only integrals over $u_{\beta k}$ remains. ($k, -k$ both included $\downarrow$)

$$\langle u^2 \rangle = \sum_{\alpha,k} \frac{\prod_\beta \int du_{\beta k} du^*_{\beta k}\; u_\alpha(k)\, u^*_\alpha(k)\; e^{-\beta V \sum_{\alpha\beta} u_\alpha(k)\, \Phi_{\alpha\beta}(k)\, u^*_\beta(k)}}{\prod_\beta \int du_{\beta k} du^*_{\beta k}\; e^{-\beta V \sum_{\alpha\beta} u_\alpha(k)\, \Phi_{\alpha\beta}(k)\, u^*_\beta(k)}}$$

To evaluate the above, one needs to know the Gaussian integrals: (Homework)

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

$$\int dz \int dz^* \; e^{-A|z|^2} = \frac{\pi}{A^2}$$

$$\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \left(-\frac{d}{d\alpha}\right) \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \frac{\sqrt{\pi}}{2} \frac{1}{\alpha^{3/2}}$$

$$\frac{\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx}{\int_{-\infty}^{\infty} e^{-\alpha x^2} dx} = \frac{1}{2\alpha} \quad \cdot\cdot \quad \frac{\iint dz\, dz^*\, |z|^2\, e^{-A|z|^2}}{\iint dz\, dz^*\, e^{-A|z|^2}} = \frac{1}{A}$$

$$\frac{\prod_i \iint dz_i dz_i^* \; e^{\sum A_{ij} z_i^* z_j} \cdot z_\alpha z_\beta^*}{\prod_i \iint dz_i dz_i^* \; e^{\sum_{ij} A_{ij} z_i^* z_j}} = (A^{-1})_{\alpha\beta}$$

Hence

$$\langle u^2 \rangle = \frac{1}{\beta V} \sum_{\alpha, K} (\Phi^{-1})_\alpha (K)$$

$$= \frac{2K_BT}{V} \sum_K \frac{1}{\mu K^2} + \frac{1}{(\lambda+2\mu) K^2}$$

($\frac{1}{\mu} \to \frac{1}{c_{00}}$, $\frac{1}{\lambda+2\mu} \to \frac{1}{c_{11}}$)

$$= 2K_BT \left(\frac{1}{\mu} + \frac{1}{\lambda+2\mu}\right) \int \frac{d^dK}{(2\pi)^d} \frac{1}{K^2} \quad \cdots (13)$$

($\sim 1/\epsilon^2$)

$$\left(\frac{1}{V}\sum_K = \int \frac{d^dK}{(2\pi)^d} \qquad d = \text{dimension}\right)$$

Mermin–Wagner theorem

Eq. (13) has an important implication:

at $d=2$ or below $\therefore \int \frac{d^2K}{(2\pi)^2} \frac{1}{K^2} = \int_0^{\frac{2\pi}{a}} \frac{2\pi K dK}{(2\pi)^2 K^2} = \infty$

$\langle u^2 \rangle = \infty$?!

It means $\langle n_G \rangle = 0$. Physically, it means that fluctuations are so large that atoms can become itinerary. The crystal orders are thus destroyed. Mermin & Wagner rigorously (at finite temperature!).

Showed that this happens for low dimensions & it's known as Mermin-Wagner theorem (order can't survive in low enough dimension).

The critical dimension when it happens is termed as the lower critical dimension d_c.

For crystals, $d_c = 2$

The physics why it happens for low dimensions is precisely because in lower dimension, # of neighbourings becomes small so that binding & the ability of locking into the order state becomes progressively weak as d goes down!

Quasi long-range order

Even though $\langle u^2 \rangle = \infty$, the eventual state for 2D crystal is not a liquid. Instead, we often term it as 2D solid.

In this case, one still sees quasi-peaks in X-ray scattering expt.

To see this, we start from the scattering intensity

$$\frac{I_G}{I_0} = \langle n_G n_{-G} \rangle \qquad n_G = \sum_i e^{i\vec{G}\cdot(\vec{r}_i+\vec{u}_i)}$$

$$\vec{u}_i \equiv \vec{u}(\vec{r}_i)$$

$$= \sum_{ij} e^{i\vec{G}\cdot(\vec{r}_i-\vec{r}_j)} \langle e^{i\vec{G}\cdot(\vec{u}_i-\vec{u}_j)} \rangle$$

$$= \sum_{ij} e^{i\vec{G}\cdot(\vec{r}_i-\vec{r}_j)} \; e^{\frac{1}{2}\langle(\vec{G}\cdot(\vec{u}_i-\vec{u}_j))^2\rangle}$$

For isotropic solids, take $\vec{G} = G\hat{x}$ $\quad \langle (u_{ix}-u_{jx})^2 \rangle = \frac{1}{2}\langle(\vec{u}_i-\vec{u}_j)^2\rangle$

$$\therefore \frac{I_G}{I_0} = \sum_{ij} e^{i\vec{G}\cdot(\vec{r}_i-\vec{r}_j)} \; \underbrace{e^{-\frac{1}{4}G^2\langle(\vec{u}_i-\vec{u}_j)^2\rangle}}$$

Debye-Waller factor.

Now $\frac{1}{2}\langle(\vec{u}_i-\vec{u}_j)^2\rangle = \frac{1}{2}\sum_{k,k'} \langle \vec{u}_k (e^{i\vec{k}\cdot\vec{r}_i} - e^{i\vec{k}\cdot\vec{r}_j}) \cdot \vec{u}_{k'} (e^{i\vec{k}'\cdot\vec{r}_i} - e^{i\vec{k}'\cdot\vec{r}_j}) \rangle$

$$= \frac{1}{2}\sum_k \langle \vec{u}_k \cdot \vec{u}_{-k} \rangle (e^{i\vec{k}\cdot\vec{r}_i} - e^{i\vec{k}\cdot\vec{r}_j})(e^{-i\vec{k}\cdot\vec{r}_i} - e^{-i\vec{k}\cdot\vec{r}_j})$$

↑ $k=-k'$

$$= \sum_k \langle \vec{u}_k \cdot \vec{u}_{-k} \rangle (1 - \cos\vec{k}\cdot(\vec{r}_i-\vec{r}_j))$$

$$= \int \frac{d^2k}{(2\pi)^2} \frac{k_B T}{c^2 k^2} (1 - e^{i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)}) \rightarrow \frac{k_B T}{2\pi c^2} \ln\left|\frac{\vec{r}_i-\vec{r}_j}{a}\right|$$

↑ (13)

$\sin\vec{k}\cdot(\vec{r}_i-\vec{r}_j)$ is odd in $\vec{k}$

as $|\vec{r}_i-\vec{r}_j| \to \infty$

a = lattice constant

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$$\therefore \frac{I_G}{I_0} \simeq \sum_{ij} e^{i\vec{G}\cdot(\vec{r}_i-\vec{r}_j)} e^{-\frac{1}{2}G^2 \frac{k_B T}{2\pi C^2} \ln \frac{|\vec{r}_i-\vec{r}_j|}{a}}$$

$$= \sum_{ij} \frac{1}{\left(\frac{|r_i-r_j|}{a}\right)^{\eta_G}} e^{i\vec{G}(\vec{r}_i-\vec{r}_j)}$$

$$\eta_G = k_B T \frac{G^2}{4\pi C^2} = \frac{k_B T G^2}{4\pi} \left(\frac{1}{\mu} + \frac{1}{\lambda+2\mu}\right)$$

$\therefore$ For $q \sim G$,

$$\frac{I_q}{I_0} \simeq \sum_{ij} e^{i\vec{q}\cdot(\vec{r}_i-\vec{r}_j)} \frac{1}{\left(\frac{|\vec{r}_i-\vec{r}_j|}{a}\right)^{\eta_G}}$$

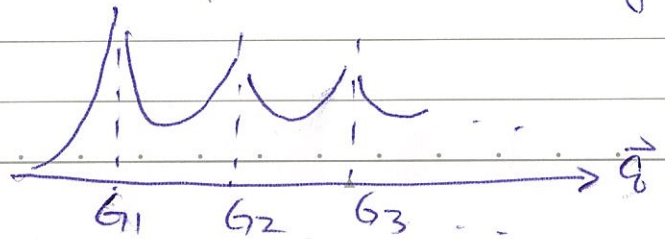
$$= \sum_{ij} e^{i(\vec{q}-\vec{G})\cdot(\vec{r}_i-\vec{r}_j)} \frac{1}{\left|\frac{\vec{r}_i-\vec{r}_j}{a}\right|^{\eta_G}} \underbrace{e^{i\vec{G}\cdot(\vec{r}_i-\vec{r}_j)}}_{\substack{\| \\ 2\pi N \\ \| \\ 1}}$$

$$\sim \int d^2r \; e^{i(\vec{q}-\vec{G})\cdot\vec{r}} \frac{1}{r^{\eta_G}}$$

rescale $\vec{r} \to |\vec{q}-\vec{G}|\vec{r} = \vec{r}'$

$$\frac{I_q}{I_0} \sim \frac{1}{|\vec{q}-\vec{G}|^{2-\eta_G}}$$

Therefore, instead of being delta-type divergent at G, it becomes power-law divergent!



We term this as quasi long-range order!
(crystal)

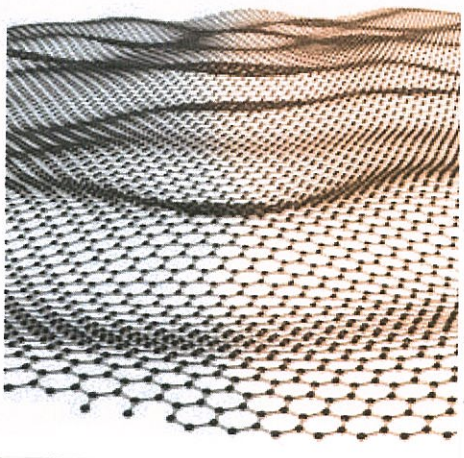
Graphene and its discovery

The Mermin-Wagner theorem has led physicists to believe that 2D crystals don't exist.
(perfect)

Hence it is a surprising when graphene is discovered in 2004 by Geim's group (Science 306, 666, 2004)

The existence of graphene actually does not violate the Mermin-Wagner theorem because its formation is done on top of 3D crystals and is "peeled off" later.

If it's suspended as a free 2D crystal, one sees ripples as required by Mermin-Wagner theorem!



← rippling in free-standing graphene

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Elastic waves of lattices

(elastic theory)
The continuum description is valid when $K \to 0$; specifically, $\lambda \gg a$. The behavior only depends on the symmetries of underlying crystals or liquid/gas.

Hence the sound wave is quite universal.

The elastic wave gets drastic change when one goes to atomic scale, i.e., $\lambda \sim a$.

To describe it, we assume that a static potential $U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ can describe the potential energy for atoms (/ions) for any moment. This is roughly correct as electrons move much faster ($\sim 10^8$ cm/sec) than atoms, one can treat the system in the adiabatic approximation — electrons move in together with atoms. (this is apparently not exactly correct for metal & covalent crystal. but is not too outrageous).

For small displacements, $\vec{r}_i \to \vec{r}_i + \vec{u}(\vec{r}_i)$,

$U(\vec{r}_1+\vec{u}(\vec{r}_1), \vec{r}_2+\vec{u}(\vec{r}_2), \cdots, \vec{r}_N+\vec{u}(\vec{r}_N))$

$= U(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) + \sum_i \vec{u}(\vec{r}_i) \cdot \frac{\partial}{\partial \vec{r}_i} U(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$

$+ \frac{1}{2!} \sum_{i,j} (\vec{u}(\vec{r}_i) \cdot \frac{\partial}{\partial \vec{r}_i})(\vec{u}(\vec{r}_j) \cdot \frac{\partial}{\partial \vec{r}_j}) U(\vec{r}_1, \cdots, \vec{r}_N) + \cdots$

(doesn't act on $U(\vec{r}_j)$)

Because $\{\vec{r}_1, \cdots, \vec{r}_N\}$ is a equilibrium configuration,

$\frac{\partial}{\partial \vec{r}_i} U(\vec{r}_1, \cdots, \vec{r}_N) = 0$.

Therefore, if we set $U(\vec{r}_1 \cdots, \vec{r}_N) = 0$ and neglect higher orders

$U \cong \frac{1}{2} \sum_{i,j} u_\alpha(\vec{r}_i) D_{\alpha\beta}(\vec{r}_1, \cdots \vec{r}_N) u_\beta(\vec{r}_j)$.

For translational invariant systems, we can write $D_{\alpha\beta}(\vec{r}_1, \cdots, \vec{r}_N) = D_{\alpha\beta}(\vec{r}_i - \vec{r}_j)$

Hence $U^h = \frac{1}{2} \sum_{\substack{i,j \\ \alpha\beta}} u_\alpha(\vec{r}_i) D_{\alpha\beta}(\vec{r}_i - \vec{r}_j) u_\beta(\vec{r}_j)$ --(14)

The approximation that neglects higher orders is termed as harmonic approximation.

