PHY 711 Classical Mechanics and Mathematical Methods
10-10:50 AM MWF in Olin 103

Discussion for Lecture 18 – Chap. 4 (F & W)

Analysis of motion near equilibrium –

Normal Mode Analysis

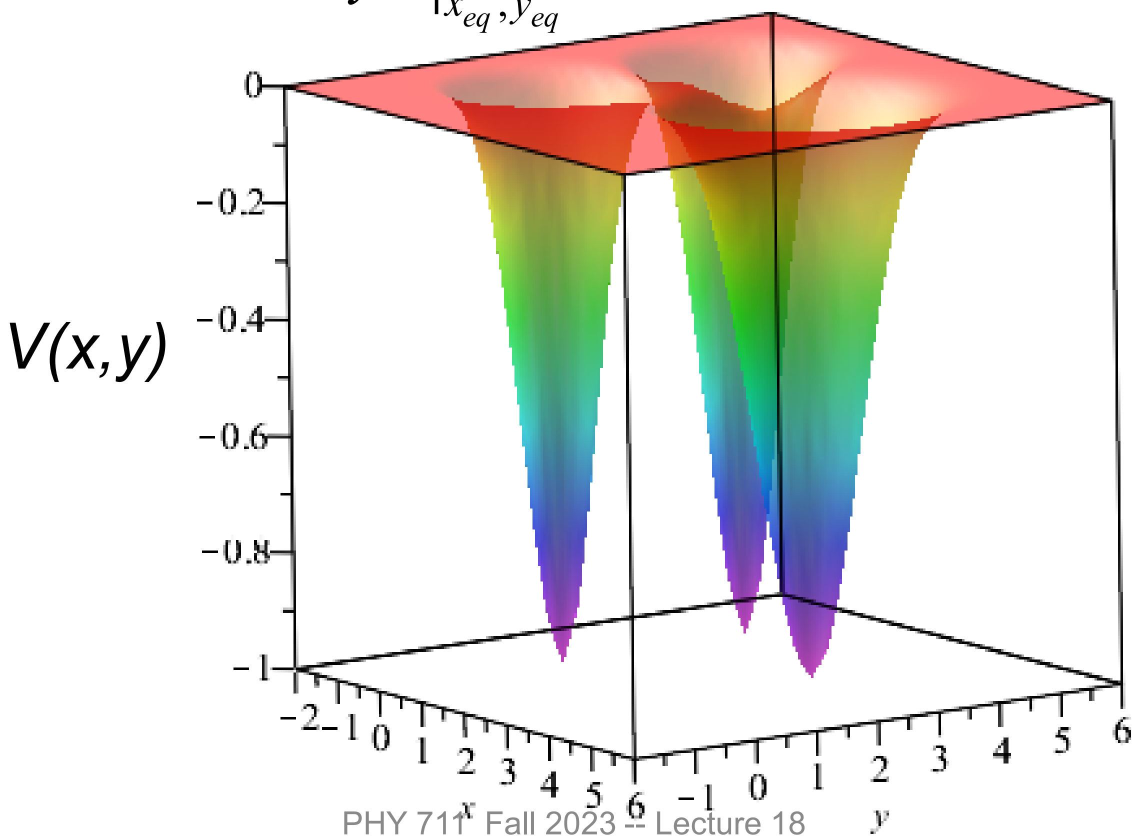
1. Normal modes for finite 2 and 3 dimensional systems
2. Normal modes for extended systems

