

Why Phonons?

- Phonons contribute to the free energy \rightarrow **Thermodynamics** (T, P) including thermal expansion, stability
- Vibrational frequencies determine **thermal transport** and **superconducting properties**
- **Comparison with experiment**: interpretation of spectroscopic techniques (infrared, Raman, inelastic x-ray / neutron scattering) requires accounting for phonons.
- Phonons participate in **optical properties** (e.g. indirect s/c)
- Phonons explain **acoustic waves** in crystals.
- Phonons are needed to work out transition rates (**kinetics**).
- Phonons determine structural **phase transitions** (mode softening)
- Strongly **anharmonic systems**: beyond 2nd order (harmonicity). Also: close to instability, light atoms (H), high T, near melting.

Separation of electrons and nuclei

• $\hat{H} = \hat{H}_e + \hat{H}_n + \hat{H}_{en}$ $\hat{H} \psi(R, x) = E \psi(R, x)$

\swarrow electronic coordinates
 \searrow nuclei coordinates

$$\hat{H}_e = \hat{T}_e + U_{ee}, \quad \hat{H}_n = \hat{T}_n + U_{nn}, \quad \hat{H}_{en} = U_{en}$$

$$\begin{aligned}
 & \downarrow & & \downarrow & & \downarrow \\
 & -\sum_i \frac{\hbar^2}{2m} \Delta_i & & -\sum_A \frac{\hbar^2}{2M_A} \Delta_A & & -\sum_i \sum_A \frac{z_A e^2}{|R_A - r_i|} \\
 & & & & & \downarrow \\
 & & & & & \frac{1}{2} \sum_{A, B} \frac{z_A z_B e^2}{R_{AB}}
 \end{aligned}$$

• A way to exact solution:

$$\left[\hat{T}_e(x) + U_{ee}(x) + U_{en}(x, R) + U_{nn}(R) \right] \psi_\zeta(x, R) = U_\zeta(R) \psi_\zeta(x, R)$$

R-fixed

This corresponds to classical nuclei. m (electron) $\ll M$ (nucleus)

Quantum nuclei:

$$\psi(R, x) = \sum_\zeta \chi_\zeta(R) \psi_\zeta(x, R) \Rightarrow \text{Schrödinger eq.}$$

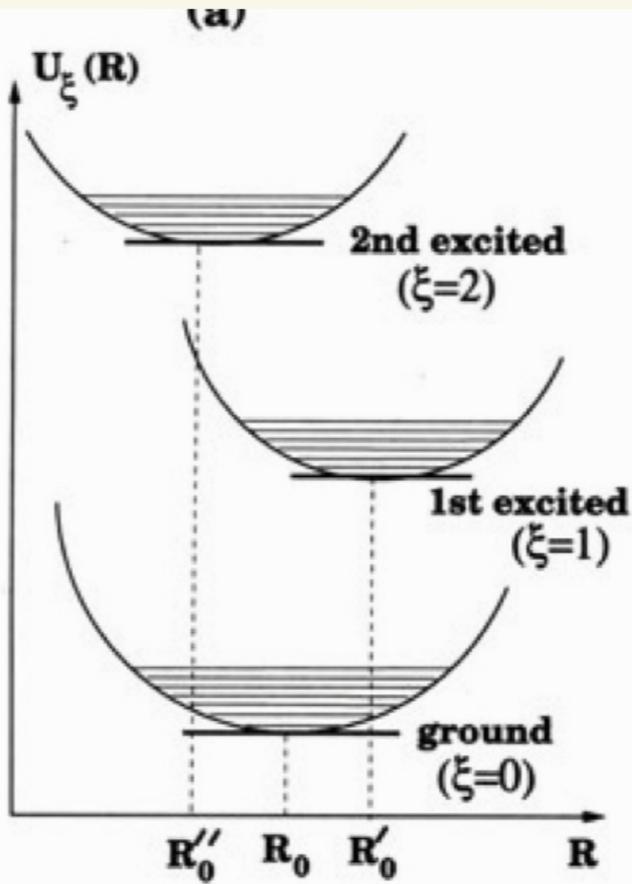
\swarrow Exact non-adiabatic equations
(v. complex!)

- $U_\xi(R)$ - adiabatic potential for the electronic state ξ

$$\Psi(R, x) = \Psi_\xi(x, R) \chi_{\xi\alpha\epsilon}(R)$$

$$\left[\hat{T}_n + U_\xi(R) + \Lambda_{\xi\xi}(R) \right] \chi_{\xi\alpha\epsilon} = E_{\xi\alpha\epsilon} \chi_{\xi\alpha\epsilon}$$

PES $E_\xi(R)$

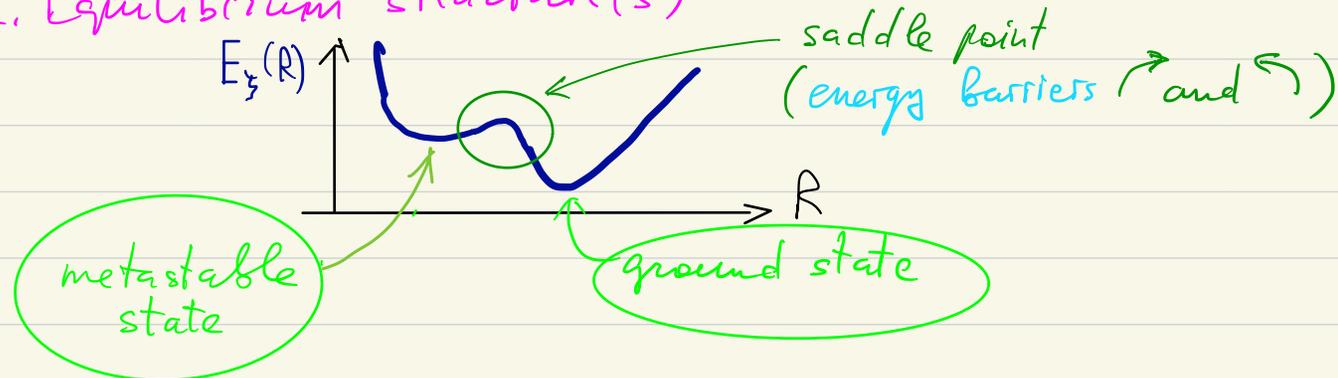


$$\hbar\omega / |E_0(R) - E_1(R)| \ll 1$$

← when the adiabatic approximation is valid

What can we learn from PES?