<u>Symmetries of $D_{\alpha\beta}$</u>

Obviously, one has $D_{\alpha\beta}(\vec{r}_i - \vec{r}_j) = D_{\beta\alpha}(\vec{r}_j - \vec{r}_i)$

If Bravais lattice has inversion symmetry,

$\therefore D_{\alpha\beta}(\vec{R}) = D_{\alpha\beta}(-\vec{R})$

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Furthermore, when $\vec{u}(\vec{r}_i) = \vec{d}$ = constant vector,

$$U(\vec{r}_1+\vec{d}, \vec{r}_2+\vec{d}, \ldots, \vec{r}_N+\vec{d}) = U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$

Hence $\sum_{ij} d_\alpha \Phi_{\alpha\beta}(\vec{r}_i-\vec{r}_j) d_\beta = 0$ i.e. $\sum_R D_{\alpha\beta}(\vec{R}) = 0$

Connection with theory of elasticity

Since $\sum_R D_{\alpha\beta}(\vec{R}) = 0$, we can write

$$U^h = \frac{1}{2} \sum_{ij} (u_\alpha(r_i) - u_\alpha(r_j)) D_{\alpha\beta}(r_i - r_j) (u_\beta(\vec{r}_i) - u_\beta(\vec{r}_j))$$

If we consider $u(r)$ that varies slightly from i to j over the range of $D_{\alpha\beta}(r_i-r_j)$ (i.e. $\lambda \gg a$),

$$u_\alpha(r_i) \cong u_\alpha(r_j) + R_\mu \frac{\partial}{\partial x_\mu} u_\alpha \Big|_{r=r_j}, \quad \vec{R} = \vec{r}_i - \vec{r}_j$$

Since $\sum_{ij} u_\alpha(r_j) D_{\alpha\beta}(r_i-r_j) u_\beta(r_j)$

$$= \sum_j u_\alpha(r_j) u_\beta(r_j) \sum_R D_{\alpha\beta}(\vec{R}) = 0, \text{ we find}$$

$$U^h = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \left(\frac{\partial u_\alpha(\vec{r})}{\partial x_\beta}\right) \left(\frac{\partial u_\gamma(r)}{\partial x_\delta}\right) E_{\alpha\beta\gamma\delta}$$

$$E_{\alpha\beta\gamma\delta} = -\sum_R R_\beta D_{\alpha\gamma}(\vec{R}) R_\delta$$

$\because e_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}\right)$, $\frac{\partial u_\alpha}{\partial x_\beta} = e_{\alpha\beta} + w_{\alpha\beta}$

$w_{\alpha\beta} \equiv \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x_\beta} - \frac{\partial u_\beta}{\partial x_\alpha}\right)$

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For pure rotation, $\omega_{\alpha\beta} \neq 0$, $e_{\alpha\beta} = 0$. Hence one has

$$\sum_{\alpha\beta\gamma\delta} \frac{\partial u_\alpha}{\partial x_\beta} C_{\alpha\beta\gamma\delta} = \sum_{\alpha\beta\gamma\delta} \frac{\partial u_\beta}{\partial x_\alpha} C_{\alpha\beta\gamma\delta}$$

By appropriate exchange indices, we find

$$U^h = \frac{1}{2} \sum \frac{\partial u_\alpha}{\partial x_\beta} C_{\alpha\beta\gamma\delta} \frac{\partial u_\gamma}{\partial x_\delta} = \frac{1}{2} \sum \frac{\partial u_\beta}{\partial x_\alpha} C_{\beta\alpha\gamma\delta} \frac{\partial u_\gamma}{\partial x_\delta}$$

$$= \frac{1}{2} \cdot \frac{1}{4} \sum \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) \left(C_{\alpha\beta\gamma\delta} + C_{\beta\alpha\gamma\delta} \right) \frac{\partial u_\gamma}{\partial x_\delta}$$

$$= \frac{1}{2} \times \frac{1}{16} \sum \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) \left(C_{\alpha\beta\gamma\delta} + C_{\beta\alpha\gamma\delta} + C_{\alpha\beta\delta\gamma} + C_{\beta\alpha\delta\gamma} \right)$$

$$\left(\frac{\partial u_\gamma}{\partial x_\delta} + \frac{\partial u_\delta}{\partial x_\gamma} \right)$$

$$= \frac{1}{2V} \sum_{\alpha\beta\gamma\delta} e_{\alpha\beta} C_{\alpha\beta\gamma\delta} e_{\gamma\delta} = \frac{1}{2} \int_V \sum_{\alpha\beta\gamma\delta} e_{\alpha\beta} C_{\alpha\beta\gamma\delta} e_{\gamma\delta}$$

with $C_{\alpha\beta\gamma\delta} = \frac{1}{4} \left(C_{\alpha\beta\gamma\delta} + C_{\beta\alpha\gamma\delta} + C_{\alpha\beta\delta\gamma} + C_{\beta\alpha\delta\gamma} \right)$.

which is exactly the starting potential of the theory of elasticity.

Equipartion theorem: The failure of the law of Dulong & Petti

One of the important consequences of Eq. (14) is the law. the Dulong & Petti, regard the temperature dependence of specific heat.

Classically, one has

$u \equiv$ thermal energy density $= \frac{1}{V} \frac{\int d^3T H e^{-\beta H}}{\int d^3T\, e^{-\beta H}}$

$= -\frac{1}{V} \frac{\partial}{\partial \beta} \ln \int d^3T\, e^{-\beta H}$

where $d^3T \equiv \int d^3u(r_1) \int d^3p_1 \cdots \int d^3u(r_N) \int d^3p_N$

$$H = \sum_i \frac{\vec{p}_i^{\,2}}{2M} + \underbrace{U(r_1, r_2, \ldots, r_N)}_{U^{eq}} + U^h$$

$$= \sum_i \frac{\vec{p}_i^{\,2}}{2M} + U^{eq} + \frac{1}{2} \sum_{\substack{ij \\ \alpha\beta}} u_\alpha(r_i)\, D_{\alpha\beta}(r_i - r_j)\, u_\beta(r_j)$$

It's clear that all the temperature dependence can be deduced by redefining $\vec{p}_i$ & $\vec{u}(r_i)$:

$$\sqrt{\beta}\, \vec{p}_i = \vec{p}_i', \quad \sqrt{\beta}\, \vec{u}(r_i) = \vec{u}'(r_i)$$

$$d^3\vec{u}(\vec{r}_i) = \beta^{-3/2}\, d^3\vec{u}'(\vec{r}), \quad d^3\vec{p}_i = \beta^{-3/2}\, d^3\vec{p}_i'$$

$$\int dT\, e^{-\beta H} = \underbrace{(\beta^{-\frac{3}{2}})^{2N}}_{e^{-\beta U^{eq}}} \underbrace{\int dT'\, e^{-\left(\sum_i \frac{\vec{p}'^{\,2}}{2M} + \frac{1}{2}\sum_{\substack{ij \\ \alpha\beta}} u_\alpha(r_i) D_{\alpha\beta}(r_i - r_j) u_\beta(r_j)\right)}}_{\beta\text{-independent}}$$

$$\therefore u = \frac{-1}{V} \frac{\partial}{\partial \beta} \ln \left[e^{-\beta U^{eq}}\, \beta^{-3N} \times \text{const} \right]$$

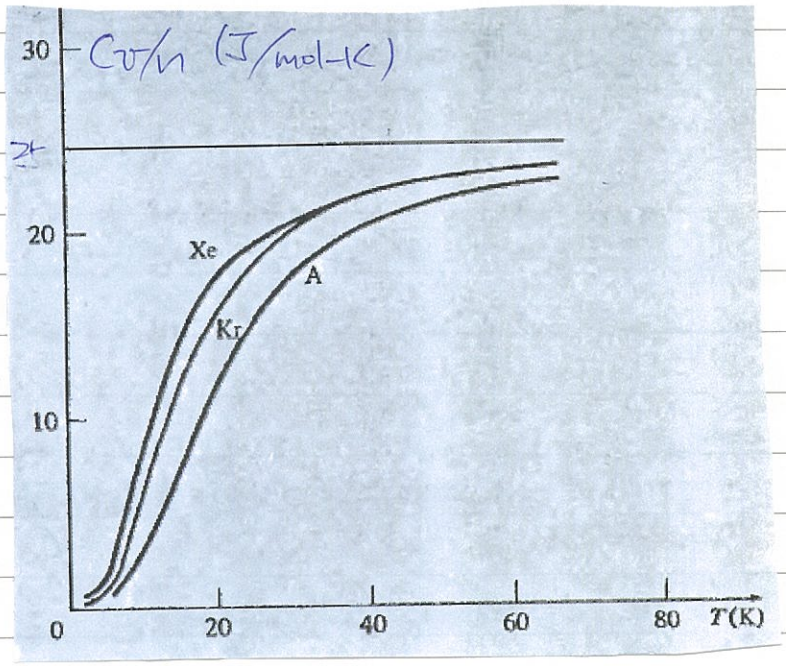
$$= \frac{U^{eq}}{V} + \frac{3N}{V} k_B T$$

$C_V = \frac{du}{dT} = 3n k_B$, i.e, each degree of freedom contributes $\frac{1}{2} k_B T$, total: $\frac{1}{2} k_B T \times 2 \times 3N$

(potential energy + kinetic)

The result $C_V = 3nk_B$ is know as the law of Dulong & Petti, which turns out not to be consistent with expts: $C_V/n = 3k_B = 5.96$ cal/mol-K ≈ 25.032 J/mol-K

1 Cal = 4.2 Joule



One can see (i) $T \lesssim 10$ K, C_V is not temperature independent

(ii) $T \to \infty$, $C_V \to 25.032$. The difference can be explained by failure of harmonic approximation!

The failure at low temperatures is due to failure of Dulong & Petti's law

the usage of classical mechanics. But at high temperature classical theory is seen to be qualitatively fine. Hence, arguments based on classical statistical mechanics still work. (such as Mermin-Wagner theorem... etc.)

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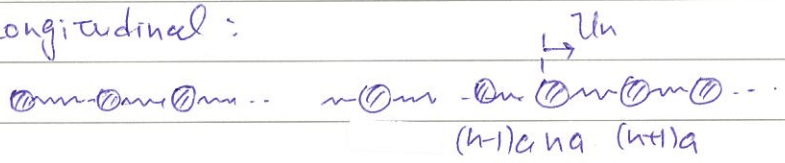
We shall first focus on features of elastic waves on Bravais lattice classically, and come back to quantum description shortly.

To illustrate the generic features of elastic waves on Bravais lattice, We consider a one-dimensional monatomic Bravais lattice.

Elastic waves on 1D monatomic Bravais lattice

Longitudinal:

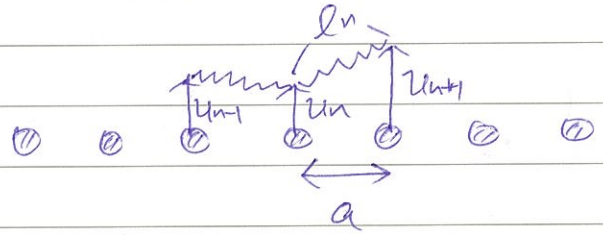


Assume that $D_{\alpha\beta}(k-k') \neq 0$ only when $j = (\pm 1)$

$$U = \frac{1}{2} K \sum_n (u_n - u_{n+1})^2$$

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

Transverse:



$$U = \frac{1}{2} K \sum_n (l_n^2 - a^2)$$

$$l_n^2 = a^2 + (u_{n+1} - u_n)^2$$

$$\therefore U = \frac{1}{2} K \sum_n (u_{n+1} - u_n)^2$$

$$\therefore M\frac{d^2u_n}{dt^2} = -\frac{\partial U}{\partial u_n} = K(u_{n+1} + u_{n-1} - 2u_n) \quad \cdots (1)$$

is correct for both transverse & longitudinal waves.
(isotropic case)

We seek the traveling wave solutions for eq. (15),

$$u_n(t) \propto Re\left[e^{i(kna-\omega t)}\right] \text{ or } Im[\cdots]$$

After being substituted into eq. (15), we find

$$Re\left[-M\omega^2 e^{ina k}\right] = +K\left[e^{ia(n+1)k} + e^{ia(n-1)k} - 2e^{iakn}\right]$$

$$\therefore -M\omega^2 = K\left(e^{iak} + e^{-iak} - 2\right)$$

$$= 2K(\cos ka - 1)$$

$$\omega^2 = \frac{2K}{M}(1-\cos ka) = \frac{4K}{M}\sin^2\frac{ka}{2}$$

$$\omega = 2\sqrt{\frac{K}{M}}\left|\sin\frac{ka}{2}\right|$$

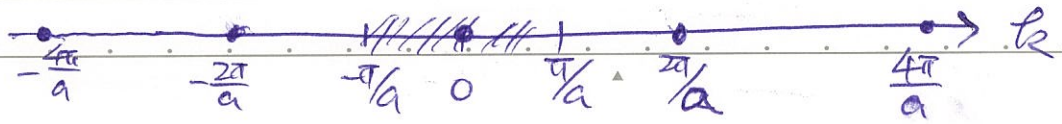
(it's sufficient to take positive ω, $-\omega$ corresponds to negative $v_g = \frac{d\omega}{dk}$)

Effective range of k

As a function k, u is periodic in k:

$$e^{ina\left(k+\frac{2\pi m}{a}\right)} = e^{ina k}, \quad \omega\left(k+\frac{2\pi m}{a}\right) = \omega(k)$$

Therefore, it's sufficient to restrict k to $-\pi/a < k \le \pi/a$ in the reciprocal lattice.