	Date	F&W	Topic	HW
1	Mon, 8/28/2023		Introduction and overview	#1
2	Wed, 8/30/2023	Chap. 3(17)	Calculus of variation	#2
3	Fri, 9/01/2023	Chap. 3(17)	Calculus of variation	#3
4	Mon, 9/04/2023	Chap. 3	Lagrangian equations of motion	#4
5	Wed, 9/06/2023	Chap. 3 & 6	Lagrangian equations of motion	#5
6	Fri, 9/08/2023	Chap. 3 & 6	Lagrangian equations of motion	#6
7	Mon, 9/11/2023	Chap. 3 & 6	Lagrangian to Hamiltonian formalism	#7
8	Wed, 9/13/2023	Chap. 3 & 6	Phase space	
9	Fri, 9/15/2023	Chap. 3 & 6	Canonical Transformations	#8
10	Mon, 9/18/2023	Chap. 5	Dynamics of rigid bodies	#9
11	Wed, 9/20/2023	Chap. 5	Dynamics of rigid bodies	#10
12	Fri, 9/22/2023	Chap. 5	Dynamics of rigid bodies	#11
13	Mon, 9/25/2023	Chap. 1	Scattering analysis	#12
14	Wed, 9/27/2023	Chap. 1	Scattering analysis	#13
15	Fri, 9/29/2023	Chap. 1	Scattering analysis	#14
16	Mon, 10/2/2023	Chap. 4	Small oscillations near equilibrium	
17	Wed, 10/4/2023	Chap. 4	Normal mode analysis	Mid term start
18	Fri, 10/6/2023	Chap. 4	Normal mode analysis	
22	Mon, 10/9/2023	Chap. 7	Normal modes of continuous string	
20	Wed, 10/11/2023		Review and summary	Mid term due
	Fri, 10/13/2023	Fall Break		

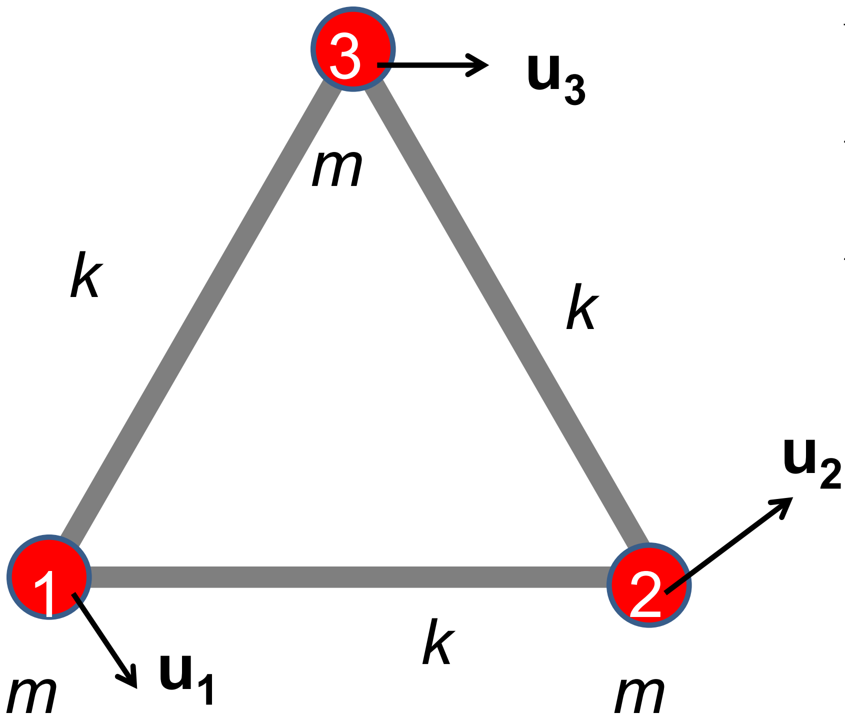
Now consider a potential system in 2 dimensions near its equilibrium point --

$$V(x,y) \approx V(x_{eq}, y_{eq}) + \tfrac{1}{2}\left(x - x_{eq}\right)^2 \left.\frac{\partial^2 V}{\partial x^2}\right|_{x_{eq}, y_{eq}}$$

$$+ \tfrac{1}{2}\left(y - y_{eq}\right)^2 \left.\frac{\partial^2 V}{\partial y^2}\right|_{x_{eq}, y_{eq}} + \left(x - x_{eq}\right)\left(y - y_{eq}\right)\left.\frac{\partial^2 V}{\partial x \partial y}\right|_{x_{eq}, y_{eq}}$$



