Problem 4.

(a) Number of motion modes :

① Translational Motion in x, y, z directions

$$N_{tr} = 3$$

② Rotational Motion : L_x, L_y, L_z (angular momentum)

$$N_{rot} = 3 \quad (n > 2)$$
$$\text{or } 2 \quad (n = 2)$$

③ The others are vibrational :

$$N_{total} = 3\,(\text{3-dim space}) \times n - N_{tr} - N_{rot}$$
$$= 3n - 6$$

(b) $L = T - V$

$$= \sum_{i=1}^{n} \sum_{j=1}^{3} \frac{m}{2}\dot{x}_{i,j}^2 - \frac{k}{2}\left[(x_{i,j} - x_{[i+1],j})^2 + (x_{i,j} - x_{[i-1],j})^2\right]$$

$[i \pm 1]$ means some cyclic rotation

$$\Rightarrow \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}_{i,j}}\right) - \frac{\partial L}{\partial x_{i,j}} = 0$$

$$\Rightarrow m\ddot{x}_{i,j} + k\,(2x_{i,j} - x_{i-1,j} - x_{i+1,j}) = 0$$

Assume $x_{i,j}(t) = q_{i,j} \cdot e^{i\omega t} + c.c.$

$$[\vec{x}](t) = [\vec{q}]\, e^{i\omega t} + c.c.$$

← column vector of $(3 \times n)$-dim

$\Rightarrow -\omega^2 \underline{\mathbb{M}}\, \vec{q} + \underline{\mathbb{K}}\, \vec{q} = 0$

Where $\underline{\mathbb{M}} = m \underline{\mathbb{1}}$

$\underline{\mathbb{K}} = k \cdot \left(2\underline{\mathbb{1}} - \delta_{u,[v+1]} \otimes \underline{\mathbb{1}}_j - \delta_{u,[v-1]} \otimes \underline{\mathbb{1}}_j\right)$

$\delta_{u,[v\pm1]}$ iterates different atoms, and

$\underline{\mathbb{1}}_j$ is the identity matrix of 3-dim space

In $n=4$ case, we can specifically write the $\underline{\mathbb{M}}, \underline{\mathbb{K}}$ matrices as:

$$\underline{\mathbb{M}} = m \overbrace{\begin{bmatrix} 1 & & & \\ & \ddots & & \\ & & \ddots & \\ & & & 1 \end{bmatrix}}^{3\times4} \Big\} 3\times4$$

$$\underline{\mathbb{K}} = k \begin{bmatrix} 2 & -1 & 0 & -1 \\ -1 & 2 & -1 & 0 \\ 0 & -1 & 2 & -1 \\ -1 & 0 & -1 & 2 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

We can solve the eigenfrequencies and eigenvectors of $\underline{\mathbb{K}}$ of 3-dims separately

$$\underline{\mathbb{K}}_0 := k \begin{bmatrix} 2 & -1 & 0 & -1 \\ -1 & 2 & -1 & 0 \\ 0 & -1 & 2 & -1 \\ -1 & 0 & -1 & 2 \end{bmatrix}$$

has eigen frequencies & vectors:

$\omega_1 = 0, \quad \omega_2 = \sqrt{2}\sqrt{\frac{k}{m}}, \quad \omega_3 = 2\sqrt{\frac{k}{m}}$

$\vec{q}_1 = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix} \quad \vec{q}_2 = \begin{bmatrix} 1 \\ 0 \\ -1 \\ 0 \end{bmatrix} \quad \vec{q}_3 = \begin{bmatrix} -1 \\ 1 \\ -1 \\ 1 \end{bmatrix}$

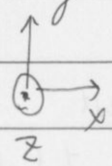
$\omega_4 = \sqrt{2}\sqrt{\frac{k}{m}}$

$\vec{q}_4 = \begin{bmatrix} 0 \\ 1 \\ 0 \\ -1 \end{bmatrix}$

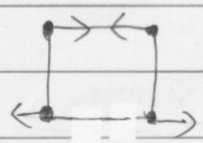
But we need to know these are eigenfreqs & vecs among atoms of a certain dim (x or y or z)