1. Equilibrium structure(s)

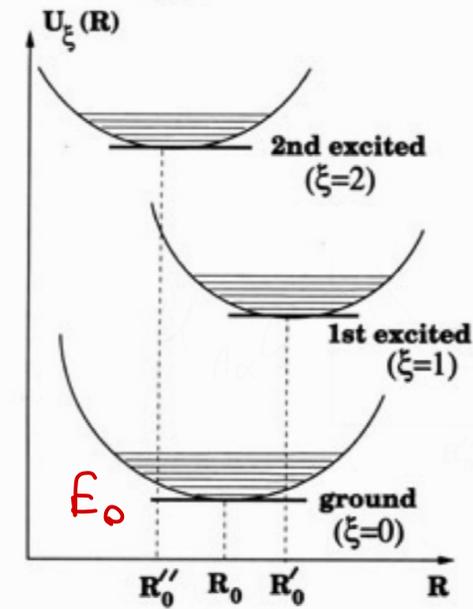


2. Thermodynamics (EOS)

3. Vibrations \Rightarrow thermal properties, transition rates (kinetics), stability

- Solve the equations for $\chi_{\xi}(R)$ for the given PES ξ (e.g. ground state)

$$[\hat{T}_n + E(R)] \chi_{\xi}(R) = E_{\xi} \chi_{\xi}(R)$$



- Expand the PES in atomic displacements: $U_{A\alpha} = R_{A\alpha} - R_{A\alpha}^0$

$$E(R) = E_0 + \sum_{A\alpha} \underbrace{\left(\frac{\partial E}{\partial R_{A\alpha}} \right)^0}_{=0} U_{A\alpha} + \frac{1}{2} \sum_{A\alpha, A'\alpha'} \underbrace{\left(\frac{\partial^2 E}{\partial R_{A\alpha} \partial R_{A'\alpha'}} \right)^0}_{(\Phi_{A\alpha, A'\alpha'})} U_{A\alpha} U_{A'\alpha'} + \text{(Anharmonic terms)}$$

\uparrow
- atomic forces

force constant matrix \Rightarrow vibrations

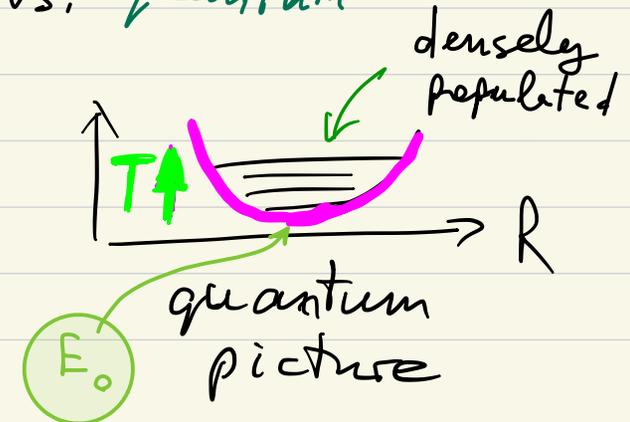
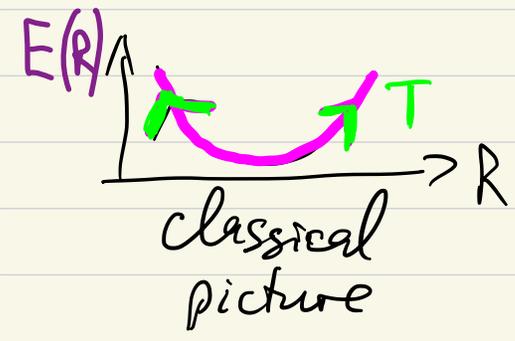
(=0 at the minimum)

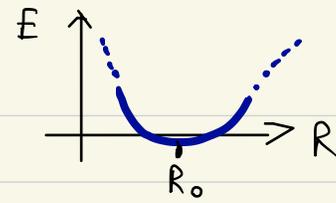
Comparison:
classical vs. quantum

$$E_{\xi} = E_0 + (\text{due to vibrations})$$

\hookrightarrow PES minimum

2nd order: harmonic approximations





A-atom
 $\alpha - x, y, z$

• We consider a simple PES, e.g. the ground state.

$$E = E_0 + \frac{1}{2} \sum_{ij} \Phi_{ij} u_i u_j \quad j, i \equiv (A, \alpha) \quad \leftarrow \text{harmonic approximation}$$

quadratic form $\Phi_{ij} = \Phi_{ji}$ (Φ - symmetric matrix)

• Translational symmetry: $\vec{u}_A \equiv \vec{v}$ for $\forall i$

$$\text{The force } F_{A\alpha} = -\frac{\partial E}{\partial u_{A\alpha}} = -\sum_{A'\alpha'} \Phi_{A\alpha, A'\alpha'} u_{A'\alpha'} = -\sum_{\alpha'} v_{\alpha'} \left(\sum_{A'} \Phi_{A\alpha, A'\alpha'} \right) = 0 \Rightarrow \sum_{A'} \Phi_{A\alpha, A'\alpha'} = 0$$

• Periodic systems (crystals) $i, j \Rightarrow (\vec{L}, s, \alpha)$ \vec{L} - unit cell; $\alpha - x, y, z$
 s - atom within the cell

(a) displace 1 atom $u_{Ls\alpha} \neq 0 \Rightarrow \Delta E = \frac{1}{2} \Phi_{s\alpha, s\alpha}^{LL} u_{Ls\alpha}^2 \Rightarrow \Phi_{s\alpha, s\alpha}^{LL}$ does not depend on L

(b) displace 2 atoms $u_{Ls\alpha}$ and $u_{L's'\alpha'} \neq 0 \Rightarrow \Delta E = \frac{1}{2} (\Phi_{Ls\alpha, Ls\alpha}^{LL} u_{Ls\alpha}^2 + \Phi_{L's'\alpha', L's'\alpha'}^{L'L'} u_{L's'\alpha'}^2) + \Phi_{Ls\alpha, L's'\alpha'}^{LL'} u_{Ls\alpha} u_{L's'\alpha'}$

$\Rightarrow \Phi^{LL'}$ can only depend on the difference $L-L' \Rightarrow \Phi^{LL'} \equiv \Phi^{L-L'}$

[we may first consider $L=L'$ but $s \neq s'$; then $L \neq L'$]

Classical picture

$$H = \sum_i \frac{p_i^2}{2M_i} + \frac{1}{2} \sum_{ij} \Phi_{ij} u_i u_j \quad i \equiv (\alpha) \quad p_i = M_i \dot{u}_i$$

$$\dot{p}_k = F_k, \quad F_k = -\frac{\partial}{\partial u_k} \left[\frac{1}{2} \sum_{ij} \Phi_{ij} u_i u_j \right] = -\sum_i \Phi_{ki} u_i \Rightarrow \boxed{M_{\cdot k} \ddot{u}_k = -\sum_i \Phi_{ki} u_i}$$

Change to matrix notations: $M \ddot{U} = -\Phi U$

$$M = \begin{pmatrix} M_1 & & 0 \\ & M_2 & \\ 0 & & \ddots \end{pmatrix} \quad u = \begin{pmatrix} u_1 \\ u_2 \\ \vdots \end{pmatrix} \quad \Phi = \begin{pmatrix} \Phi_{11} & \Phi_{12} & \dots \\ \Phi_{21} & \Phi_{22} & \dots \\ \dots & \dots & \dots \end{pmatrix}$$

$$V = M^{1/2} U \Rightarrow M^{1/2} \ddot{V} = -\Phi M^{-1/2} V \Rightarrow \boxed{\ddot{V} = -DV}$$

Dynamical matrix $\boxed{D = M^{-1/2} \Phi M^{-1/2}}$

$$D_{ij} = \frac{1}{\sqrt{M_i M_j}} \Phi_{ij}$$

Trial solution: $V(t) = Y e^{i\omega t}$, $-\omega^2 Y = -DY$ or $\boxed{DY = \omega^2 Y}$ Eigenproblem

\Rightarrow normal modes are: $u = M^{-1/2} V$, $V = Y e^{i\omega t} \Rightarrow u = M^{-1/2} Y e^{i\omega t}$

$\boxed{u^{(x)} = M^{-1/2} Y_\lambda e^{i\omega_\lambda t}}$ \Rightarrow full solution is a linear combination