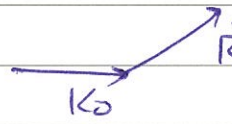


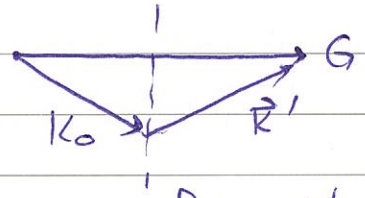
Therefore, unlike ideal lattices, wave # of displacement u $\hookrightarrow -\frac{\pi}{a} < k \leq \frac{\pi}{a}$

The region is termed as 1st Brillouin zone.

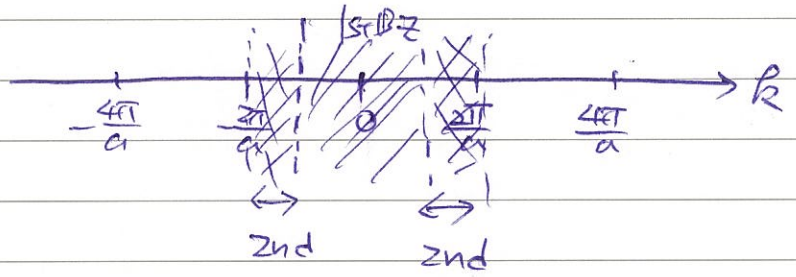
which is the Wigner-Seitz primitive cell of the reciprocal lattice. Higher Brillouin zones can be also constructed: The 2nd B.Z. = {points} that can be reached from 1st B.Z. by crossing only one Bragg plane ($\frac{2\pi m}{a}$)

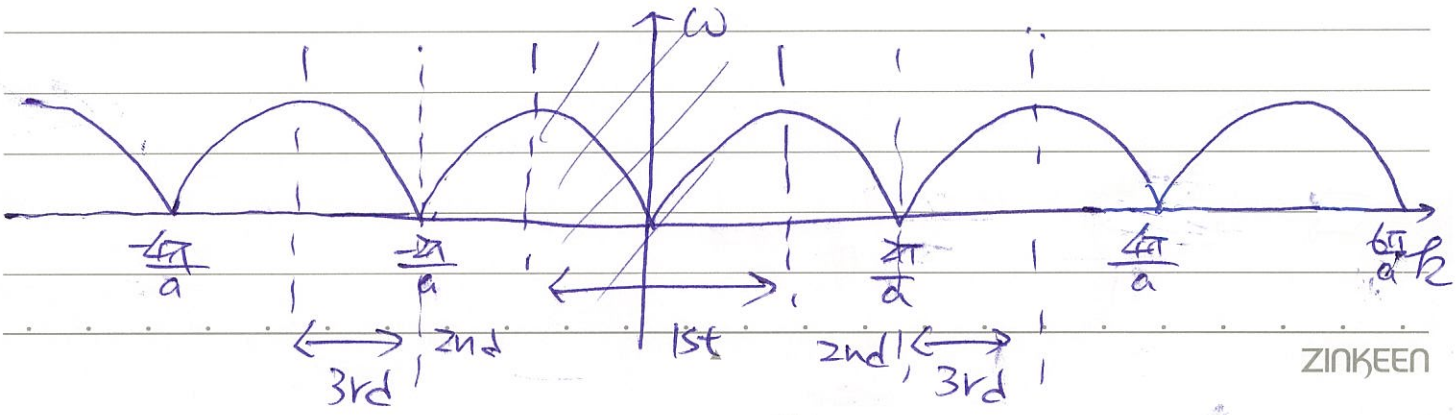
The nth B.Z. = {points} that can be reached from the origin by crossing n-1 Bragg planes.

Bragg plane: scattering expt. 

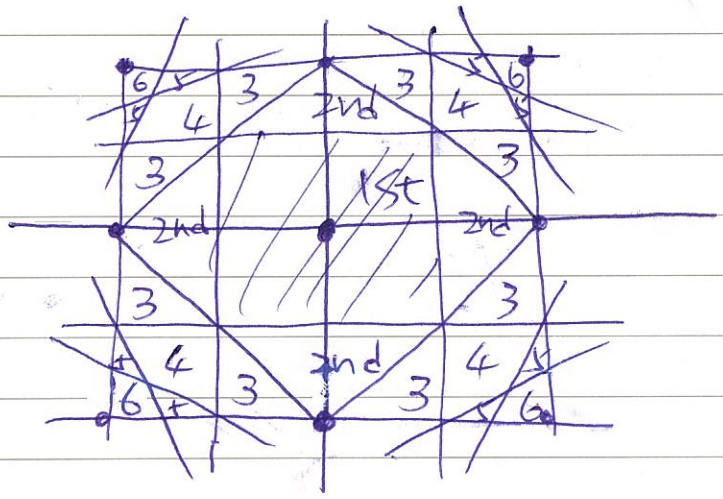


Bragg plane = planes bisecting origin to any reciprocal lattice vector

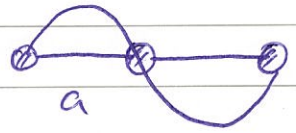
Example 



Example : 2D Square lattice



Note that even though u & ω is periodic in k, large ks in higher B.Z. actually have no meaning in classical waves. For instance,



$\lambda = 2a$, $k = \frac{2\pi}{2a} = \frac{\pi}{a}$

$3\lambda = 2a$ $k = \frac{2\pi}{\frac{2a}{3}} = \frac{3\pi}{a} = \frac{\pi}{a} + \frac{2\pi}{a}$

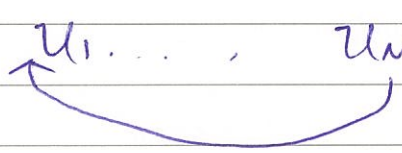
↔ moving one λ

are equivalent because there is no atom inside the spacing a!

Therefore, the 1st B.Z. is physical and has real meaning.

Boundary conditions For finite systems in we can simulate it with finite systems with N atoms & periodic boundary

Condition



$\therefore$ We require $e^{ik(N+1)a} = e^{ika}$, $e^{ikNa} = 1$

Hence $kNa = 2\pi m$, $m =$ integers

$$-\frac{\pi}{a} < k = \frac{m}{N}\frac{2\pi}{a} \leq \frac{\pi}{a}$$

$$-N < 2m \leq 2N$$

$N =$ even, $m = -\frac{N}{2}+1, -\frac{N}{2}+2, \ldots, \frac{N}{2}$ # of $k = N$

$N =$ odd, $m = -\frac{N}{2}+\frac{1}{2}, \ldots, \frac{N}{2}-\frac{1}{2}$, " $= N$

$\therefore$ Each B.Z. has N allowed k. → Exercise

(Note that open boundary condition also allows N solutions)

· Longitudinal + 2 transverse $\Rightarrow$ total # of k

$= 3N$ degree of freedoms

Velocity : v_p = Phase velocity $= \frac{\omega}{k} = 2\sqrt{\frac{K}{M}}\frac{1}{k}\left|\sin\frac{ka}{2}\right|$

$\rightarrow \sqrt{\frac{K}{M}}\, a$, $k \to 0$

Group velocity $v_g = \frac{d\omega}{dk} = a\sqrt{\frac{K}{M}}\cos\frac{ka}{2}$

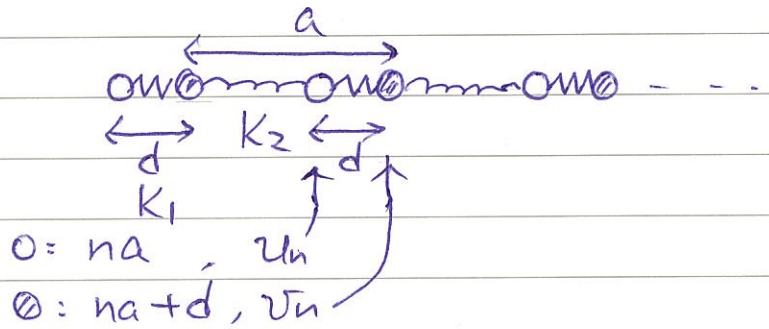
$\rightarrow a\sqrt{\frac{K}{M}}$ as $k \to 0^+$

$\parallel$

Sound wave velocity

1D Bravais lattice with a basis

Consider two atoms in a basis,



$$U = \frac{K_1}{2}\sum_n (u_n - v_n)^2 + \frac{K_2}{2}\sum_n (v_n - u_{n+1})^2$$

$$K.E. = \frac{1}{2}m_1\sum_n \dot{u}_n^2 + \frac{1}{2}m_2\sum_n \dot{v}_n^2$$

$$m_1\frac{d^2u_n}{dt^2} = -K_1(u_n - v_n) - K_2(u_n - v_{n-1})$$

$$m_2\frac{d^2v_n}{dt^2} = -K_1(v_n - u_n) - K_2(v_n - u_{n+1})$$

Try traveling waves: $u_n = u e^{i(nka-\omega t)}$

$v_n = v e^{i(nka-\omega t)}$

$$-m_1\omega^2 u = -K_1(u-v) - K_2(u - v e^{-ika})$$

$$-m_2\omega^2 v = -K_1(v-u) - K_2(v - u e^{ika})$$

$$(K_1+K_2-m_1\omega^2)u - (K_1+K_2e^{-ika})v = 0$$

$$(K_1+K_2e^{ika})u - (K_1+K_2-m_2\omega^2)v = 0$$

$$\therefore \begin{vmatrix} K_1+K_2-m_1\omega^2 & -(K_1+K_2e^{-ika}) \\ K_1+K_2e^{ika} & -(K_1+K_2-m_2\omega^2) \end{vmatrix} = 0$$

$$(K_1+K_2-m_1\omega^2)(K_1+K_2-m_2\omega^2)-(K_1+K_2e^{ika})(K_1+K_2e^{-ika})=0$$

$$m_1m_2(\omega^2)^2-(K_1+K_2)(m_1+m_2)\omega^2+2K_1K_2(1-\cos ka)=0$$

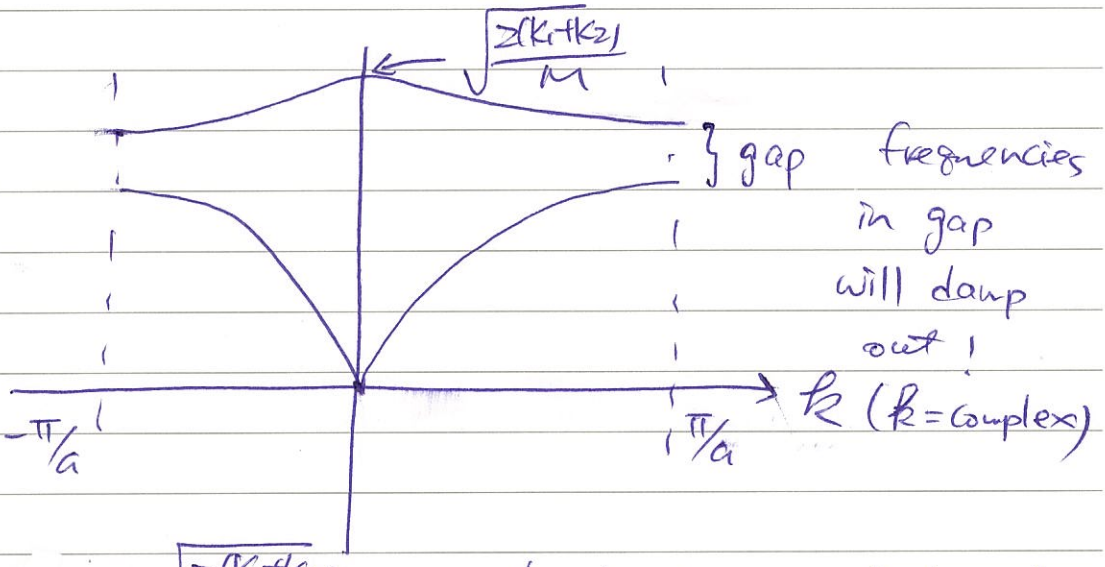
$$\omega^2=\frac{(K_1+K_2)(m_1+m_2)\pm\left[(m_1+m_2)^2(K_1+K_2)^2-8K_1K_2m_1m_2(1-\cos ka)\right]^{\frac{1}{2}}}{2m_1m_2}$$

To illustrate important features, we shall set $m_1=m_2=M$, then

$$\omega^2=\frac{K_1+K_2}{M}\pm\frac{1}{M}\sqrt{K_1^2+K_2^2+2K_1K_2\cos ka}$$

$\downarrow$ $|K_1+K_2e^{ika}|^2$

with $$\frac{U}{v}=\mp\frac{K_1+K_2e^{-ika}}{|K_1+K_2e^{ika}|}$$



We have

frequencies in gap will damp out!