To obtain the vibrational modes, we need to superimpose the degenerate $\vec{q}_{i,j}$ of $j=1,2,3$, so that the total translational momentum & angular mom. are conserved

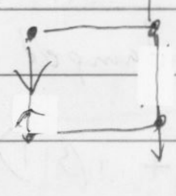
$\therefore$ We have the following 6 modes:



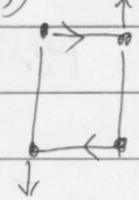
① $\omega_1 = 2\sqrt{\frac{k}{m}}$



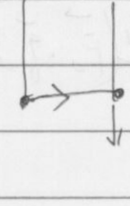
② $\omega_2 = 2\sqrt{\frac{k}{m}}$



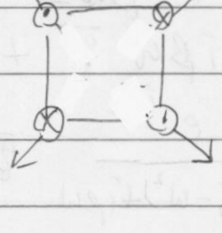
③ $\omega_3 = \sqrt{2}\sqrt{\frac{k}{m}}$



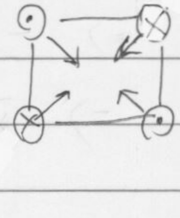
④ $\omega_4 = \sqrt{2}\sqrt{\frac{k}{m}}$



⑤ $\omega_5 = 2\sqrt{\frac{k}{m}}$



⑥ $\omega_6 = 2\sqrt{\frac{k}{m}}$



(C) Assume $\vec{x} = \sum\limits_{\text{all modes } s} \overset{\text{oscillation amp.}}{u_s} \, \overset{\text{dimensionless unit eigenvector of } \mathbb{K}}{\vec{q}_s} \cdot e^{i\omega t} + \text{c.c.}$

$$\underline{\mathbb{K}} \, \vec{q}_s = m \omega_s^2 \, \vec{q}_s$$

adding the damping factor

$$m \ddot{x}_{i,j} + \beta \dot{x}_{i,j} + k(2x_{i,j} - x_{[i+1],j} - x_{[i-1],j}) = F_{ext\,i,j}$$

$$-M D_t^2 \vec{x} + \beta D_t \vec{x} + \mathbb{K} \vec{x} = \vec{F}_{ext}$$

$$\Rightarrow \left(\sum_s -\omega^2 \underline{M} u_s \vec{q}_s + i\beta\omega \mathbb{1} u_s \vec{q}_s + \underline{\mathbb{K}} u_s \vec{q}_s \right) e^{i\omega t} + \text{c.c.}$$

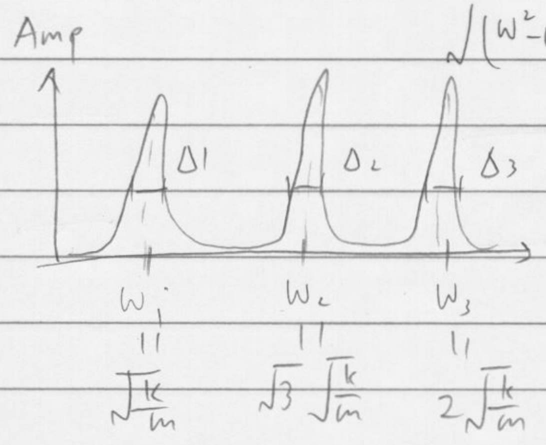
$$= \sum_s (\vec{F}_{ext} \cdot \vec{q}_s) \, \vec{q}_s$$

$$\Rightarrow [m(\omega_s^2 - \omega^2) + i\beta\omega] u_s = F_{0,s}$$

$$\vec{F}_{ext} \cdot \vec{q}_s = e^{i\omega t} \cdot F_{0,s} + \text{c.c.}$$

$$\Rightarrow u_s = \frac{F_{0,s}}{m(\omega^2 - \omega_s^2) + i\beta\omega} = \frac{F_{0,s}/m}{(\omega^2 - \omega_s^2) + i(\frac{\beta}{m})\omega}$$

$$\therefore |\vec{x}_s| = |u_s| \propto \frac{1}{\sqrt{(\omega^2 - \omega_s^2)^2 + \omega^2 (\frac{\beta}{m})^2}}$$



$\Delta s \propto \beta$

for Benzene ($n=6$)