- Full solution can also be obtained as follows:

$$u = M^{-1/2} V, \quad \ddot{V} = -D V \quad D Y_\lambda = \omega_\lambda^2 Y_\lambda, \quad Y_\lambda^T Y_{\lambda'} = \delta_{\lambda\lambda'}$$

$$D = \sum_\lambda \omega_\lambda^2 Y_\lambda Y_\lambda^T \quad (\text{spectral theorem})$$

$$\ddot{V} = - \sum_\lambda \omega_\lambda^2 Y_\lambda Y_\lambda^T V \Rightarrow \ddot{V} = - \sum_\lambda \omega_\lambda^2 Y_\lambda \underbrace{(Y_\lambda^T V)}_{y_\lambda \text{ (scalar)}} \quad \Big| \quad Y_{\lambda'}^T \times$$

$$\ddot{y}_\lambda = - \sum_{\lambda'} \omega_\lambda^2 \underbrace{(Y_{\lambda'}^T Y_\lambda)}_{\delta_{\lambda\lambda'}} y_{\lambda'} \Rightarrow \boxed{\ddot{y}_{\lambda'} = - \omega_{\lambda'}^2 y_{\lambda'}} \quad (\text{harmonic oscillator})$$

with the scalar solution: $y_\lambda(t) = A_\lambda e^{i\omega_\lambda t} + B_\lambda e^{-i\omega_\lambda t} = A_\lambda e^{i\omega_\lambda t} + \text{c.c.}$
(must be real)

$V(t)$ is obtained via: $y_\lambda = Y_\lambda^T V \quad \Big| \quad \sum_\lambda Y_\lambda \times$

$$\sum_\lambda Y_\lambda y_\lambda = \underbrace{\left(\sum_\lambda Y_\lambda Y_\lambda^T \right)}_E V \equiv V \Rightarrow V(t) = \sum_\lambda y_\lambda(t) Y_\lambda$$

$$u(t) = M^{-1/2} V = M^{-1/2} \sum_\lambda Y_\lambda (A_\lambda e^{i\omega_\lambda t} + B_\lambda e^{-i\omega_\lambda t}) = M^{-1/2} \sum_\lambda Y_\lambda y_\lambda(t)$$

$$= \sum_\lambda (A_\lambda u^{(\lambda)}(t) + \text{c.c.}) \quad (\text{must be real})$$

Normal modes

$$y_\lambda = Y_\lambda^T V = Y_\lambda^T M^{1/2} U \quad \rightarrow \quad y_\lambda = \sum_i \sqrt{m_i} Y_{\lambda i} u_i$$

u_i ordinary displacements

$$u_i = \frac{1}{\sqrt{m_i}} \sum_\lambda Y_{\lambda i} y_\lambda \quad \leftarrow \quad \text{normal coordinates}$$

The vibrational frequencies: $|D - \omega^2 E| = 0$ E - identity matrix

$$D = D^T \text{ (symmetric) } \Rightarrow$$

Eigenvectors Y_λ can be all chosen orthonormal:

$$Y_\lambda^T Y_{\lambda'} = \delta_{\lambda\lambda'}$$

orthogonality

$$E = \sum_\lambda Y_\lambda Y_\lambda^T$$

completeness

Modal matrix of D :

$$U = (Y_1 Y_2 \dots Y_n)$$

$$U^T = U^{-1}$$

Stability

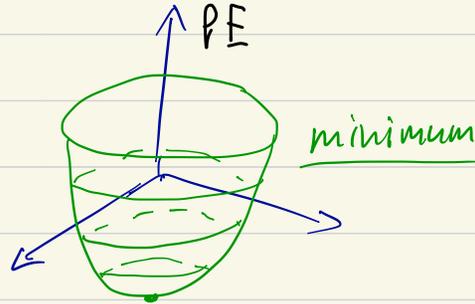
$$PE = \frac{1}{2} U^T \Phi U = \frac{1}{2} U^T (M^{1/2} \mathcal{D} M^{1/2}) U = \frac{1}{2} (M^{1/2} U)^T \mathcal{D} (M^{1/2} U)$$

$$\mathcal{D} = \sum_x \omega_x^2 Y_x Y_x^T \quad (\text{spectral theorem})$$

$$PE = \frac{1}{2} (M^{1/2} U)^T \sum_x \omega_x^2 Y_x Y_x^T (M^{1/2} U) = \frac{1}{2} \sum_x \omega_x^2 \underbrace{(M^{1/2} Y_x^T U)^T}_{\text{scalar} \Rightarrow y_x} \underbrace{(M^{1/2} Y_x^T U)}_{y_x} = \sum_x \frac{\omega_x^2 y_x^2}{2}$$

$$\boxed{D^T = D \Rightarrow \omega_x^2 \in \mathbb{R} \text{ (real)}}$$

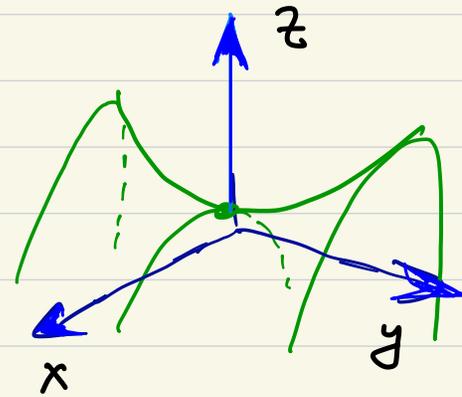
(a) $\omega_x^2 > 0$ for $\forall x \Rightarrow$ stable



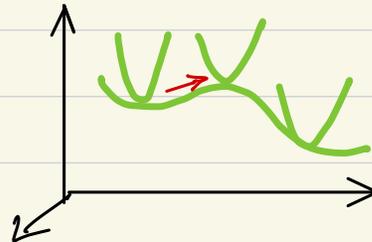
(b) $\exists \omega_x^2 < 0 \Rightarrow$ unstable

$$e^{\pm i \omega_x t} \Rightarrow e^{\pm i(i|\omega_x|)t} = e^{\mp |\omega_x| t}$$

dissociative solution



(c) $\exists \omega_x$ - small \Rightarrow soft mode



• for finite systems (e.g. molecules):

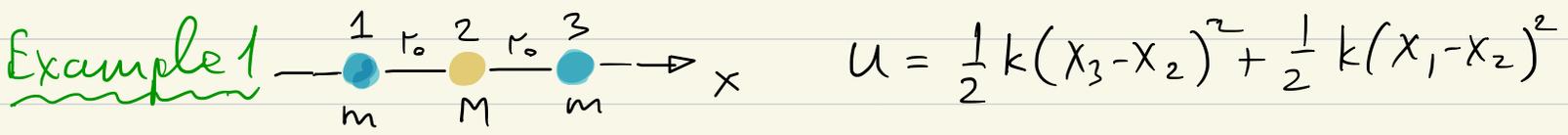
(a) translational invariance: momentum $\vec{P} = \sum_A m_A \dot{\vec{u}}_A = 0 \Rightarrow \boxed{\sum_A m_A u_{A\alpha} = 0}$ 3 DoF less

(b) rotational invariance: angular momentum $\vec{M} = \sum_A m_A [\vec{r}_A \times \dot{\vec{u}}_A] = 0$

Small vibrations: $\vec{M} = \sum_A m_A [(\vec{r}_A^0 + \vec{u}_A) \times \dot{\vec{u}}_A] \approx \sum_A m_A [\vec{r}_A^0 \times \dot{\vec{u}}_A] = \frac{d}{dt} \sum_A m_A [\vec{r}_A^0 \times \vec{u}_A] \equiv 0$
 $\Rightarrow \boxed{\sum_A m_A [\vec{r}_A^0 \times \vec{u}_A] = 0}$

Total # of DoF = $3N - 6$ (non-linear molecules)
 Linear molecules: $3N - 5$ (one rotation less)

3 DoF less as well



Condition: $m(x_1 + x_3) + M x_2 = 0 \Rightarrow x_2$ can be eliminated.