$k\to 0$ $\quad \omega\to\sqrt{\frac{2(K_1+K_2)}{M}}$ $\quad (+)\Rightarrow$ optical branch (ionic crystals, its long wavelength interact with E.M.)

$\cos ka=1-\frac{(ka)^2}{2}$

& $\sqrt{\frac{K_1K_2}{2M(K_1+K_2)}}\,ka$ $\quad (-)\Rightarrow$ acoustical branch

Furthermore, $\frac{u}{v} \to \mp 1$

∴ acoustic mode + ○ ◎ ○ ◎ → → → → move together

optical mode − ○ ◎ ○ ◎ → ← → ←

$k = \pi/a$ $\quad \frac{u}{v} = \mp 1$

$$\omega^2 = \frac{K_1 + K_2}{M} \pm \frac{1}{M}\sqrt{(K_1 - K_2)^2}$$

$$\omega = \sqrt{\frac{2K_1}{M}} \qquad \frac{u}{v} = -1$$

$$\omega = \sqrt{\frac{2K_2}{M}} \qquad \frac{u}{v} = 1$$

$K_1 >> K_2$

$\omega \simeq \sqrt{\frac{2K_1}{M}}$ (almost flat) $\quad \frac{u}{v} = -1$ optical mode

$\omega \simeq \sqrt{\frac{2K_2}{M}} \sin\frac{ka}{2} \quad \frac{u}{v} = 1$ acoustical mode

General consideration:

In general, using eq. (14), one has (Bravais lattice) Monatomic

$$M\frac{d^2 u_\alpha}{dt^2} = -\sum_j D_{\alpha\beta}(r_i - r_j)\, u_\beta(r_j)$$

We look the solution $\vec{u}(r_j, t) = \vec{\epsilon}\, e^{i(\vec{k}\cdot\vec{r}_j - \omega t)}$

$\vec{\epsilon}$ = polarization vector of the normal mode

Using the periodic boundary condition, we have $u(\vec{r}+N_i\vec{a}_i) = u(\vec{r})$, for Bravais lattice

$$\therefore \vec{k} = \frac{n_1}{N_1}\vec{g}_1 + \frac{n_2}{N_2}\vec{g}_2 + \frac{n_3}{N_3}\vec{g}_3$$

$$\vec{g}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$$

ω^2 is determined by the eigenvalue problem:

$$[M\omega^2 \mathbb{I} - D(k)] \cdot \vec{\epsilon} = 0$$

where $D_{\alpha\beta}(\vec{k}) = \sum_R D_{\alpha\beta}(\vec{R})\, e^{i\vec{k}\cdot\vec{R}}$

$\because D(-\vec{R}) = D(\vec{R})$, $\sum_R D(\vec{R}) = 0$

$$\therefore D(k) = \frac{1}{2}\sum_R D(\vec{R})\left[e^{i\vec{k}\cdot\vec{R}} + e^{-i\vec{k}\cdot\vec{R}} - 2\right]$$

$$= -2\sum_R D(\vec{R}) \sin^2\left(\frac{1}{2}\vec{k}\cdot\vec{R}\right)$$

$\therefore D(-k) = D(k)$ = real, symmetric $D_{\alpha\beta} = D_{\beta\alpha}$

$\therefore$ For each $\vec{k}$, there must be 3 eigenvectors $\vec{\epsilon}_1, \vec{\epsilon}_2$ & $\vec{\epsilon}_3$ such that $D(k)\,\vec{\epsilon}_i(k) = \lambda_i(k)\,\vec{\epsilon}_i(k)$

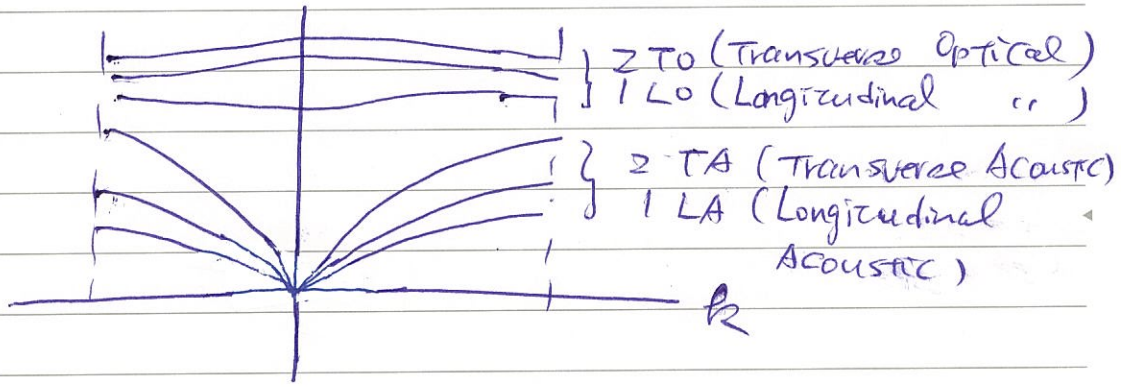
$\vec{\epsilon}_i \cdot \vec{\epsilon}_j = \delta_{ij}$. $\therefore \omega_i(k) = \sqrt{\frac{\lambda_i(k)}{M}}$.

For general 3D lattice with a basis

If there are p atoms (ions) in a basis,

There will be 3p branches. Among them, 3 are acoustic, the other 3(p-1) are optical, because for a p-atomic molecule, there are 3 translational degrees of freedom but 3(p-1) vibrational degrees of freedom.

As an example, typical dispersion curves for p=2 is



Quantization of elastic waves : phonons in solids

As indicated by the failure of the law of Dulong & Petit, one sees that C_V gradually increases with T. It hints that energy for each degree of freedom is not the same and is gradually excited. This seems to point to that one needs to take "energy quanta"

into consideration. Hence we need to treat elastic waves quantum mechanically.

We shall illustrate it by considering 1D monoatomic Bravais lattice.

In this case,

$$\hat{H} = \sum_n \frac{\hat{P}_n^2}{2M} + \frac{1}{2}K(\hat{U}_n - \hat{U}_{n+1})^2$$

with $[\hat{U}_n, \hat{P}_{n'}] = \delta_{nn'} i\hbar$

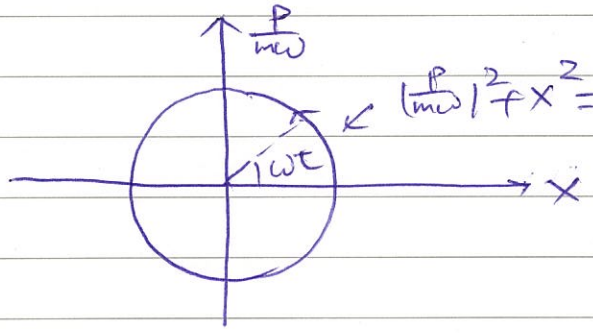
$[\hat{U}_n, \hat{X}_{n'}] = 0, \quad [\hat{P}_n, \hat{P}_{n'}] = 0$

$\hat{H}$ is a generalization of a simple harmonic oscillator.

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$$

Classically, $E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2$, hence

$$\left(\frac{p}{m\omega}\right)^2 + x^2 = \text{const}$$



it suggests that the equation of motion is circular motion with "normal modes" $x \pm i\frac{p}{m\omega}$.

The quantum mechanical solution to this problem follows exactly the hint above by trying the factorization

$$\hat{H}_0 = \frac{1}{2m}(\hat{p}+im\omega\hat{x})(\hat{p}-im\omega\hat{x}) - \underbrace{\frac{1}{2m}im\omega[\hat{x},\hat{p}]}_{\text{purely due to Quantum Mechanics}}$$

$$= \frac{1}{2m}(m\omega)^2\left[\hat{x}-\frac{i\hat{p}}{m\omega}\right]\left[\hat{x}+\frac{i\hat{p}}{m\omega}\right] + \frac{1}{2}\hbar\omega \qquad \text{"} \ \frac{1}{2}\hbar\omega$$

$$= \hbar\omega\left[\frac{m\omega}{2\hbar}\left[\hat{x}-\frac{i\hat{p}}{m\omega}\right]\left[\hat{x}+\frac{i\hat{p}}{m\omega}\right]\right] + \frac{1}{2}\hbar\omega$$

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

$$\hat{a}^+ = \text{"} \ \left(\hat{x}-\frac{i\hat{p}}{m\omega}\right)$$

$$H_0|n\rangle = \hbar\omega(n+1/2)|n\rangle$$

are known as annihilation & creation operators. The energy eigenstate is also an eigenstate to $a^+a = \hat{a}\hat{a}|n\rangle = n|n\rangle$

It is then clear that to solve $\hat{H}$, one needs to find normal modes first. This is equivalently diagonalizing $\hat{H}$.

Let N = # of atoms, we form the Fourier transformation of x_n & p_n:

$$\hat{u}_K = \frac{1}{\sqrt{N}}\sum_n \hat{u}_n e^{i k(na)}$$

$$\hat{p}_K = \frac{1}{\sqrt{N}}\sum_n \hat{p}_n e^{i k(na)}$$

Clearly, because $\hat{u}_n^+ = \hat{u}_n$, $\hat{p}_n^+ = \hat{p}_n$, we have

$$\hat{u}_k^+ = \hat{u}_{-k}, \quad \hat{p}_k^+ = \hat{p}_k \quad \text{(not self-adjoint!)}$$

Furthermore, $[\hat{u}_k, \hat{p}_{k'}] = \frac{1}{N}\sum_{n,m}[u_n, p_m]\, e^{ik(na)} e^{ik'(ma)}$

$$= \frac{1}{N}\sum_{n,m} i\hbar\,\delta_{n,m}\, e^{ik(na)} e^{ik'(ma)}$$

$$= i\hbar\,\delta_{k,-k'}$$

$$\therefore [\hat{u}_k, \hat{p}_{k'}^+] = i\hbar\delta_{k,k'} \quad \text{or} \quad [\hat{u}_k^+, \hat{p}_{k'}] = i\hbar\delta_{k,k'}$$

$$[\hat{u}_k, \hat{u}_{k'}^+] = 0, \quad [\hat{p}_k, \hat{p}_{k'}^+] = 0, \quad [\hat{u}_k, \hat{u}_{k'}] = 0, \quad [p_k, \hat{p}_{k'}] = 0$$

Now, $\sum_n \hat{p}_n^2 = \frac{1}{N}\sum_{kk'} \hat{p}_k \hat{p}_{k'} \sum_n e^{i(k+k')na} = \sum_k \hat{p}_k \hat{p}_{-k} = \sum_k \hat{p}_k^+ \hat{p}_k$

$$\sum_n (\hat{u}_n - \hat{u}_{n+1})^2 = 2\sum_n \hat{u}_n^2 - 2\sum_n \hat{u}_n \hat{u}_{n+1} \qquad [u_n, u_{n+1}] = 0$$

$$\sum_n \hat{u}_n \hat{u}_{n+1} = \sum_k \sum_{k'} \Big(\frac{1}{N}\sum_n e^{ik(na)} e^{ik'(n+1)a}\Big) \hat{u}_k \hat{u}_{k'}$$

($\frac{1}{N}\sum_n e^{ik(na)} e^{ik'(n+1)a} = \delta_{k,-k'} e^{ik'a}$)

$$= \sum_{k'} \hat{u}_{k'}^+ \hat{u}_{k'} e^{ik'a}$$

$$= \sum_k \hat{u}_k \hat{u}_{-k} e^{-ika} = \frac{1}{2}\sum_k \hat{u}_k^+ \hat{u}_k (e^{ika} + e^{-ika})$$

$$= \sum_k \cos ka\, \hat{u}_k^+ \hat{u}_k$$

$$\therefore \hat{H} = \frac{1}{2M}\sum_k \hat{p}_k^+ \hat{p}_k + \frac{1}{2} M\omega^2 \sum_k \underbrace{2(1-\cos ka)}_{4\omega^2 \sin^2 \frac{ka}{2}} \hat{u}_k^+ \hat{u}_k$$

(k ↑)

$$= \sum_k \Big(\frac{1}{2M}\hat{p}_k^+ \hat{p}_k + \frac{1}{2} M\omega_k^2 \hat{u}_k^+ \hat{u}_k\Big) \qquad \omega_k = 2\omega\Big|\sin\frac{ka}{2}\Big|$$

Factoring $\hat{H}$, we get

$$\hat{H} = \sum_K \frac{1}{2M} \left(\hat{P}_K^+ + i m\omega_K \hat{U}_K^+\right)\left(\hat{P}_K - i m\omega_K \hat{U}_K\right) - \frac{i}{2}\omega_K\left(\hat{U}_K^+ \hat{P}_K - \hat{P}_K^+ \hat{U}_K\right)$$

Here $\hat{U}_K^+ \hat{P}_K - \hat{P}_K^+ \hat{U}_K$

$$= \frac{1}{N}\sum_{n,m} U_n P_m e^{-iK(n-m)a} - P_m X_n e^{-iK(m-n)a}$$

$$= \frac{1}{N}\sum_{n,m} [U_n, P_m] \cos K(n-m)a$$

$$+ \frac{i}{N}\sum_{n,m} \{U_n, P_m\} \sin K(n-m)a$$

$\because \sum_K \omega_K \sin K(n-m)a = 0 \qquad \omega_{-K} = \omega_K$

$$\sum_{n,m} \underbrace{[U_n, P_m]}_{i\hbar\delta_{n,m}} \cos K(n-m)a = \sum_n i\hbar = i\hbar N$$

$\therefore \quad \hat{U}_K^+ \hat{P}_K - \hat{P}_K^+ \hat{U}_K = i\hbar$

Hence if we set $\hat{a}_K = \sqrt{\frac{M\omega_K}{2\hbar}}\left(\hat{U}_K + \frac{i\hat{P}_K}{m\omega_K}\right)$

we find $\hat{a}_K^+ \neq$ " $\left(\hat{U}_K - \frac{i\hat{P}_K}{m\omega_K}\right)$ $\left(\because \hat{P}_K^+ = \hat{P}_K,\ \hat{U}_K^+ = \hat{U}_K\right)$

instead $\hat{a}_{-K}^+ = \sqrt{\frac{m\omega_K}{2\hbar}}\left(\hat{U}_K - \frac{i\hat{P}_K}{m\omega_K}\right)$, $\hat{a}_K^+ = \sqrt{\frac{m\omega_K}{2\hbar}}\left(\hat{U}_K^+ - \frac{i\hat{P}_K^+}{m\omega_K}\right)$, $[a_K, a_{K'}^+] = \delta_{K,K'}$,

we find $\hat{H} = \sum_K \hbar\omega_K \left(a_K^+ a_K + \frac{1}{2}\right)$

Hence for each K, the energy is characterized by $\hbar\omega_K$. This is equivalent to think the system is composed of particles called phonons. Adding one phonon would increase

the energy of the system by $\hbar\omega_k$.