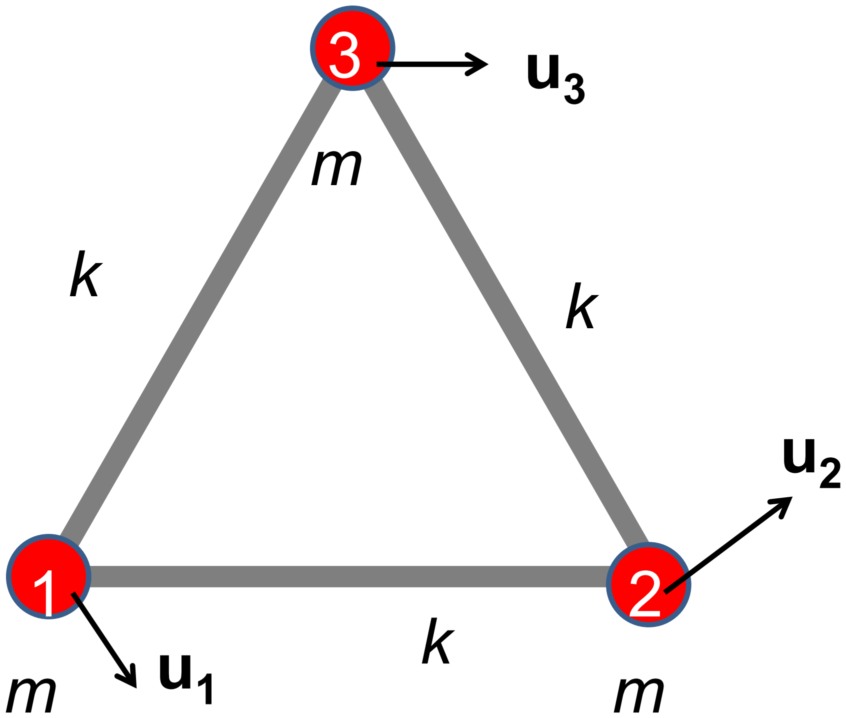
Example – normal modes of a system with the symmetry of an equilateral triangle



Degrees of freedom for 2-dimensional motion:

$$2N = 6$$

Some details for this case of the equilateral triangle --

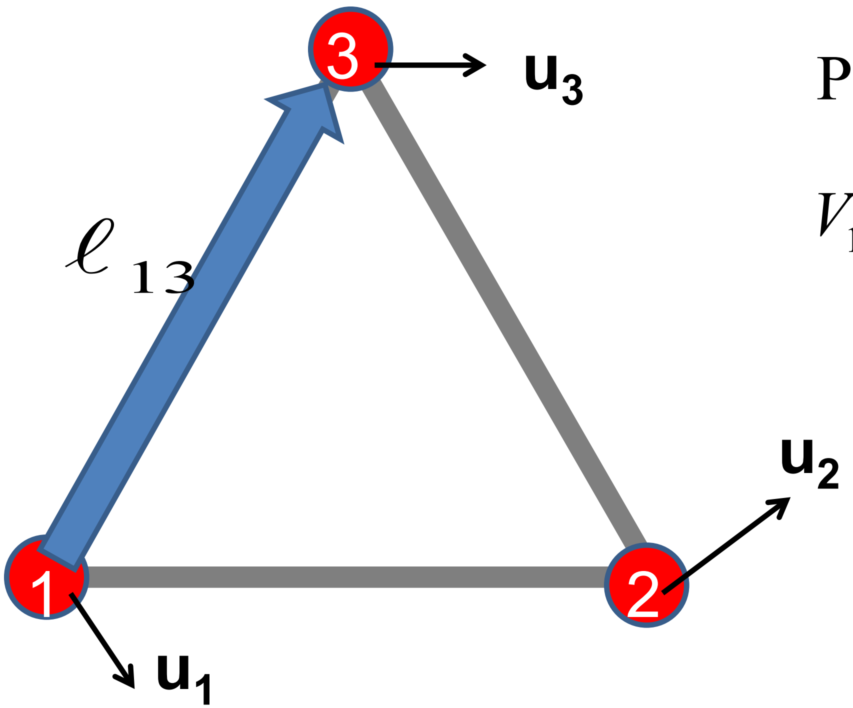


$$\ell_{12} = |\ell_{12}|\hat{\mathbf{x}}$$

$$\ell_{13} = |\ell_{13}|\left(\frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right)$$

$$\ell_{23} = |\ell_{23}|\left(-\frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right)$$