$KE = \frac{1}{2} m (\dot{x}_1^2 + \dot{x}_3^2) + \frac{1}{2} M \dot{x}_2^2 = \frac{mM}{4M} \dot{Q}_a^2 + \frac{m}{4} \dot{Q}_b^2$, $J = M + 2m$

$PE = U = \frac{kM^2}{4M^2} Q_a^2 + \frac{k}{4} Q_b^2$

New variables:

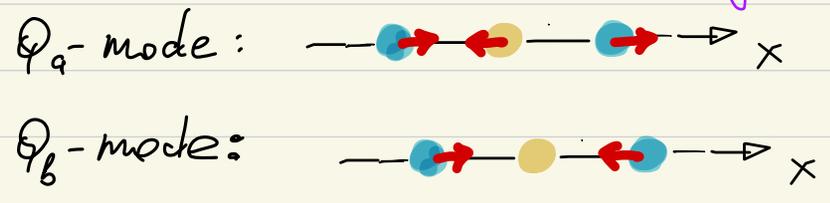
$Q_a = x_1 + x_3$
 $Q_b = x_1 - x_3$

$x_1 = \frac{1}{2} (Q_a + Q_b)$
 $x_3 = \frac{1}{2} (Q_a - Q_b)$
 $x_2 = -\frac{m}{M} Q_a$

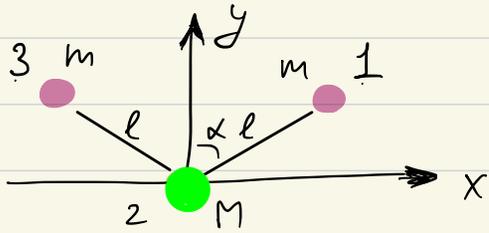
The Hamiltonian: $H = H_a + H_b$, $H_a = \frac{mM}{4M} \dot{Q}_a^2 + \frac{kM^2}{4M^2} Q_a^2$, $H_b = \frac{m}{4} \dot{Q}_b^2 + \frac{k}{4} Q_b^2$ (separable form)

Q_a, Q_b - normal coordinates with frequencies:

$\omega_a^2 = \frac{kM}{mM}$ and $\omega_b^2 = \sqrt{\frac{k}{m}}$



Example 2



Translational invariance:

$$m(x_1 + x_3) + Mx_2 = 0, \quad m(y_1 + y_3) + My_2 = 0$$

Rotational invariance:

$$m \left[\vec{r}_1^0 \times \begin{pmatrix} x_1 \\ y_1 \end{pmatrix} \right] + m \left[\vec{r}_3^0 \times \begin{pmatrix} x_3 \\ y_3 \end{pmatrix} \right] + M \left[\vec{r}_2^0 \times \begin{pmatrix} x_2 \\ y_2 \end{pmatrix} \right] = 0$$

$$\begin{pmatrix} l \sin \alpha \\ l \cos \alpha \end{pmatrix} \quad \begin{pmatrix} -l \sin \alpha \\ l \cos \alpha \end{pmatrix} \quad \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\sin \alpha (y_1 - y_3) - \cos \alpha (x_1 + x_3) = 0$$

Instead of 6 variables, we have only 3.

← 3 conditions

• Introduce new variables:

$$\begin{aligned} Q_a &= x_1 + x_3 \\ Q_{s2} &= y_1 + y_3 \\ Q_{s1} &= x_1 - x_3 \end{aligned}$$



$$\begin{cases} x_1 = \frac{1}{2}(Q_a + Q_{s1}) \\ y_1 = \frac{1}{2}(Q_{s2} + Q_a \operatorname{ctg} \alpha) \end{cases} \quad \begin{cases} x_2 = -\frac{m}{M} Q_a \\ y_2 = -\frac{m}{M} Q_{s2} \end{cases} \quad \begin{cases} x_3 = \frac{1}{2}(Q_a - Q_{s1}) \\ y_3 = \frac{1}{2}(Q_{s2} - Q_a \operatorname{ctg} \alpha) \end{cases}$$

• Considering \vec{r}_{12} and \vec{r}_{32} in the 1st order with respect to displacements x_1, y_1, x_2, y_2 and x_3, y_3 :

$$\delta l_{12} = (x_1 - x_2) \sin \alpha + (y_1 - y_2) \cos \alpha$$

$$\delta l_{32} = -(x_3 - x_2) \sin \alpha + (y_3 - y_2) \cos \alpha$$

The angle's $\Delta 321$ change can be obtained e.g. from $\cos(2\alpha + \delta\alpha) = \vec{r}_{12} \cdot \vec{r}_{32} / r_{12} r_{32} =$

$$\delta\alpha = \frac{1}{l} \left\{ [-(x_3 - x_2) + (x_1 - x_2)] \cos \alpha - [(y_3 - y_2) + (y_1 - y_2)] \sin \alpha \right\}$$

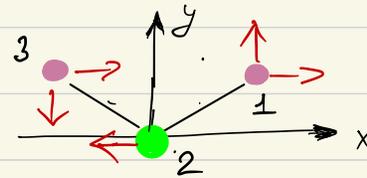
$$PE = \frac{k_1}{2} (\delta l_{12}^2 + \delta l_{32}^2) + \frac{k_2}{2} (e \delta \alpha)^2 = \frac{k_1}{4} \left(\frac{2m}{M} + \frac{1}{s^2} \right) \left(1 + \frac{2m}{M} s^2 \right) Q_a^2 + \frac{Q_{s1}^2}{4} (k_1 s^2 + 2k_2 c^2) + \left(\frac{\mu}{2M} \right)^2 Q_{s2}^2 (k_1 c^2 + 2k_2 s^2) + \frac{\mu}{2M} (k_1 - 2k_2) c s Q_{s1} Q_{s2}, \text{ where } c \equiv \cos \alpha, s \equiv \sin \alpha$$

$$\bullet KE = \frac{m}{2} (\dot{y}_1^2 + \dot{y}_3^2) + \frac{M}{2} \dot{l}_2^2 = \dot{Q}_a^2 \frac{M}{4} \left(\frac{2m}{M} + \frac{1}{s^2} \right) + \frac{m}{4} \dot{Q}_{s1}^2 + \frac{\mu m}{4M} \dot{Q}_{s2}^2$$

$$\bullet \text{EoM } \mathcal{L} = KE - PE, \quad \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{q}} = \frac{\partial \mathcal{L}}{\partial q} \quad (q \rightarrow Q_a, Q_{s1}, Q_{s2})$$

Q_a coordinate is already separated,

normal mode 1 $\Rightarrow \omega_a^2 = \frac{k_1}{m} \left(1 + \frac{2m}{M} \sin^2 \alpha \right)$ (63)