In general, the system is characterized by

$$(n_{k_1}, n_{k_2}, n_{k_3}, \cdots, n_{k_i}, \cdots)$$
$$n_k = 0, 1, 2, 3, \cdots \quad \text{with } k \text{ in 1st B.Z.}$$

Space formed by the above states is called Fock space.

phonons in higher BZ don't exist

Note that given a_k, a_k^+, one can express u_n & P_n in terms of a_k & a_k^+.

$$\because \hat{u}_k = \sqrt{\frac{\hbar}{2M\omega_k}}\left(\hat{a}_k + \hat{a}_{-k}^+\right)$$

$$\hat{P}_k = -i\sqrt{\frac{\hbar M\omega_k}{2}}\left(\hat{a}_{-k}^+ - \hat{a}_k\right)$$

$$\hat{u}_n = \frac{1}{\sqrt{N}}\sum_k \sqrt{\frac{\hbar}{2M\omega_k}}\left(a_k + a_{-k}^+\right)e^{-ik(na)}$$

$$= \frac{1}{\sqrt{N}}\sum_k \sqrt{\frac{\hbar}{2M\omega_k}}\left(a_k e^{-ik(na)} + a_k^+ e^{ik(na)}\right)$$

$$\hat{P}_n = \frac{-i}{\sqrt{N}}\sum_k \sqrt{\frac{\hbar M\omega_k}{2}}\left(a_k e^{-ik(na)} - a_k^+ e^{+ik(na)}\right)$$

In general, each k is associated with polarization of phonons λ. One has $H = \sum_{k,\lambda} \hbar\omega_{k,\lambda}\left(a_{k\lambda}^+ a_{k\lambda} + \frac{1}{2}\right)$ and replace $\sum_k$ by $\sum_{k,\lambda}$, ω_k by $\omega_{k\lambda}$ in $\hat{u}_n$ & $\hat{P}_n$. $\in$ 1st BZ $\hat{a}_k$ by $\hat{a}_{k\lambda}\vec{\epsilon}_{k\lambda}$, $\vec{\epsilon}_{k\lambda}$ = polarization vector

Example: Debye-Waller Factor at $T=0$

$\therefore \langle n_G \rangle = \langle 0 | e^{i\vec{G}\cdot(\vec{r}_i + \vec{u}(r_i))} | 0 \rangle = e^{i\vec{G}\cdot\vec{r}_i} \langle 0 | e^{i\vec{G}\cdot\vec{u}(r_i)} | 0 \rangle$

$|0\rangle$ = Ground state with all $n=0$

One needs to evalue $S \equiv \langle e^{i\vec{G}\cdot\vec{u}_n} \rangle_0$

where $\vec{u}_n$ is the displacement operator:

$$\vec{u}_n = \frac{1}{\sqrt{N}} \sum_{k\lambda} \sqrt{\frac{\hbar}{2M\omega_{k\lambda}}} \left(\hat{a}_{k\lambda} \vec{\epsilon}_{k\lambda} e^{-i\vec{k}\cdot\vec{R}_n} + \hat{a}^+_{k\lambda} \vec{\epsilon}^{\,*}_{k\lambda} e^{i\vec{k}\cdot\vec{R}_n} \right)$$

According to the cumulant expansion, one has

$$S \simeq e^{-\frac{1}{2}\langle (\vec{G}\cdot\vec{u}_n)^2 \rangle_0}$$

$$\langle (\vec{G}\cdot\vec{u}_n)^2 \rangle_0 = \frac{1}{N} \sum_{\substack{k,k' \\ \lambda\lambda'}} \sqrt{\frac{\hbar}{2M\omega_{k\lambda}}} \sqrt{\frac{\hbar}{2M\omega_{k'\lambda'}}}$$

$$\times \langle \left[\hat{a}_{k\lambda} (\vec{G}\cdot\vec{\epsilon}_{k\lambda}) e^{-i\vec{k}\cdot\vec{R}_n} + \hat{a}^+_{k\lambda} (\vec{G}\cdot\vec{\epsilon}^{\,*}_{k\lambda}) e^{i\vec{k}\cdot\vec{R}_n} \right]$$

$$\left[\hat{a}_{k'\lambda'} (\vec{G}\cdot\vec{\epsilon}_{k'\lambda'}) e^{-i\vec{k}'\cdot\vec{R}_n} + \hat{a}^+_{k'\lambda'} (\vec{G}\cdot\vec{\epsilon}^{\,*}_{k'\lambda'}) e^{i\vec{k}'\cdot\vec{R}_n} \right] \rangle_0$$

$\because \langle \hat{a}_{k\lambda} \hat{a}^+_{k'\lambda'} \rangle_0 = \delta_{kk'}\delta_{\lambda\lambda'}$ $\quad \langle \hat{a}_{k\lambda} \hat{a}_{k'\lambda'} \rangle_0 = 0$

$\langle \hat{a}^+_{k\lambda} \hat{a}_{k'\lambda'} \rangle_0 = 0$ $\quad \langle \hat{a}^+_{k\lambda} \hat{a}^+_{k'\lambda'} \rangle_0 = 0$

$$\therefore \langle (\vec{G}\cdot\vec{u}_n)^2 \rangle_0 = \frac{1}{N} \sum_{k\lambda} \frac{\hbar}{2M\omega_{k\lambda}} |\vec{G}\cdot\vec{\epsilon}_{k\lambda}|^2$$

$$= \sum_\lambda \frac{\hbar}{2M} \int \frac{d^dk}{(2\pi)^d \omega_\lambda(k)} |\vec{G}\cdot\vec{\epsilon}_{k\lambda}|^2$$

Since any crystal must contain acoustic mode with $\min \omega_\lambda(k) \leq ck$ for $k \to 0$,

we have $\langle (\vec{G}\cdot\vec{u}_n)^2 \rangle_0$

$$\gtrsim \frac{\hbar}{2M} \int \frac{d^d k}{(2\pi)^d ck} \sum_\lambda |\vec{G}\cdot\vec{\epsilon}_{k\lambda}|^2$$

$$\because \sum_\lambda \epsilon_\lambda^{\alpha *}(k)\,\epsilon_\lambda^{\beta}(k) = \frac{1}{M}\delta_{\alpha\beta}$$

$$\sum_\lambda |\vec{G}\cdot\vec{\epsilon}_{k\lambda}|^2 = \frac{1}{M}|\vec{G}|^2$$

$$\therefore \langle (\vec{G}\cdot\vec{u}_n)^2 \rangle_0 \gtrsim \frac{\hbar |\vec{G}|^2}{2M^2} \int \frac{d^d k}{(2\pi)^d ck}$$

which diverges at $d = 2$!

Crystal momentum

Do phonons carry momentum?

Phonons are quantized elastic waves. Just like elastic waves, each atom doesn't have net motion. For phonons at 1st B.Z., total momentum of all atoms $= 0$ for any energy eigenstate:

$$\langle \sum_n \hat{p}_n \rangle$$

$$= \frac{-i}{\sqrt{N}} \sum_k \sqrt{\frac{\hbar M \omega_k}{2}} \left\langle a_k \sum_n e^{-ikna} - a_k^\dagger e^{ikna} \right\rangle$$

$$= 0 \quad (\because \langle a_k \rangle = 0,\ \langle a_k^\dagger \rangle = 0)$$

However, just as electromagnetic waves, the wave itself can carry energy and momentum. There will be energy/momentum flow associated with the wave $e^{\pm i(Kx-\omega t)}$!

For phonons, the associated momentum is $\hbar(K \pm G)$ with K being labelling of $\hat{a}_{K\lambda}$. $\hbar K$ are termed as crystal momentum to distinguish them from momentum of atoms.

The existence of crystal momentum can be rigorously formulated by defining the "momentum" operator: $\vec{P}_c = \sum_{K,\lambda} \hbar \vec{K}\, \hat{a}^+_{K\lambda} \hat{a}_{K\lambda}$, with $\hat{a}^+_{K\lambda}\hat{a}_{K\lambda} = \hat{n}_{K\lambda}$.

Now, because of the identity

$$e^{i\alpha a^+a}\, a\, e^{-i\alpha a^+a}\,|n\rangle$$

$$= e^{i\alpha a^+a}\, a\, e^{-i\alpha n}\,|n\rangle = e^{-i\alpha n} e^{i\alpha a^+a}\, n\,|n-1\rangle$$

$$= n\, e^{-i\alpha n} e^{i\alpha(n-1)}\,|n\rangle = e^{-i\alpha}\, n\,|n\rangle = e^{-i\alpha} a\,|n\rangle$$

$$\therefore\ e^{i\alpha a^+a}\, a\, e^{-i\alpha a^+a} = e^{-i\alpha} a,\quad e^{i\alpha a^+a}\, a^+ e^{-i\alpha a^+a} = e^{i\alpha} a^+.$$

Different $a_{k\lambda}$'s commute, we have

$$e^{i\vec{P}_c\cdot\vec{R}}\, a_{k\lambda}\, e^{-i\vec{P}_c\cdot\vec{R}} = e^{-i\vec{k}\cdot\vec{R}}\, a_{k\lambda}$$

$$e^{i\vec{P}_c\cdot\vec{R}}\, a^{+}_{k\lambda}\, e^{-i\vec{P}_c\cdot\vec{R}} = e^{+i\vec{k}\cdot\vec{R}}\, a^{+}_{k\lambda}$$

Since $\vec{u}_n = \frac{1}{\sqrt{N}} \sum_{k\lambda} \sqrt{\frac{\hbar}{2M\omega_{k\lambda}}} \left(a_{k\lambda}\, \vec{\epsilon}_{k\lambda}\, e^{-i\vec{k}\cdot\vec{R}_n} + a^{+}_{k\lambda}\, \vec{\epsilon}^{\,*}_{k\lambda}\, e^{i\vec{k}\cdot\vec{R}_n} \right)$,

we have $e^{i\vec{P}_c\cdot\vec{R}}\, \vec{u}_n\, e^{-i\vec{P}_c\cdot\vec{R}} = \vec{u}(\vec{R}_n + \vec{R})$

Similarly $e^{i\vec{P}_c\cdot\vec{R}}\, \vec{p}_n\, e^{-i\vec{P}_c\cdot\vec{R}} = \vec{p}(\vec{R}_n + \vec{R})$.

In other words, $e^{i\vec{P}_c\cdot\vec{R}}$ acts as a translational operator.