Example – normal modes of a system with the symmetry of an equilateral triangle -- continued



$$\boldsymbol{\ell}_{13} = |\boldsymbol{\ell}_{13}| \left(\frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}} \right)$$

Potential contribution for spring 13:

$$V_{13} = \frac{1}{2}k\left(\left|\boldsymbol{\ell}_{13} + \mathbf{u}_3 - \mathbf{u}_1\right| - \left|\boldsymbol{\ell}_{13}\right|\right)^2$$

$$\approx \frac{1}{2}k\left(\frac{\boldsymbol{\ell}_{13}\cdot(\mathbf{u}_3 - \mathbf{u}_1)}{|\boldsymbol{\ell}_{13}|}\right)^2$$

$$\approx \frac{1}{2}k\left(\frac{1}{2}(u_{x3} - u_{x1}) + \frac{\sqrt{3}}{2}(u_{y3} - u_{y1})\right)^2$$

Some details for spring 13:

$$\left(\left|\boldsymbol{\ell}_{13}+\mathbf{u}_3-\mathbf{u}_1\right|-\left|\boldsymbol{\ell}_{13}\right|\right)^2 \equiv \left(\left(\boldsymbol{\ell}_{13}+\mathbf{u}_{13}\right)^{1/2}-\left|\boldsymbol{\ell}_{13}\right|\right)^2$$

negligible

$$\left(\left|\boldsymbol{\ell}_{13}+\mathbf{u}_{13}\right|\right)^{1/2} = \left|\boldsymbol{\ell}_{13}\right|\left(1+\frac{2\boldsymbol{\ell}_{13}\cdot\mathbf{u}_{13}}{\left|\boldsymbol{\ell}_{13}\right|^2}+\frac{\left|\mathbf{u}_{13}\right|^2}{\left|\boldsymbol{\ell}_{13}\right|^2}\right)^{1/2}$$

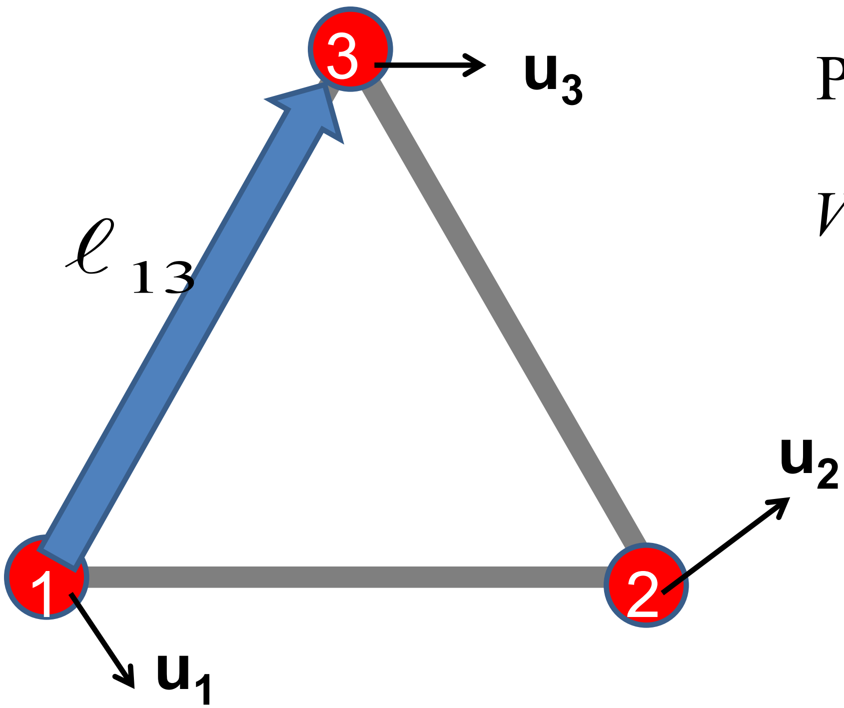
Assume $\left|\mathbf{u}_{13}\right| \ll \left|\boldsymbol{\ell}_{13}\right|$