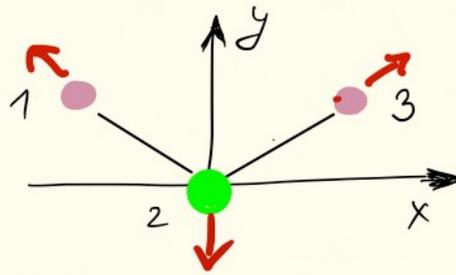
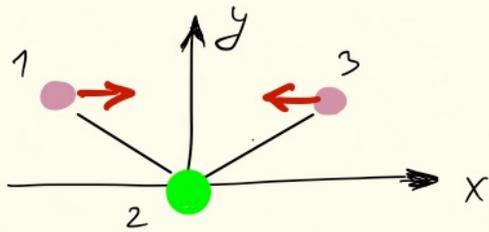
$Q_{s1} = Q_{s2} = 0$ $x_1 = x_3, \quad y_1 = -y_3$ $y_2 = 0, \quad x_2 \sim -x_1$
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Q_{s1} and Q_{s2} are still coupled:

$$\frac{d^2}{dt^2} \begin{pmatrix} Q_{s1} \\ Q_{s2} \end{pmatrix} = \begin{pmatrix} -\frac{1}{m} (k_1 s^2 + 2k_2 c^2) & -\frac{\mu}{mM} (k_1 - 2k_2) s c \\ -\frac{1}{m} (k_1 - 2k_2) c s & -\frac{\mu}{mM} (k_1 c^2 + 2k_2 s^2) \end{pmatrix} \begin{pmatrix} Q_{s1} \\ Q_{s2} \end{pmatrix} = -A \begin{pmatrix} Q_{s1} \\ Q_{s2} \end{pmatrix}$$

Vibrations $\begin{pmatrix} Q_{s1} \\ Q_{s2} \end{pmatrix} = Y e^{i\omega t}$ are obtained from $A Y = \omega^2 Y$, yielding

$$\omega^4 - \left[\frac{k_1}{m} \left(1 + \frac{2m}{M} c^2 \right) + \frac{2k_2}{m} \left(1 + \frac{2m}{M} s^2 \right) \right] \omega^2 + \frac{2\mu k_1 k_2}{M m^2} = 0$$



$$\Phi_a = 0 \Rightarrow \begin{cases} x_1 = \frac{1}{2} \Phi_{s1} \\ y_1 = \frac{1}{2} \Phi_{s2} \end{cases} \begin{cases} x_2 = 0 \\ y_2 = -\frac{m}{M} \Phi_{s2} \end{cases} \begin{cases} x_3 = -\frac{1}{2} \Phi_{s1} \\ y_3 = \frac{1}{2} \Phi_{s2} \end{cases} \quad \begin{matrix} \Phi_{s1} \sim \Phi_{s2} \\ \text{(from eigenvectors)} \\ \text{of } 2 \times 2 \end{matrix}$$

• A realistic force field model for H_2O :

$$U(x_1, x_2, \Delta\theta) \simeq U_0 + \frac{1}{2} k_r (\delta l_{12}^2 + \delta l_{32}^2) + \frac{1}{2} k_\theta \ell^2 \delta \alpha^2 + k_r' \delta l_{12} \delta l_{32} + k_{r\theta} \ell (\delta l_{12} + \delta l_{32}) \delta \alpha \quad (67)$$

$$k_r \simeq 52.76 ; k_\theta = 4.75 ; k_r' = -0.63 ; k_{r\theta} = 1.42 \text{ (eV/\AA}^2\text{)} ; \ell = 0.9576 \text{ \AA}$$

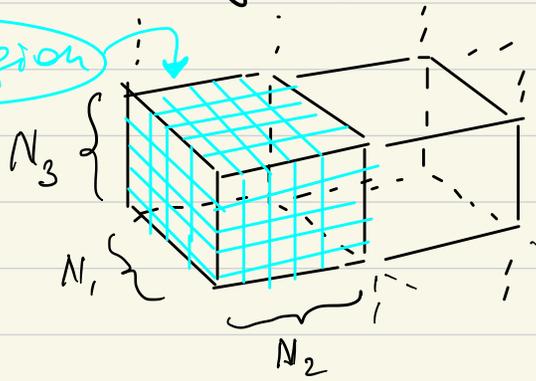
● Crystals

$i \equiv (L, s, \alpha)$ $DY = \omega^2 Y$

$\Rightarrow \sum_{L', s', \alpha'} D_{s\alpha, s'\alpha'}^{L-L'} Y_{s'\alpha'}^{L'} = \omega^2 Y_{s\alpha}^L$

Born, von Karman boundary conditions:

main region



$N = N_1 N_2 N_3$ primitive cells

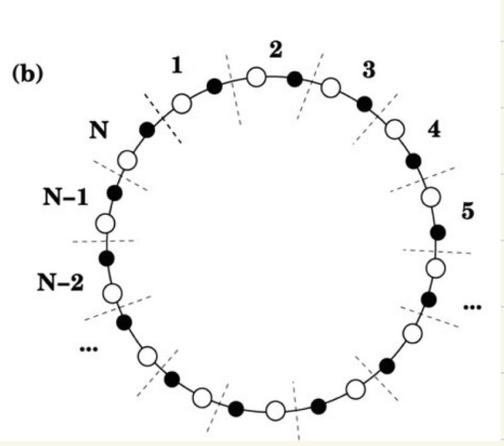
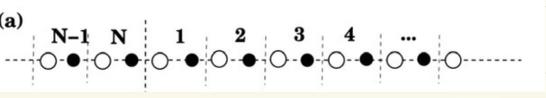
$\vec{a}_1, \vec{a}_2, \vec{a}_3$ - primitive lattice vectors

Bvk conditions:

$$U_{\vec{L} + N_1 \vec{a}_1} = U_{\vec{L}}$$

$$U_{\vec{L} + N_2 \vec{a}_2} = U_{\vec{L}}$$

$$U_{\vec{L} + N_3 \vec{a}_3} = U_{\vec{L}}$$



Reciprocal space: $\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$

\vec{b}_j - primitive reciprocal lattice vectors

Brillouin zone (BZ): $\vec{k} \in BZ$

Let us take some \vec{k} and apply $\sum_{\vec{L}} e^{-i\vec{k}\vec{L}}$ to both sides of

$$\sum_{L, L'} D^{L-L'} Y^{L'} e^{-i\vec{k}\vec{L}} = \omega^2 \left[\sum_{\vec{L}} e^{-i\vec{k}\vec{L}} Y_{\vec{L}} \right] \Rightarrow \left(\sum_{L''} D^{L''} e^{-i\vec{k}\vec{L}''} \right) \left(\sum_{L'} e^{-i\vec{k}\vec{L}'} Y^{L'} \right) = \omega^2 \left(\sum_{\vec{L}} e^{-i\vec{k}\vec{L}} Y_{\vec{L}} \right)$$

$$\Rightarrow \sum_{s', \alpha'} D_{s\alpha, s'\alpha'}^{\vec{k}} Y_{s'\alpha'}^{\vec{k}} = \omega_{\vec{k}}^2 Y_{s\alpha}^{\vec{k}}, \quad D^{\vec{k}} = \sum_{\vec{L}} D^{\vec{L}} e^{-i\vec{k}\vec{L}} \quad Y^{\vec{k}} = \sum_{\vec{L}} e^{-i\vec{k}\vec{L}} Y^{\vec{L}}$$

$$D^{\vec{k}} Y^{\vec{k}} = \omega_{\vec{k}}^2 Y^{\vec{k}}$$

finite size!

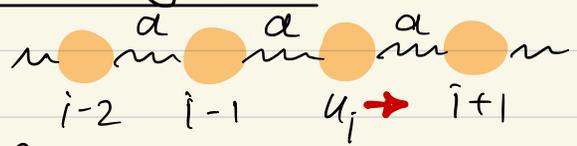
normal modes & their frequencies are characterised by the wave vector \vec{k} .