For crystals, $\vec{R}$ has to be a <u>lattice vector $\vec{R}_0$</u>

for H to be invariant:

$$e^{i\vec{P}_c\cdot\vec{R}_0}\, H[u_n, p_n]\, e^{-i\vec{P}_c\cdot\vec{R}_0}$$

$$= H\left[u(\vec{R}_n - \vec{R}_0),\, p(\vec{R}_n - \vec{R}_0)\right] = H$$

Therefore, if $|E\rangle$ is an energy eigenstate, $H|E\rangle = E|E\rangle$

$e^{i\vec{P}_c\cdot\vec{R}_0}|E\rangle$ is also an eigenstate.

and <u>$e^{i\vec{P}_c\cdot\vec{R}_0}$ is a constant of motion</u>

Since $e^{i\vec{G}\cdot\vec{R}_0} = 1$ for any reciprocal lattice vector, one concludes the conservation of $\vec{K}$ is ....

up to some reciprocal lattice vector:

$$\sum_{k\lambda} \vec{k} \hat{n}_{k\lambda}' = \sum_{k\lambda} \vec{k} \hat{n}_{k\lambda} + \vec{G}.$$

In the scattering expt. (for instance, the neutron scattering), the total translational operator that is invariant under $H_{crystal} + \frac{\vec{p}^2}{2m_n}$ ← neutron is $e^{\frac{i}{\hbar}\vec{p}\cdot\vec{R}_0 + i\vec{P}_c\cdot\vec{R}_0}$. Therefore, the conservation of momentum becomes

$$\vec{p}' + \hbar \sum_{k\lambda} \vec{k} \hat{n}_{k\lambda}' = \vec{p} + \hbar \sum_{k\lambda} \vec{k} \hat{n}_{k\lambda} + \hbar \vec{G} \quad \cdots (11)$$

The momentum $\hbar\vec{G}$ is absorbed by the whole crystal (translated by some lattice vector!) as this also happens for elastic scattering from the ideal and fixed crystal:

$$\vec{R}_0 - \vec{r} = \vec{G} !$$

The crystal momentum $\hbar \sum_{k\lambda} \vec{k} \hat{n}_{k\lambda}$ is entirely due to relative motion of atoms in crystal.

Umklapp process in scattering

In the process of scattering, the potential encountered by the incident particle (such as neutrons) is $U(\vec{r}) = \sum_n V_a(\vec{r} - \vec{r}_n - \vec{u}_n)$ ....

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Incident particles (neutron) : $I = \frac{\hbar k_0}{m_n} \frac{1}{V}$ . . . . . .

$\left(\frac{1}{\sqrt{V}} e^{-i\vec{k}_0 \cdot \vec{r}} \right)$

If P is the transition probability from $\vec{k}_0 \to \vec{k}$, per unit time,

then transition per unit time, around $\vec{k}$, $\vec{k}+d\vec{k}$

$$= P \cdot \sum_{(\vec{k}, \vec{k}+d\vec{k})} = P \frac{V d^3\vec{k}}{(2\pi)^3}$$

$$\therefore \frac{V d^3\vec{k}}{(2\pi)^3} = \frac{V \hbar^3 k^2 dk\, d\Omega}{(2\pi\hbar)^3} = \frac{V \hbar k' d\Omega}{(2\pi\hbar)^3} m_n \cdot \underbrace{\frac{d\frac{\hbar^2 k^2}{2m_n}}{}}_{E_n}$$

$$= \frac{V m_n \hbar k' dE_n d\Omega}{(2\pi\hbar)^3}$$

$$\therefore \frac{d\sigma}{d\Omega dE_n} = \frac{\frac{V m_n \hbar k'}{(2\pi\hbar)^3} P}{\frac{\hbar k_0}{m_0} \frac{1}{V}} = \frac{k}{k_0} \frac{(V m_n)^2}{(2\pi\hbar)^3} P(\vec{k}_0 \to \vec{k})$$

Now, according to Fermi's Golden Rule,

$$P(\vec{k}_0 \to \vec{k}) = \sum_f \frac{2\pi}{\hbar} \delta(E^f - E^i) \left| \langle \psi^f | \hat{V} | \psi^i \rangle \right|^2$$

We need to find the transition amplitude (Scattering Amplitude) $\langle \psi^f | \hat{V} | \psi^i \rangle$

Both $|\psi^i\rangle$ & $|\psi^f\rangle$ are the form $|k\rangle \otimes |\text{Crystal}\rangle$

$$|\psi^i\rangle = |\vec{k}_0\rangle |\Phi_i\rangle$$

$$|\psi^f\rangle = |\vec{k}\rangle |\Phi_f\rangle$$

. . . . . .

$\therefore \langle \psi^f | U | \psi^i \rangle$

$$= \int \frac{d\vec{r}}{V} e^{-i\vec{K}_0 \cdot \vec{r}} \langle \Phi^f | v(\vec{r}) | \Phi^i \rangle e^{i\vec{K}\cdot\vec{r}}$$

$\uparrow$

$\begin{cases} \frac{1}{\sqrt{V}} e^{i\vec{K}_0 \cdot \vec{r}} \\ \frac{1}{\sqrt{V}} e^{i\vec{K}\cdot\vec{r}} \end{cases}$

$$= \frac{1}{V} \sum_n \int d\vec{r}\; e^{i(\vec{K}-\vec{K}_0)\cdot\vec{r}} \langle \Phi^f | v_a(\vec{r} - \vec{r}_n - \vec{u}_n) | \Phi^i \rangle$$

$$= \frac{1}{V} \sum_n \langle e^{i(\vec{K}-\vec{K}_0)(\vec{r}_n + \vec{u}_n)} \rangle_{fi} \underbrace{\int d\vec{r}\, e^{i(\vec{K}-\vec{K}_0)\cdot\vec{r}} v_a(\vec{r})}$$

Atomic form factor,
$\equiv v_a(\vec{K}-\vec{K}_0)$

Let the change of neutron energy be $\hbar\omega_n = \frac{\hbar^2 k^2}{2m_n} - \frac{\hbar^2 k_0^2}{2m_n}$.

E_c = energy of crystals.

We find

$$P(\vec{K}_0 \to \vec{K}) = \frac{2\pi N}{\hbar V} |v_a(\vec{K}-\vec{K}_0)|^2 \frac{1}{N} \sum_f \delta(E_c^f - E_c^i + \hbar\omega_n) \underbrace{\left| \sum_n e^{i(\vec{K}-\vec{K}_0)(\vec{r}_n+\vec{u}_n)} \right|^2_{fi}}_{S}$$

One defines the elastic structure factor

$$S(\vec{q},\omega) = \frac{1}{N} \sum_f \delta(E_c^f - E_c^i + \hbar\omega) \left| \sum_n \langle \Phi_f | e^{i\overbrace{(\vec{K}-\vec{K}_0)}^{\vec{q}}(\vec{r}_n+\vec{u}_n)} | \Phi_i \rangle \right|^2$$

$$= \frac{1}{N} \sum_f \int \frac{dt}{2\pi} e^{it(E_c^f - E_c^i + \hbar\omega)} \sum_{nn'} e^{i\vec{q}(\vec{r}_n - \vec{r}_{n'})}$$

$$\times \langle \Phi^i | e^{-i\vec{q}\cdot\vec{u}_{n'}} | \Phi^f \rangle \langle \Phi^f | e^{i\vec{q}\cdot\vec{u}_n} | \Phi^i \rangle$$

Replacing E_c^f & E_c^i by H_c, we find

$$S(\vec{q},\omega) = \frac{1}{N}\int \frac{dt}{2\pi\hbar} e^{i\omega t} \sum_{nn'} e^{i\vec{q}\cdot(\vec{r}_n - \vec{r}_{n'})} \langle \Phi^i | e^{-i\vec{q}\cdot\vec{u}_{n'}} | \Phi^f \rangle$$

$$\langle \Phi^f | e^{iH_c t/\hbar} e^{i\vec{q}\cdot\vec{u}_n} e^{-iH_c t/\hbar} | \Phi^i \rangle$$

$$e^{i\vec{q}\cdot\vec{u}_n(t)}$$

$$\therefore S(\vec{q},\omega) = \frac{1}{N}\int \frac{dt}{2\pi\hbar} e^{i\omega t} \sum_{n,n'} e^{i\vec{q}\cdot(\vec{r}_n - \vec{r}_{n'})} \langle \Phi^i | e^{-i\vec{q}\cdot\vec{u}_{n'}} e^{i\vec{q}\cdot\vec{u}_n(t)} | \Phi^i \rangle$$

Therefore, the relevant quantity is

$$\langle e^{-i\vec{q}\cdot\vec{u}_n} e^{i\vec{q}\cdot\vec{u}_n(t)} \rangle$$

Note that $\hat{a}_{k\lambda}(t) = e^{-i\omega_{k\lambda}t}\hat{a}_{k\lambda}$, $\hat{a}^+_{k\lambda}(t) = e^{i\omega_{k\lambda}t}\hat{a}^+_{k\lambda}$

$$[a_{k\lambda}, a^+_{k'\lambda'}] = \delta_{kk'}\delta_{\lambda\lambda'}$$

$$\therefore \vec{u}_n(t) = \frac{1}{\sqrt{N}} \sum_{p\lambda} \sqrt{\frac{\hbar}{2M\omega_{p\lambda}}} \left[\hat{a}_{p\lambda}\vec{\epsilon}_{p\lambda} e^{-i(\vec{p}\cdot\vec{r}_n + \omega_{p\lambda}t)} + \hat{a}^+_{p\lambda}\vec{\epsilon}^*_{p\lambda} e^{i(\vec{p}\cdot\vec{r}_n + \omega_{p\lambda}t)} \right]$$

$$[\vec{q}\cdot\vec{u}_{n'}, \vec{q}\cdot\vec{u}_n(t)] = \frac{1}{N}\sum_{p\lambda} \frac{\hbar}{2M\omega_{p\lambda}} \left[e^{i\omega_{p\lambda}t} - e^{-i\omega_{p\lambda}t} \right] (\vec{\epsilon}_{p\lambda}\cdot\vec{q})(\vec{\epsilon}^*_{p\lambda}\cdot\vec{q})$$

$e^{i\vec{p}\cdot(\vec{r}_n - \vec{r}_{n'})}$ $\quad$ $e^{i\vec{p}\cdot(\vec{r}_{n'} - \vec{r}_n)}$

$$= \text{const} \quad (\text{not an operator})$$

Now, $e^A e^B = e^{A+B} e^{\frac{1}{2}[A,B]}$ $\quad [A,B] = \text{const}$

$$\therefore \langle e^A e^B \rangle = \langle e^{A+B} \rangle e^{\frac{1}{2}[A,B]}$$

$$= e^{\frac{1}{2}\langle (A+B)^2 \rangle + \cdots} e^{\frac{1}{2}[A,B]}$$

$$= e^{\frac{1}{2}\langle A^2 + AB + BA + B^2 \rangle + \frac{1}{2}[A,B]} + \cdots$$

$$= e^{\frac{1}{2}\langle A^2 + 2AB + B^2 \rangle} + \cdots$$

$\because \langle [\vec{u}_n(0)\cdot\vec{q}]^2 \rangle = \langle (\vec{u}_n(t)\cdot\vec{q})^2 \rangle$

Therefore,

$$\langle e^{-i\vec{q}\cdot\vec{u}_{n'}} e^{i\vec{q}\cdot\vec{u}_n(t)} \rangle$$

$$= e^{-(\vec{q}\cdot\vec{u}_n)^2} e^{\langle (\vec{q}\cdot\vec{u}_{n'})(\vec{q}\cdot\vec{u}_n(t)) \rangle}$$

Debye-Waller factor e^{-2W}

$$2W = \langle (\vec{q}\cdot\vec{u}_n)^2 \rangle$$

$$= \frac{1}{N} \sum_{pp'\lambda\lambda'} \sqrt{\frac{\hbar}{2M\omega_{p\lambda}}} \sqrt{\frac{\hbar}{2M\omega_{p'\lambda'}}}$$

$$\langle [\hat{a}_{p\lambda}(\vec{q}\cdot\vec{\epsilon}_{p\lambda}) e^{i\vec{p}\cdot\vec{r}_n} + \hat{a}^+_{p\lambda}(\vec{q}\cdot\vec{\epsilon}^*_{p\lambda}) e^{-i\vec{p}\cdot\vec{r}_n}]$$

$$[\hat{a}_{p'\lambda'}(\vec{q}\cdot\vec{\epsilon}_{p'\lambda'}) e^{-i\vec{p}'\cdot\vec{r}_{n'}} + \hat{a}^+_{p'\lambda'}(\vec{q}\cdot\vec{\epsilon}^*_{p'\lambda'}) e^{i\vec{p}'\cdot\vec{r}_{n'}}] \rangle$$

$$\langle \hat{a}_{p\lambda}\hat{a}^+_{p'\lambda'} \rangle = \delta_{pp'}\delta_{\lambda\lambda'}(n_{p\lambda}+1)$$

$$\langle \hat{a}^+_{p\lambda}\hat{a}_{p'\lambda'} \rangle = \delta_{pp'}\delta_{\lambda\lambda'} n_{p\lambda}$$

$$2W = \sum_{p\lambda} \frac{1}{N} \frac{\hbar^2 |\vec{q}\cdot\vec{\epsilon}_{p\lambda}|^2}{2M\hbar\omega_{p\lambda}} (2n_{p\lambda}+1)$$

$$\therefore S(\vec{q},\omega) = \sum_{nn'} \frac{1}{N} e^{i\vec{q}\cdot(\vec{r}_n - \vec{r}_{n'})} \int \frac{dt}{2\pi\hbar} e^{i\omega t} e^{-2W} e^{\langle (\vec{q}\cdot\vec{u}_{n'})(\vec{q}\cdot\vec{u}_n(t)) \rangle}$$

For small displacement $\vec{u}$, we can expand

$$e^{\langle (\vec{q}\cdot\vec{u}_{n'})(\vec{q}\cdot\vec{u}_n(t)) \rangle} = 1 + \langle (\vec{q}\cdot\vec{u}_{n'})(\vec{q}\cdot\vec{u}_n(t)) \rangle + \cdots$$

Zeroth order — zero phonon process

. . This is the case of ideal lattice . . . . .

$$S(q=K-K_0,\omega)=\sum_{n,n'}\frac{1}{N}e^{i\vec{q}\cdot(\vec{r}_n-\vec{r}_{n'})}\left[\int\frac{dt}{2\pi\hbar}e^{i\omega t}\right]e^{-2W}\cdots$$

$\sum_{n,n'}\frac{1}{N}e^{i\vec{q}\cdot(\vec{r}_n-\vec{r}_{n'})}=\sum_G\delta_{q,G}$

$\int\frac{dt}{2\pi\hbar}e^{i\omega t}=\delta(\hbar\omega)$ ← elastic

graphically: $\vec{K}$, $-\vec{G}$, $\vec{K}_0$

$\vec{K}=\vec{K}_0+\vec{G}$

$\vec{G}$ is absorbed by the whole lattice.