$$\approx \left|\boldsymbol{\ell}_{13}\right|\left(1+\frac{\boldsymbol{\ell}_{13}\cdot\mathbf{u}_{13}}{\left|\boldsymbol{\ell}_{13}\right|^2}\right) = \left|\boldsymbol{\ell}_{13}\right| + \frac{\boldsymbol{\ell}_{13}\cdot\mathbf{u}_{13}}{\left|\boldsymbol{\ell}_{13}\right|}$$

$$\Rightarrow \left(\left(\boldsymbol{\ell}_{13}+\mathbf{u}_{13}\right)^{1/2}-\left|\boldsymbol{\ell}_{13}\right|\right)^2 = \left(\frac{\boldsymbol{\ell}_{13}\cdot\mathbf{u}_{13}}{\left|\boldsymbol{\ell}_{13}\right|}\right)^2$$

Note that this analysis of the leading term is true in 1, 2, and 3 dimensions.

Example – normal modes of a system with the symmetry of an equilateral triangle -- continued



$$\boldsymbol{\ell}_{13} = |\boldsymbol{\ell}_{13}|\left(\frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right)$$

Potential contribution for spring 13:

$$V_{13} = \frac{1}{2}k\left(|\boldsymbol{\ell}_{13} + \mathbf{u}_3 - \mathbf{u}_1| - |\boldsymbol{\ell}_{13}|\right)^2$$

$$\approx \frac{1}{2}k\left(\frac{\boldsymbol{\ell}_{13}\cdot(\mathbf{u}_3 - \mathbf{u}_1)}{|\boldsymbol{\ell}_{13}|}\right)^2$$

$$\approx \frac{1}{2}k\left(\frac{1}{2}(u_{x3} - u_{x1}) + \frac{\sqrt{3}}{2}(u_{y3} - u_{y1})\right)^2$$

Example – normal modes of a system with the symmetry of an equilateral triangle -- continued

Potential contributions: $V = V_{12} + V_{13} + V_{23}$

$$\approx \frac{1}{2}k\left(\frac{\ell_{12}\cdot(\mathbf{u}_2-\mathbf{u}_1)}{|\ell_{12}|}\right)^2 + \frac{1}{2}k\left(\frac{\ell_{13}\cdot(\mathbf{u}_3-\mathbf{u}_1)}{|\ell_{13}|}\right)^2$$

$$+\frac{1}{2}k\left(\frac{\ell_{23}\cdot(\mathbf{u}_3-\mathbf{u}_2)}{|\ell_{23}|}\right)^2$$

$$\approx \frac{1}{2}k\left(u_{x2}-u_{x1}\right)^2$$

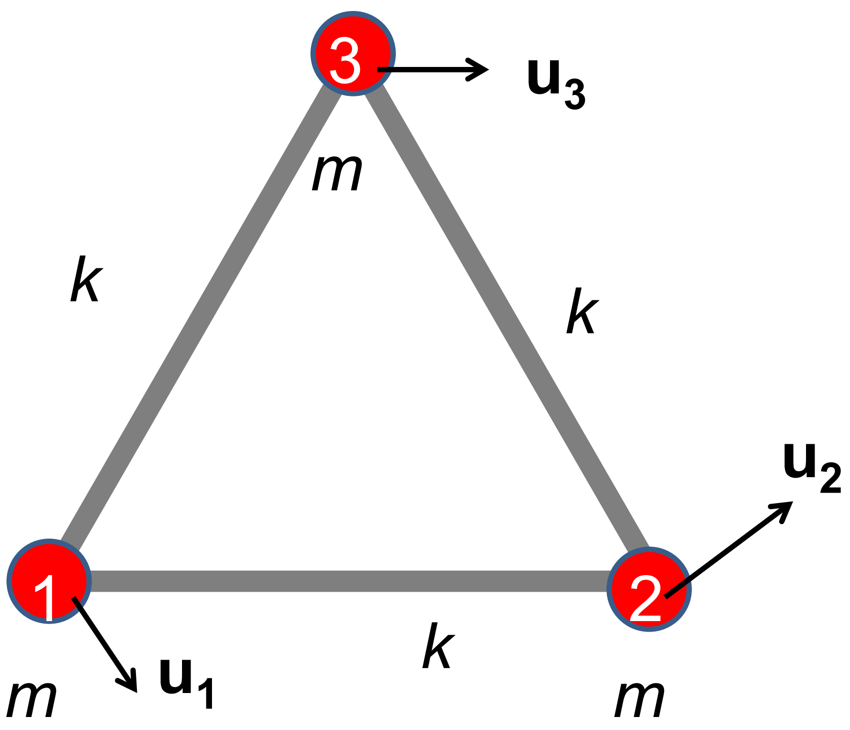
$$+\frac{1}{2}k\left(\frac{1}{2}\left(u_{x3}-u_{x1}\right)+\frac{\sqrt{3}}{2}\left(u_{y3}-u_{y1}\right)\right)^2$$