Translational symmetry!

Crystalline systems

Classical consideration

Example 3



Monoatomic lattice

$$\mathcal{L} = \sum_{n=-\infty}^{\infty} \left\{ \frac{1}{2} m \dot{u}_n^2 - \frac{1}{2} k (u_{n+1} - u_n)^2 \right\}, \quad \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{u}_n} = \frac{\partial \mathcal{L}}{\partial u_n}$$

$$\frac{\partial \mathcal{L}}{\partial \dot{u}_n} = m \dot{u}_n; \quad F_n = - \frac{\partial \mathcal{L}}{\partial u_n} = +k(u_{n+1} - u_n) - k(u_n - u_{n-1}) \Rightarrow m \ddot{u}_n = k(u_{n+1} - 2u_n + u_{n-1})$$

Use $u_n(t) = A_n e^{-i\omega t}$ with $A_n = A e^{ikan} \Rightarrow -A\omega^2 = k(e^{ika} - 2 + e^{-ika})A$

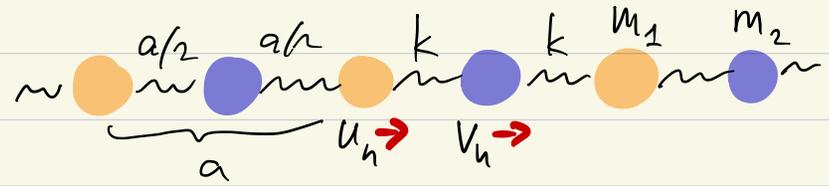
$$\omega^2 = \frac{2k}{m}(1 - \cos ka) \quad \text{and} \quad u_n^{(k)}(t) = A e^{-i\omega t} e^{ikan}$$

In the classical limit $a \rightarrow 0$ we have $u^{(k)}(t) \sim \exp[i(kx - \omega t)]$ a wave-like solution.
(acoustic wave)

Here $\omega(k)$ - dispersion relation.

$-\frac{\pi}{a} < k \leq \frac{\pi}{a}$ as otherwise solutions repeat themselves \Rightarrow BZ in 1D.

Example 4

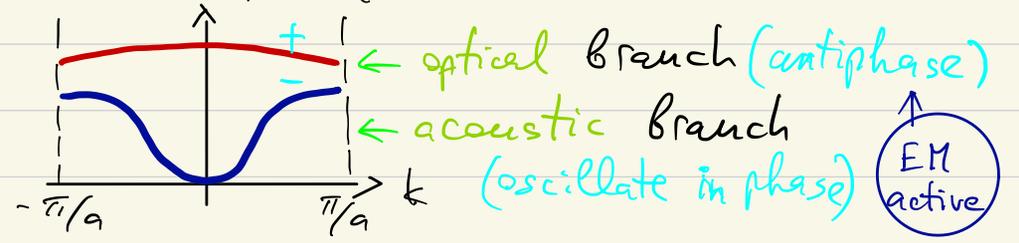


Two atoms in the basis ● v_n ● u_n

$$\begin{cases} m_1 \ddot{u}_n = k(v_n - 2u_n + u_{n-1}) \\ m_2 \ddot{v}_n = k(u_n - 2v_n + u_{n+1}) \end{cases} \Rightarrow \begin{pmatrix} u_n(t) \\ v_n(t) \end{pmatrix} = \begin{pmatrix} e_1 \\ e_2 \end{pmatrix} e^{i\omega t} e^{ikan} \Rightarrow \begin{pmatrix} 2k - m_1 \omega^2 & -k(1 + e^{-ika}) \\ -k(1 + e^{ika}) & 2k - m_2 \omega^2 \end{pmatrix} \begin{pmatrix} e_1 \\ e_2 \end{pmatrix} = 0$$

Yields two solutions: $\omega_{\pm}(k)$, $-\frac{\pi}{a} < k \leq \frac{\pi}{a}$

3D?



How can one calculate Φ ?

Example 5 Central forces

$$PE = \frac{1}{2} \sum_{AB} \sum' \phi(R_{AB}) \text{ nearest neighbours only (between unlike atoms)}$$

Expand the pairwise interaction: $\vec{R}_A = \vec{R}_A^0 + \vec{u}_A$, $\vec{R}_{AB} = \vec{R}_{AB}^0 + (\vec{u}_A - \vec{u}_B)$

$$\phi(R) = \phi(|\vec{R} + \vec{u}|) = \phi(R) + \sum_{\alpha} \left(\frac{\partial \phi}{\partial R_{\alpha}} \right)^0 u_{\alpha} + \frac{1}{2} \sum_{\alpha \alpha'} \left(\frac{\partial^2 \phi}{\partial R_{\alpha} \partial R_{\alpha'}} \right)^0 u_{\alpha} u_{\alpha'} + \dots$$

where: $\vec{u} = \vec{u}_i - \vec{u}_j$

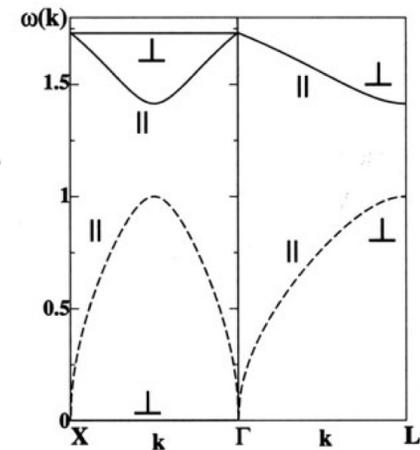
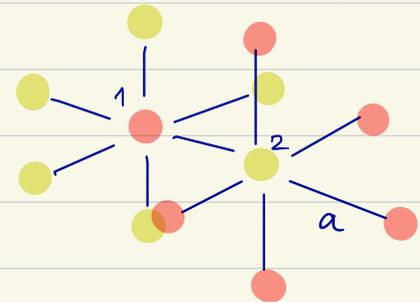
$$\frac{\partial \phi}{\partial R_{\alpha}} = \phi'(R) \frac{\partial R}{\partial R_{\alpha}} = \phi'(R) \frac{R_{\alpha}}{R}$$

$$\frac{\partial^2 \phi}{\partial R_{\alpha} \partial R_{\alpha'}} = \frac{\partial}{\partial R_{\alpha'}} \left(\phi'(R) \frac{R_{\alpha}}{R} \right) = \phi'(R) \frac{\delta_{\alpha \alpha'}}{R} + \frac{R_{\alpha} R_{\alpha'}}{R} \left(\frac{1}{R} \phi'(R) \right)' \equiv \Phi_{\alpha \alpha'}(\vec{R})$$

$$PE = \frac{1}{4} \sum_{AB} \sum'_{\alpha \alpha'} \phi_{\alpha \alpha'}(\vec{R}_{AB}^0) (\vec{u}_A - \vec{u}_B) (\vec{u}_A - \vec{u}_B) = \frac{1}{2} \sum_A \left(\sum_B \sum'_{\alpha \alpha'} \phi_{\alpha \alpha'}(R_{AB}^0) \right) u_{A\alpha} u_{A\alpha'} - \frac{1}{2} \sum_{AB} \sum'_{\alpha \alpha'} \phi_{\alpha \alpha'}(R_{AB}^0) u_{A\alpha} u_{B\alpha'}$$

$$\Rightarrow \Phi_{s\alpha, s'\alpha'}^{\vec{L}-\vec{L}'} = \delta_{LO} \delta_{ss'} \sum_{L''s''} \sum'_{\alpha \alpha'} \phi_{\alpha \alpha'}(\vec{L}_s - \vec{L}_{s''}) - \phi_{\alpha \alpha'}(\vec{L}_s - \vec{L}_{s'})$$

Binary fcc



Using ab initio methods

- Frozen phonon approximation

$U_3(R)$ - ground state property, can differentiate numerically

$F_{B\beta}^{(+)} = - \sum_{A'\alpha'} \Phi_{B\beta, A'\alpha'} u_{A'\alpha'} = - \Phi_{B\beta, A\alpha} u_{A\alpha}$

$\Phi_{B\beta, A\alpha} = - F_{B\beta}^{(+)} / u_{A\alpha}$

$u_{A\alpha} \neq 0$ only!