First order

$$S^{(1)}(\underset{\parallel}{K}-K_0,\omega)=\sum_{n,n'}\frac{1}{N}e^{i\vec{q}\cdot(\vec{r}_n-\vec{r}_{n'})}\int\frac{dt}{2\pi\hbar}e^{i\omega t}e^{-2W}\langle(\vec{q}\cdot\vec{u}_{n'})(\vec{q}\cdot\vec{u}_n(t))\rangle$$
$$q$$

$$\langle(\vec{q}\cdot\vec{u}_{n'})(\vec{q}\cdot\vec{u}_n(t))\rangle$$

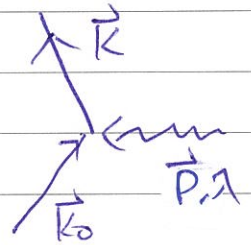
$$=\frac{1}{N}\sum_{\substack{pp'\\ \lambda\lambda'}}\sqrt{\frac{\hbar}{2M\omega_{p\lambda}}}\sqrt{\frac{\hbar}{2M\omega_{p'\lambda'}}}$$
$$\langle\left[\hat{a}_{p\lambda}(\vec{\epsilon}_{p\lambda}\cdot\vec{q})e^{-i\vec{p}\cdot\vec{r}_{n'}}+\hat{a}^{+}_{p\lambda}(\vec{q}\cdot\vec{\epsilon}^{*}_{p\lambda})e^{i\vec{p}\cdot\vec{r}_{n'}}\right]$$
$$\left[\hat{a}_{p'\lambda'}(\vec{\epsilon}_{p'\lambda'}\cdot\vec{q})e^{-i(\vec{p}'\cdot\vec{r}_n+\omega_{p'\lambda'}t)}+\hat{a}^{+}_{p'\lambda'}(\vec{q}\cdot\vec{\epsilon}^{*}_{p'\lambda'})e^{i(\vec{p}'\cdot\vec{r}_n+\omega_{p'\lambda'}t)}\right]\rangle$$

$$=\frac{1}{N}\sum_{p\lambda}\frac{\hbar^2|\vec{q}\cdot\vec{\epsilon}_{p\lambda}|^2}{2M\hbar\omega_{p\lambda}}\left[\langle a^{+}_{p\lambda}a_{p\lambda}\rangle e^{-i\omega_{p\lambda}t}+\langle\hat{a}_{p\lambda}\hat{a}^{+}_{p\lambda}\rangle e^{i\omega_{p\lambda}t}\right]\cdot$$

$\langle a^{+}_{p\lambda}a_{p\lambda}\rangle = n_{p\lambda}$, $e^{i\vec{p}\cdot(\vec{r}_{n'}-\vec{r}_n)}$, $\langle\hat{a}_{p\lambda}\hat{a}^{+}_{p\lambda}\rangle = n_{p\lambda}+1$, $e^{-i\vec{p}\cdot(\vec{r}_{n'}-\vec{r}_n)}$

$$\therefore S^{(1)}(K-K_0,\omega)$$
$$=e^{-2W}\sum_{\substack{\lambda p\\ G}}\frac{N\hbar^2|\vec{q}\cdot\vec{\epsilon}_{p\lambda}|^2}{2M\hbar\omega_{p\lambda}}\left[\delta(\hbar\omega-\hbar\omega_{p\lambda})\delta(\vec{q}-\vec{p}+\vec{G})n_{p\lambda}\right.$$
$$\left.+\delta(\hbar\omega+\hbar\omega_{p\lambda})\delta(\vec{q}+\vec{p}+\vec{G})(n_{p\lambda}+1)\right]$$

The first term corresponds to destroying a phonon (absorbing a phonon) during the scattering:



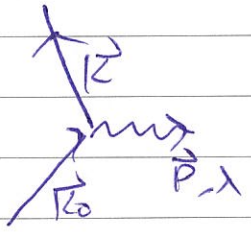
$$\vec{q} = \vec{K} - \vec{K}_0 = \vec{P}, \quad \vec{K} = \vec{K}_0 + \vec{P} \ (+G)$$

$$\hbar\omega = \frac{\hbar^2 K^2}{2m} - \frac{\hbar^2 K_0^2}{2m} = \hbar\omega_{P\lambda}$$

$$E_K = E_{K_0} + \hbar\omega_{P\lambda}$$

(absorb a phonon)

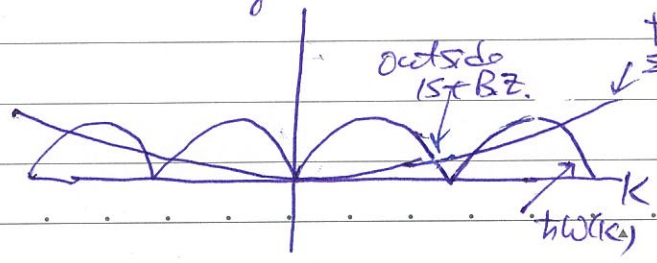
the 2nd term: emitting a phonon



$$\vec{q} = -\vec{P}, \quad \vec{K} = \vec{K}_0 - \vec{P} \ (+\vec{G})$$

$$E_K = E_0 - \hbar\omega_{P\lambda}$$

In addition, summation over n makes it possible to add $\vec{G}$ (reciprocal lattice vector) to $\vec{K}_0 \pm \vec{P}$ so that any $\vec{K} - \vec{K}_0$ can exceed 1st B.Z. This is known as umklapp scattering (process), first discussed by R. Peierls. The meaning is "turn over" in German word. In 1D, the addition of G is easily to reverse the direction of $\vec{K}_0$. The umklapp scattering is most important in phonon-phonon interaction which be discussed later. Here, as an example, the scattering for $K_0 = 0$ is: one phonon is absorbed



obviously, one has two-phonon scattering, 3-phonon scattering, ...

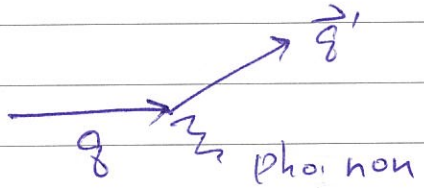
Optical measurement of phonons

visible light (usually from a high intensity laser beam)

$k \sim 10^5\ cm^{-1}$

1st B.Z. size $\sim 10^8\ cm^{-1}$

$\therefore$ only probe $k \sim 0$



phonon is acoustic $\Rightarrow$ Brillouin scattering

" " optical $\Rightarrow$ Raman "

X-ray : hard to do

$E_x \sim 10\ keV$ } $1 : 10^6$!

$\hbar\omega_{ph} \sim 10\ meV$

Contribution of phonons to specific heat

To find the specific heat due to phonons, we need to find

$$U = \frac{1}{Z} \sum_{\{n_{k\lambda}\}} \hbar\omega_{k\lambda}\left(n_{k\lambda}+\tfrac{1}{2}\right) e^{-\beta \sum_{k\lambda} \hbar\omega_{k\lambda}\left(n_{k\lambda}+1/2\right)}$$

$$Z = \sum_{n_{k_1\lambda_1}=0}^{\infty} \sum_{n_{k_2\lambda_2}=0}^{\infty} \cdots \; e^{-\beta \sum_{k\lambda} \hbar\omega_{k\lambda}\left(n_{k\lambda}+1/2\right)}$$

& $C_V = \frac{1}{V} \frac{\partial U}{\partial T}\Big|_V$

The standard trick is to write

$U = -\frac{\partial \ln Z}{\partial \beta}$. Hence one needs to find $\ln Z$. Usually, this is defined as the Free energy

$$F = -k_B T \ln Z \quad \therefore \quad U = \frac{\partial \beta F}{\partial \beta}$$

Now, Z can be found as

$$Z = \prod_{k\lambda}^{\infty} \left\{ \sum_{n=0}^{\infty} e^{-\beta \hbar\omega_{k\lambda}\left(n+1/2\right)} \right\}$$

$$= \prod_{k\lambda}^{\infty} \frac{e^{-\beta\hbar\omega_{k\lambda}/2}}{1 - e^{-\beta\hbar\omega_{k\lambda}}}$$

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$$F = -k_B T \ln Z = \sum_{k\lambda} \frac{1}{2}\hbar\omega_{k\lambda} + k_B T \ln\left(1 - e^{-\beta\hbar\omega_{k\lambda}}\right)$$

Contribution of zero-point energy

$$\therefore U = \frac{\partial(\beta F)}{\partial \beta} = \sum_{k\lambda} \frac{1}{2}\hbar\omega_{k\lambda} + \frac{\hbar\omega_{k\lambda}}{e^{\beta\hbar\omega_{k\lambda}} - 1}$$

$$= \sum_{k\lambda} \hbar\omega_{k\lambda}\left(\langle n_{k\lambda}\rangle + 1/2\right), \quad \langle n_{k\lambda}\rangle = \frac{1}{e^{\beta\hbar\omega_{k\lambda}} - 1}$$

$$\therefore C_V = \frac{1}{V}\sum_{k\lambda} \hbar\omega_{k\lambda} \frac{\partial\langle n_{k\lambda}\rangle}{\partial T}$$

$$= \int_0^\infty d\omega \sum_{k\lambda} \delta(\omega - \omega_{k\lambda}) \frac{1}{V}\hbar\omega \cdot \frac{\partial\langle n\rangle}{\partial T}$$

The quantity $\frac{1}{V}\sum_{k\lambda} \delta(\omega - \omega_{k\lambda}) = D(\omega)$

is the density of state for phonon. and it must satisfy $3N = V\int_0^\infty d\omega\, D(\omega)$ --- (16)

$$\therefore C_V = \int_0^\infty d\omega\, D(\omega) \frac{\partial}{\partial T}\left(\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right) \quad --- (17)$$

The optical modes $\lesssim 16$ THz (1 THz $= 4.2$ meV)
~ 67 meV Room T $= \frac{1}{40}$ eV $= 25$ meV

∴ For high temperature ($k_B T \gg$ all $\hbar\omega \sim 300$K), $\beta\hbar\omega \ll 1$

$$\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \sim \frac{\hbar\omega}{\beta\hbar\omega} \sim k_B T$$

$$\therefore C_V \sim \int_0^\infty d\omega\, D(\omega) \times k_B = \frac{3Nk_B}{V} = 3nk_B$$

⇒ recover Dulong & Petit's law

For low Temperature, one needs to ..... consider the acoustic modes $\omega_\lambda = C_\lambda |K|$.

Since typical $C \sim 1000$ m/sec, for $T = 10K$,

ν (freequence) $= \frac{10 K_B}{4.2 meV} \sim 0.208$ THz,

$\lambda \sim 4ff\text{Å} >> a$. Therefore, $O(10K)$ is a rough (upper) boundary for low T.

$$D(\omega) = \frac{1}{V} \sum_{K\lambda} \delta(\omega - \omega_{K\lambda}) = \int \frac{d^3K}{(2\pi)^3} \sum_\lambda \delta(\omega - \omega_\lambda(|K|))$$

$$= \int \frac{d^3K}{(2\pi)^3} \sum_\lambda \delta(\omega - C_\lambda |K|)$$

$$= \sum_\lambda \frac{4\pi \left(\frac{\omega}{C_\lambda}\right)^2 \frac{1}{C_\lambda}}{(2\pi)^3} = \frac{\omega^2}{2\pi^2} \sum_\lambda \left(\frac{1}{C_\lambda^3}\right) \equiv \frac{3\omega^2}{2\pi^2 C^3}$$

$$\therefore C_V = \frac{3\hbar}{2\pi^2 C^3} \frac{\partial}{\partial T} \int_0^\infty d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$

$$= \frac{3\hbar}{2\pi^2 C^3} \frac{\partial}{\partial T} \left(\frac{1}{(\beta\hbar)^4}\right) \Big|_0^\infty dx \frac{x^3}{e^x - 1} \qquad \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}$$

$$= \frac{2\pi^2}{5} K_B \left(\frac{K_B T}{\hbar C}\right)^3 \propto T^3$$

T^3 is a character of phonon's contribution to the specific heat regardless the system!

To calculate $C_V(T)$, one needs to calculate detailed temperature of $D(\omega)$ in details. Historically, before this is doable, simple guesses were employed to get the qualitative picture of $C_V(T)$:

Einstein & Debye models.