$$+\frac{1}{2}k\left(\frac{1}{2}\left(u_{x2}-u_{x3}\right)-\frac{\sqrt{3}}{2}\left(u_{y2}-u_{y3}\right)\right)^2$$

Example – normal modes of a system with the symmetry of an equilateral triangle -- continued

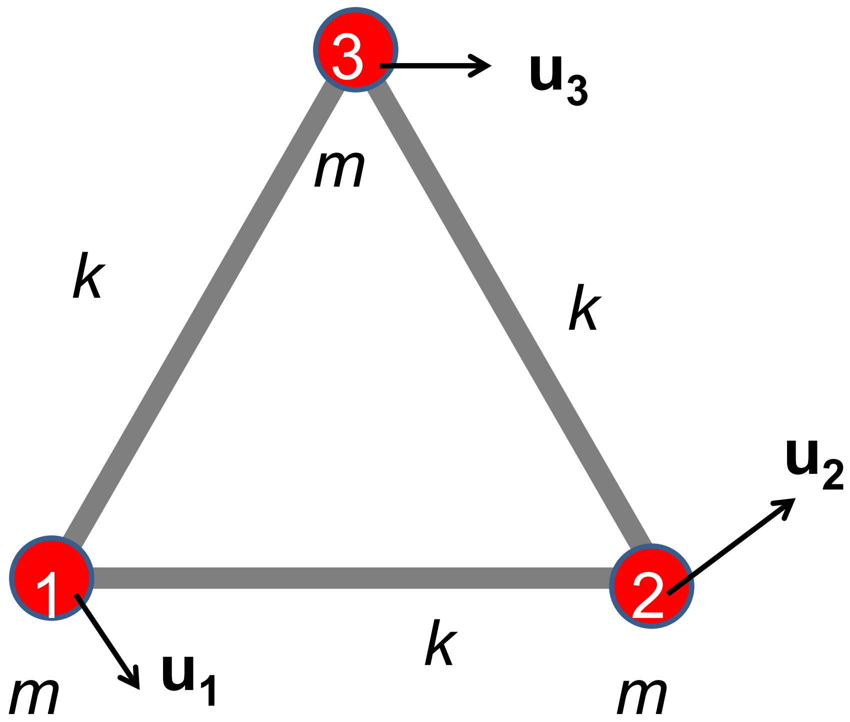
$$\frac{k}{m}\begin{bmatrix} \frac{5}{4} & -1 & -\frac{1}{4} & \frac{1}{4}\sqrt{3} & 0 & -\frac{1}{4}\sqrt{3} \\ -1 & \frac{5}{4} & -\frac{1}{4} & 0 & -\frac{1}{4}\sqrt{3} & \frac{1}{4}\sqrt{3} \\ -\frac{1}{4} & -\frac{1}{4} & \frac{1}{2} & -\frac{1}{4}\sqrt{3} & \frac{1}{4}\sqrt{3} & 0 \\ \frac{1}{4}\sqrt{3} & 0 & -\frac{1}{4}\sqrt{3} & \frac{3}{4} & 0 & -\frac{3}{4} \\ 0 & -\frac{1}{4}\sqrt{3} & \frac{1}{4}\sqrt{3} & 0 & \frac{3}{4} & -\frac{3}{4} \\ -\frac{1}{4}\sqrt{3} & \frac{1}{4}\sqrt{3} & 0 & -\frac{3}{4} & -\frac{3}{4} & \frac{3}{2} \end{bmatrix}\begin{bmatrix} u_{x1} \\ u_{x2} \\ u_{x3} \\ u_{y1} \\ u_{y2} \\ u_{y3} \end{bmatrix} = \omega^2 \begin{bmatrix} u_{x1} \\ u_{x2} \\ u_{x3} \\ u_{y1} \\ u_{y2} \\ u_{y3} \end{bmatrix}$$