Better precision:
- $u_{A\alpha}$ as well

$\Phi_{B\beta, A\alpha} \approx - (F_{B\beta}^{(+)} - F_{B\beta}^{(-)}) / u_{A\alpha}$

$$\Phi_{B\beta, A\alpha} = \begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$$

$A\alpha$

$B\beta$

It won't be symmetric. Need to **impose** the symmetrisation posteriori by either accepting \triangle , ∇ or averaging over two.

Symmetry: the number of calculations can be reduced.

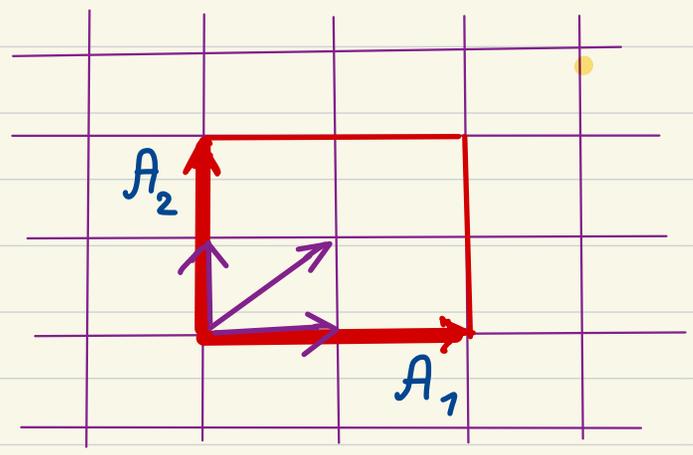
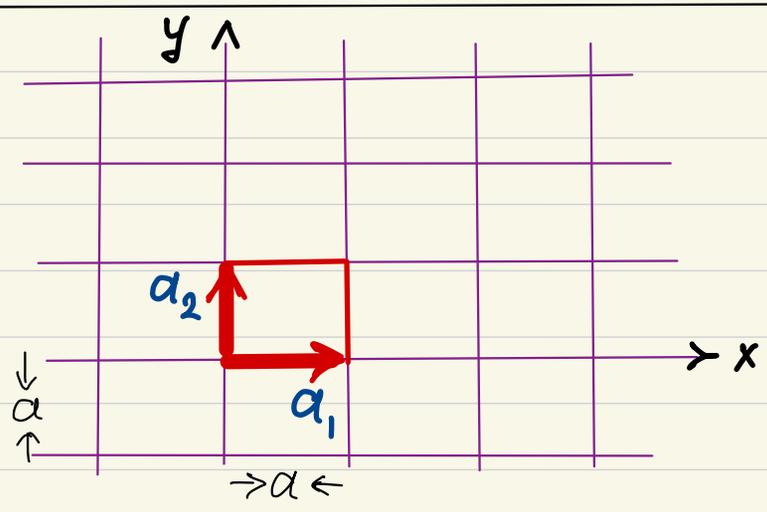
Taylor?

Interplay between primitive & super cells

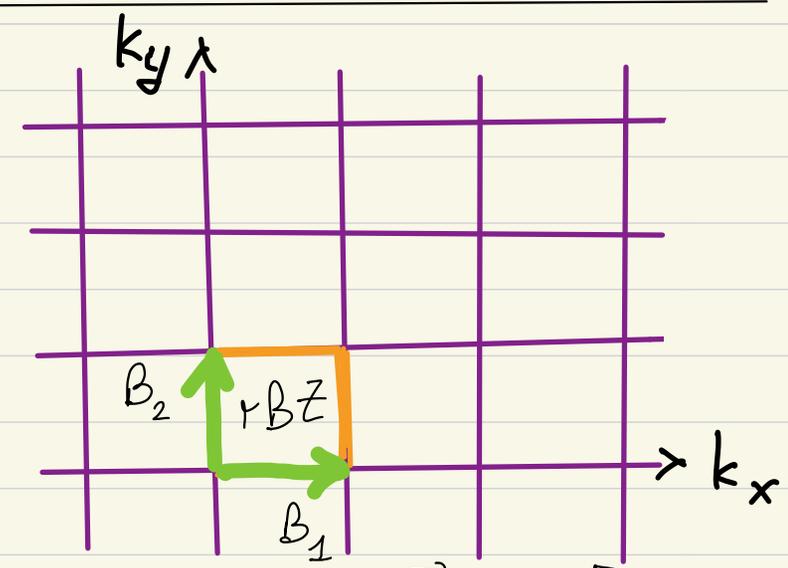
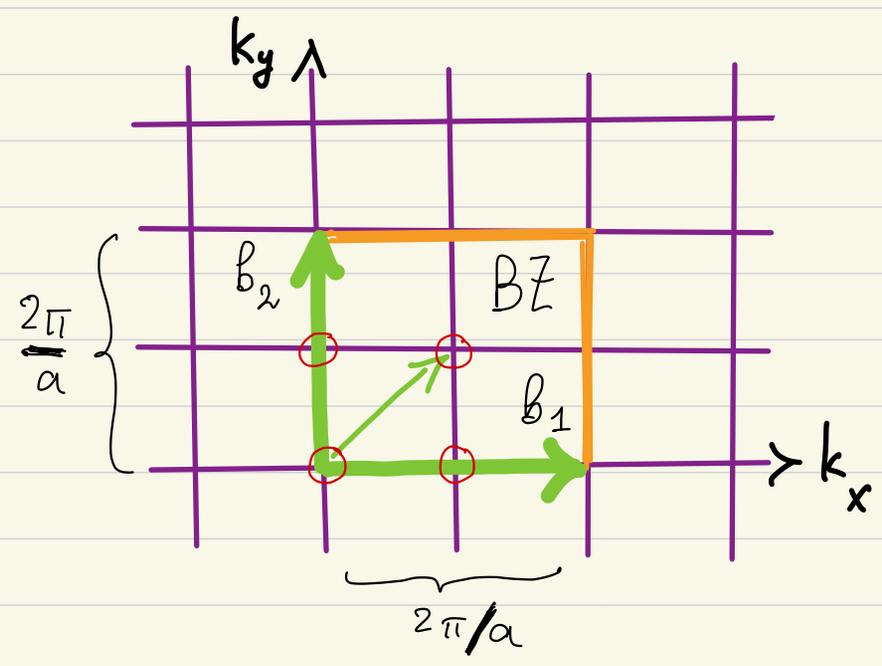
Primitive cell