Einstein : $D(\omega) = \frac{3N}{V}\delta(\omega-\omega_0)$

Debye : $D(\omega) = \frac{3\omega^2}{2\pi^2 c^3}\theta(\omega_D-\omega)$ Sudden cutoff at ω_D = "Debye frequency"

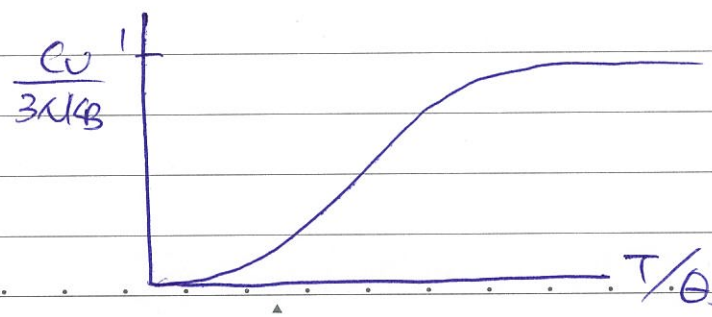
$\therefore \frac{3N}{V} = \int_0^\infty d\omega\, D(\omega) = 3n$

$\therefore \frac{\omega_D^3}{2\pi^2 c^3} = 3n, \quad n = \frac{\omega_D^3}{6\pi^2 c^3}$

$k_B\theta_D \equiv \hbar\omega_D$, θ_D = Debye temperature Characterizes the upper cut energy scale of acoustic phonons. ~ a few hundred!

In this approximation, one finds

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



Anharmonic effects

The harmonic approximation is the key approximation we have used in the above.

The approximation can't explain two important properties of solid, however.

(i) Equilibrium properties (such as thermal expansion)

Rigorously harmonic crystal ⇒ size would not depend on T !

$$U = U^{eq} + \frac{1}{2}\sum_{ij} u^{\alpha}(r_i)\, D^{\alpha\beta}(r_i - r_j)\, u^{\beta}(r_j)$$

($D^{\alpha\beta}(r_i - r_j)$: independent of u)

if solids expand, $\bar{r}_i = (1+\epsilon) r_i$, since the ($\epsilon \propto \Delta V$)
atom position $\bar{r}_i + \bar{u}(\bar{r}_i) = r_i + u(r_i)$, one

has $u(r_i) = \bar{u}(\bar{r}_i) + \epsilon r_i$

($\bar{u}$: displacement w.r.t. the new eq. position $\bar{r}_i$)

Using $\bar{u}$, we find (linear term = 0, if $\bar{r}_i$ are equilibrium)

$$U = U^{eq} + \frac{1}{2}\epsilon^2 \sum_{ij} r_i^{\alpha} D^{\alpha\beta}(r_i - r_j) r_j^{\beta} + \frac{1}{2}\sum_{ij} \bar{u}^{\alpha}(r_i)\, D^{\alpha\beta}(r_i - r_j)\, \bar{u}^{\beta}(r_j)$$

(U^{eq} + ϵ^2 term: independent of $\bar{u}$)

∴ Dynamics of oscillations in new equilibrium is the same, and doesn't depend on ϵ (ΔV) !

Hence quantities such as $\frac{\partial}{\partial V}\hbar\omega_\lambda(k)=0$ ....

(V = volume of crystal)

As a result, thermal expansion = 0:

$$\alpha \equiv \frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow 3V\alpha = \frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(-\frac{\partial P}{\partial V}\right)_T}$$

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T \quad (\text{bulk modulus})$$

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

$$\therefore 3V\alpha = -\frac{V}{B}\frac{\partial^2 F}{\partial V \partial T}$$

$$F = \sum_{k\lambda}\frac{1}{2}\hbar\omega_\lambda(k) + k_BT\ln\left(1-e^{-\beta\hbar\omega_\lambda(k)}\right)$$

$$\left(\frac{\partial F}{\partial V}\right)_T = \sum_{k\lambda}\frac{\partial \hbar\omega_\lambda(k)}{\partial V}\left(n_{k\lambda}+\frac{1}{2}\right)$$

$$\frac{\partial^2 F}{\partial V \partial T} = \sum_{k\lambda}\frac{\partial n_{k\lambda}}{\partial T}\frac{\partial \hbar\omega_\lambda(k)}{\partial V} = 0 \quad \therefore \alpha = 0 \;?!$$

$$\because C_V = \sum_{k\lambda}\underbrace{\frac{\hbar\omega_\lambda(k)}{V}\frac{\partial n_{k\lambda}}{\partial T}}_{\equiv C_{k\lambda}}$$

One usually defines the Grüneisen parameter γ by

$$\gamma = \frac{\sum_{k\lambda}\left(-\frac{\partial \ln\omega_\lambda(k)}{\partial \ln V}\right)C_{k\lambda}}{\sum_{k\lambda}C_{k\lambda}} = \frac{\sum_{k\lambda}\frac{-V}{\omega_\lambda(k)}\frac{\partial\omega_\lambda(k)}{\partial V}C_{k\lambda}}{C_V}$$

$$\therefore \frac{\partial^2 F}{\partial V \partial T} = -\gamma C_V$$

$$\therefore \alpha = \frac{\gamma C_V}{3B}$$

In reality, $\gamma \sim O(1)$, $\alpha \neq 0$. Hence it indicates that one has to go beyond the harmonic approximation.

The existence of anharmonic terms also implies DOS depends on U & T!

(iii) Transport: thermal conductivity

A rigorously harmonic crystal ⇒ { thermal conductivity $= \infty$! ; there is no thermalization!

The thermal conductivity K is defined by the heat current transport under a temperature gradient $\frac{dT}{dx}$: $J_u = -K \frac{dT}{dx}$.

i.e., the temperature gradient $\frac{dT}{dx}$ is the drive for generating heat current!

Without $\frac{dT}{dx}$, there is no current of thermal energy.

However, in the harmonic crystals, phonons are independent of each other (just like ideal gas): In terms of eq. of motion,

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

is linear in u_n!

if u_n for a phonon satisfies the equation.

v_n for another phonon " this "

u_n+v_n still satisfies the equation just like superposition! They don't affect each other.

Therefore, if initially $\sum_{k\lambda}\hbar k\, n_{k\lambda} \neq 0$, it will flow without the need of the drive $\frac{dT}{dx}$!

Since it carries thermal energy $U=\sum \hbar\omega_\lambda(k)\, n_{k\lambda}$,

$\Delta u \neq 0$, even when $\frac{dT}{dx}=0$. $\therefore$ $K=\infty$!

In addition, it also implies that distribution of phonon, $n_{k\lambda}$, will not relax to $\frac{1}{e^{\beta\hbar\omega_{k\lambda}}-1}$!

Formally, the thermal conductivity can be evaluated ...

τ = mean collision time, C = speed of sound

$\ell = \tau C$ = mean free length

Starting at x_0, the collision happens at $\sim x_0 - \ell\cos\theta$. θ = velocity of phonon $\wedge$ x-axis.

$$\therefore J_u = \langle C\cos\theta\, u(x_0 - \ell\cos\theta)\rangle$$

J_u: energy flux along x-direction; u: energy density; $\langle\,\rangle$: average over angle

$$= \int_0^\pi C\cos\theta\, u(x_0 - \ell\cos\theta)\frac{2\pi d\theta}{4\pi}\sin\theta$$

$$= \frac{1}{2}\int_{-1}^{1} y\,dy\; C\,u(x_0 - \ell y)$$

$$u(x_0 - \ell y) = u(x_0) - \ell y\frac{du}{dx} \cdots$$

$$= -C\ell\frac{du}{dx}\frac{1}{2}\int_{-1}^{1} y^2 dy$$

$$= \frac{1}{3}C\ell\frac{du}{dT}\left(-\frac{dT}{dx}\right)$$

$$= K$$

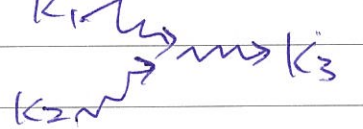
$$K = \frac{1}{3}C\ell C_v$$

Therefore, without scattering to change $\vec{k}$ of phonons, $\ell = \infty$; $K = \infty$

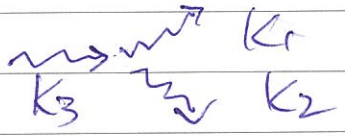
Umklapp process & thermal conductivity

It is clear that one needs to change $\vec{k}$ distribution of phonon in order to have finite k. This is possible if one includes anharmonic terms; i.e., non-linear terms, so that superposition no longer works. The lowest orders are $o(u^3)$ & $O(u^4)$.

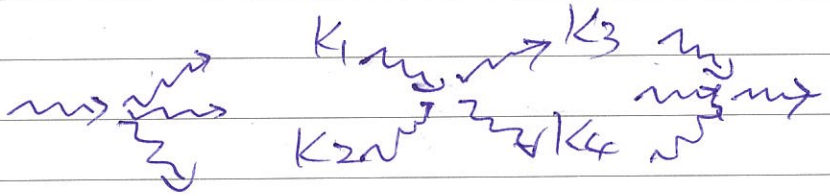
In this case, one has collisions among phonons (graphically):



$k_3 = k_1 + k_2$ $(O(u^3))$



or



$k_1 + k_2 = k_3 + k_4$

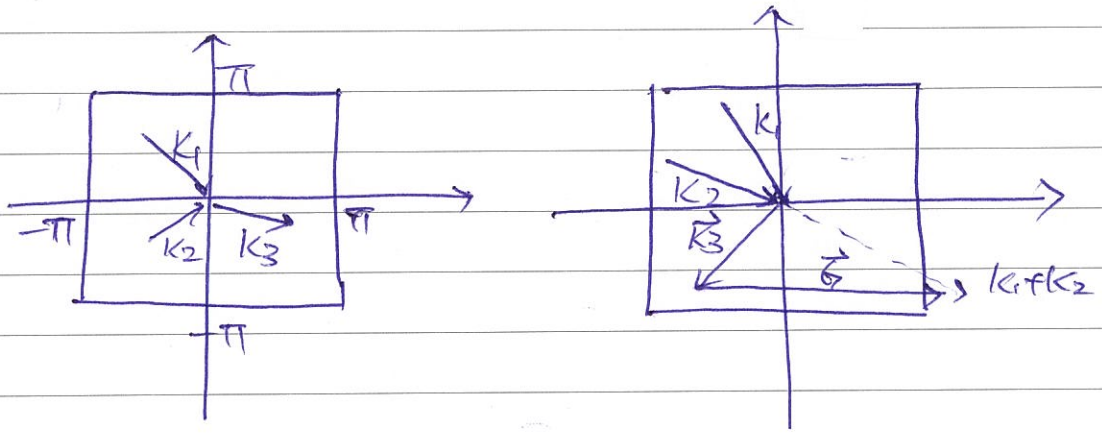
The other possibility is due to boundaries or imperfection. This possibility can be controlled by good samples & moving away from the boundary.

It may seem that collisions provide a change to get finite K. Nonetheless, for above processes, $\hbar\vec{k}$ are still conserved!

Hence total $\vec{k}$ is not consumed!

To really consume $\vec{k}$, one needs the umklapp process as first noticed by R. Peierls.

3-phonon process



Temperature dependent of K for insulator

$$K = \frac{1}{3} C G l = \frac{1}{3} C^2 G \tau$$

l = mean distance between umklapp process

$$k_1 + k_2 = k_3 + G$$

$|\vec{k}_1|, |\vec{k}_2| \sim \frac{1}{2}$ zone boundary

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At zone boundary, $\hbar\omega_\lambda(K) \sim k_B\theta_D$

∴ phonon capable of suffering umklapp process $\bar{\epsilon} \simeq \frac{1}{2}k_B\theta_D$

$T \gg \theta_D$ all modes are excited (including the above $\bar{\epsilon} = \frac{1}{2}k_B\theta_D$)

$$\langle n \rangle = \frac{1}{e^{\beta\hbar\omega} - 1} \simeq \frac{k_B T}{\hbar\omega} \propto T$$

$C_v \sim$ const.

$\frac{1}{\tau}$ (scattering rate) $\propto n^x$ (typically $1 \le x \le 2$) expt

theory: competition between u^3 & u^4

$\therefore \frac{1}{\tau} \propto T^x$ ($\langle n \rangle \sim T$)

$\rightarrow K \propto \tau \propto \frac{1}{T^x}$

$T \lesssim \theta_D$ $\bar{\epsilon} \simeq \frac{1}{2}k_B\theta_D$

$$\langle n \rangle \sim \frac{1}{e^{\frac{\theta_D}{2T}} - 1} \sim e^{-\theta_D/2T}$$

$\frac{1}{\ell} \sim \frac{1}{\tau} \sim e^{-\theta_D/2T}$, $C_v \sim$ const

$K \sim e^{T_0/T}$ $T_0 \sim \theta_D/2$

$T \to 0$ $\ell \sim e^{\theta_D/2T}$ ↑ until reach the characteristic length of sample imperfection / boundary, ℓ stops. (umklapp is frozen out) $K \propto C_v \propto T^3$

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∴ Finally