Example – normal modes of a system with the symmetry of an equilateral triangle -- continued



With help from Maple

$$\omega^2 = \begin{bmatrix} 3 \\ \frac{3}{2} \\ \frac{3}{2} \\ 0 \\ 0 \\ 0 \end{bmatrix} \frac{k}{m}$$



What can you say about the 3 zero frequency modes?

What can you say about the 3 non-zero frequency modes?

More general treatment of atomic system near equilibrium

Atoms located at the positions :

$$\mathbf{R}^a = \mathbf{R}_0{}^a + \mathbf{u}^a$$

Potential energy function near equilibriu :

$$U\left(\left\{\mathbf{R}^a\right\}\right) \approx U\left(\left\{\mathbf{R}_0{}^a\right\}\right) + \frac{1}{2}\sum_{a,b}\left(\mathbf{R}^a - \mathbf{R}_0{}^a\right)\cdot \left.\frac{\partial^2 U}{\partial \mathbf{R}^a \partial \mathbf{R}^b}\right|_{\left\{\mathbf{R}_0{}^a\right\}} \cdot \left(\mathbf{R}^b - \mathbf{R}_0{}^b\right)$$

Define :

$$D_{jk}^{ab} \equiv \left.\frac{\partial^2 U}{\partial \mathbf{R}_j{}^a \partial \mathbf{R}_k{}^b}\right|_{\left\{\mathbf{R}_0{}^a\right\}}$$

so that

$$U\left(\left\{\mathbf{R}^a\right\}\right) \approx U_0 + \frac{1}{2}\sum_{a,b,j,k} u_j^a D_{jk}^{ab} u_k^b$$

$$L\left(\left\{u_j^a, \dot{u}_j^a\right\}\right) = \frac{1}{2}\sum_{a,j} m_a \left(\dot{u}_j^a\right)^2 - U_0 - \frac{1}{2}\sum_{a,b,j,k} u_j^a D_{jk}^{ab} u_k^b$$

$$L\left(\left\{u_j^a, \dot{u}_j^a\right\}\right) = \frac{1}{2}\sum_{a,j} m_a \left(\dot{u}_j^a\right)^2 - U_0 - \frac{1}{2}\sum_{a,b,j,k} u_j^a D_{jk}^{ab} u_k^b$$

Equations of motion:

$$m_a \ddot{u}_j^a = -\sum_{b,k} D_{jk}^{ab} u_k^b$$

For a system of N atoms moving in d dimensions, we must solve a $dN \times dN$ eigenvalue problem.

Solution form:

$$u_j^a(t) = \frac{1}{\sqrt{m_a}} A_j^a e^{-i\omega t}$$

Eigenvalue problem: $$\omega^2 A_j^a = \sum_{b,k} \frac{D_{jk}^{ab}}{\sqrt{m_a m_b}} A_k^b$$

Extension of this analysis to a periodic system --

Equilibrium positions: $\mathbf{R}_0^a = \boldsymbol{\tau}^a + \mathbf{T}$

where $\boldsymbol{\tau}^a$ denotes unique sites within a unit cell

and $\mathbf{T}$ denotes all possible lattice translation vectors

Solution form for the periodic extended system:

$$u_j^a(t) = \frac{1}{\sqrt{m_a}} A_j^a e^{-i\omega t + i\mathbf{q}\cdot\mathbf{R}_0^a}$$

q maps distinct configurations of periodic states.