Extended cell

Direct space



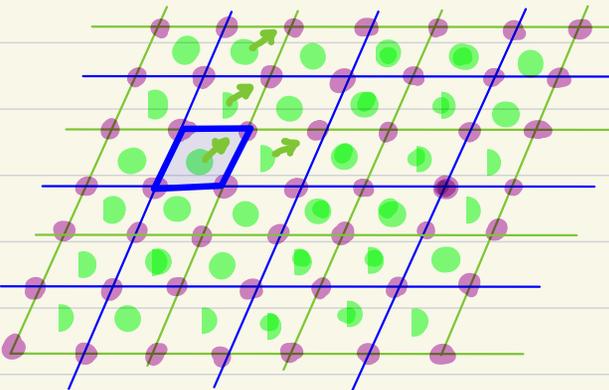
Reciprocal space



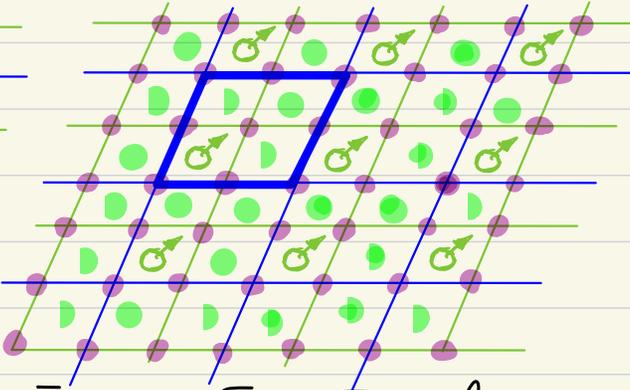
$$\vec{b}_2 = 2\vec{B}_2, \quad \vec{b}_1 = 2\vec{B}_1$$

○ BZ → rBZ are equivalent

• Periodic Boundary conditions (crystal phonons)

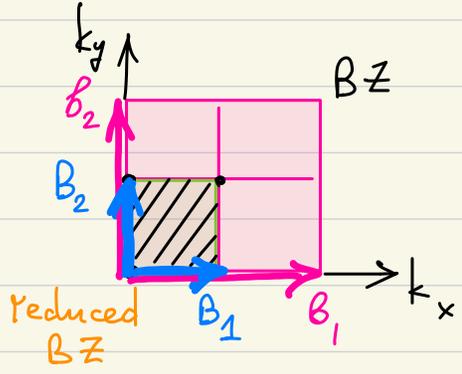


\bar{a}_1, \bar{a}_2 - primitive
 \bar{b}_1, \bar{b}_2 - reciprocal



$\bar{A}_1 = 2\bar{a}_1, \bar{A}_2 = 2\bar{a}_2$ - large
 $\bar{B}_1 = \bar{b}_1/2, \bar{B}_2 = \bar{b}_2/2$

$$\gamma^{\vec{k}} = \sum_{\vec{l}} e^{-i\vec{k}\cdot\vec{l}} \gamma^{\vec{l}} \Rightarrow \vec{k} = 0 \text{ only if } \gamma^{\vec{l}} \text{ are the same}$$



all
 $\vec{L} = \vec{N} + \vec{h}$
 large internal

$$D_{s\alpha_1 s'\alpha'}(k) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_L \Phi_{s\alpha_1 s'\alpha'}^{L,0} e^{-i\vec{k}\cdot\vec{L}} = \frac{1}{\sqrt{M_s M_{s'}}} \sum_N \sum_n \Phi_{s\alpha_1 s'\alpha'}^{N+n,0} e^{-i\vec{k}\cdot(N+n)}$$

$$= \frac{1}{\sqrt{M_s M_{s'}}} \sum_n \left[\sum_N \Phi_{s\alpha_1 s'\alpha'}^{N+n,0} e^{-i\vec{k}\cdot\vec{N}} \right] e^{-i\vec{k}\cdot\vec{n}} = \frac{1}{\sqrt{M_s M_{s'}}} \sum_n f_{s\alpha_1 s'\alpha'}^n(k) e^{-i\vec{k}\cdot\vec{n}}$$

• Displace $u_{0s_1\alpha_1}$ from $\vec{N}=0$: $F_{ns\alpha} = - \left[\sum_N \Phi_{s\alpha, s_1\alpha_1}^{N+n,0} \right] u_{0s_1\alpha_1}$

For those $k \in BZ$, for which $\exp(i\vec{k}\cdot\vec{N}) = 1$, equals $f_{s\alpha, s_1\alpha_1}^n$ exactly.

These are $k \in BZ$, which become $\sum_j m_j \vec{B}_j$ in the reduced BZ:

$$\exp\left[-i \sum_j m_j \vec{B}_j \cdot \vec{N}\right] = \exp\left[-i \sum_{jk} m_j p_k \underbrace{\vec{B}_j \cdot \vec{A}_k}_{2\pi \delta_{jk}}\right] = \exp(-2\pi i (\text{integer})) = 1$$

For crystals with PBC this method would only give vibrations for certain $\vec{k} \in \text{BZ}$. Larger UC are needed to have more \vec{k} points reproduced.
different

The method is EXACT!

Practical steps:

① given extension $\vec{A}_i = \sum_j T_{ij} \vec{a}_j$, determine all internal translations \vec{n}

② determine all $\vec{k} \in \text{BZ}$ that satisfy $e^{i\vec{k}\vec{N}} = 1$ for this extension } equivalent to
 $\vec{k} = 0$ from rBZ

③ displace atoms in the primitive unit cell $\Rightarrow f_{s\alpha, s'\alpha'}^n$

④ calculate $D_{s\alpha, s'\alpha'}(\vec{k}) \sim \sum_{\vec{n}} f_{s\alpha, s'\alpha'}^n e^{-i\vec{k}\vec{n}}$ for $\forall \vec{k} \in \text{BZ}$ equiv. to $\vec{k} = 0$ from rBZ

Playing with supercells:

- one cell \rightarrow many \vec{k} points (it will then be large)
 - many small cells designed for specific \vec{k} points
- TETR

• Small \vec{k} vectors require VERY LARGE extensions

• Numerical problems: "small" displacements; symmetrisation \boxtimes required,

• Problem: the smallest supercell to give a particular $\vec{k} \in \text{BZ}$?

• Calculating phonons at other k-points

(Interpolation)

$$D_{s\alpha, s'\alpha'}(k) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_L \Phi_{s\alpha, s'\alpha'}^{L,0} e^{-ikL}$$

$$\Phi_{s\alpha, s'\alpha'}^{n,0} = \sqrt{M_s M_{s'}} \frac{1}{N} \sum_k D_{s\alpha, s'\alpha'}(k) e^{ikn}$$

$$\approx \sqrt{M_s M_{s'}} \frac{1}{N_r} \sum_{k \in rBZ} D_{s\alpha, s'\alpha'}(k) e^{ikn}$$

symmetrize over the BZ

$$\Phi_{s\alpha, s'\alpha'}^{N+n,0} = 0 \text{ for any } N \neq 0$$

Once Φ is known in the direct space, then for any other $k \in BZ$:

$$D_{s\alpha, s'\alpha'}(k) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_N \sum_n \Phi_{s\alpha, s'\alpha'}^{N+n,0} e^{-ik(N+n)}$$

$$\approx \frac{1}{\sqrt{M_s M_{s'}}} \sum_n \Phi_{s\alpha, s'\alpha'}^{n,0} e^{-ikn}$$

$$= \frac{1}{N_r} \sum_{k_r \in rBZ} D_{s\alpha, s'\alpha'}(k_r) \left[\sum_n e^{i(k_r - k)n} \right]$$