Define:

$$W_{jk}^{ab}(\mathbf{q}) = \sum_{\mathbf{T}} \frac{D_{jk}^{ab} e^{i\mathbf{q}\cdot(\boldsymbol{\tau}^a - \boldsymbol{\tau}^b)}}{\sqrt{m_a m_b}} e^{i\mathbf{q}\cdot\mathbf{T}}$$

Eigenvalue equations:

$$\omega^2 A_j^a = \sum_{b,k} W(\mathbf{q})_{jk}^{ab} A_k^b$$

In this equation the summation is only over unique atomic sites.

$\Rightarrow$ Find "dispersion curves" $\omega(\mathbf{q})$

3-dimensional periodic lattices
Example – face-centered-cubic unit cell (Al or Ni)

Diagram of atom positions

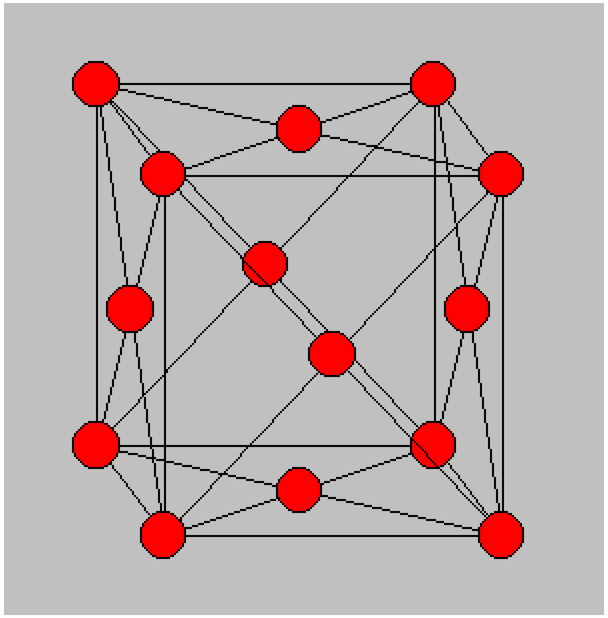
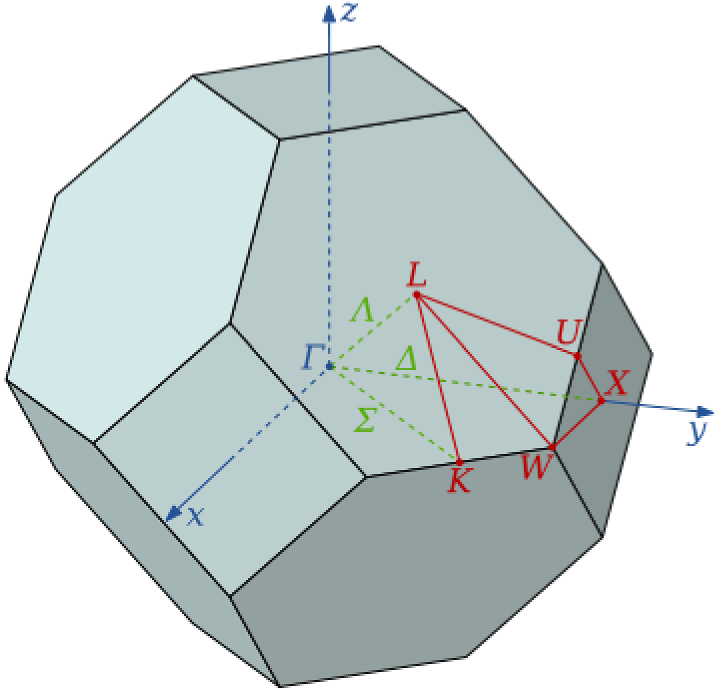


Diagram of q-space $\nu(q)$



From: PRB **59** 3395 (1999); Mishin et. al. $\nu(q)$

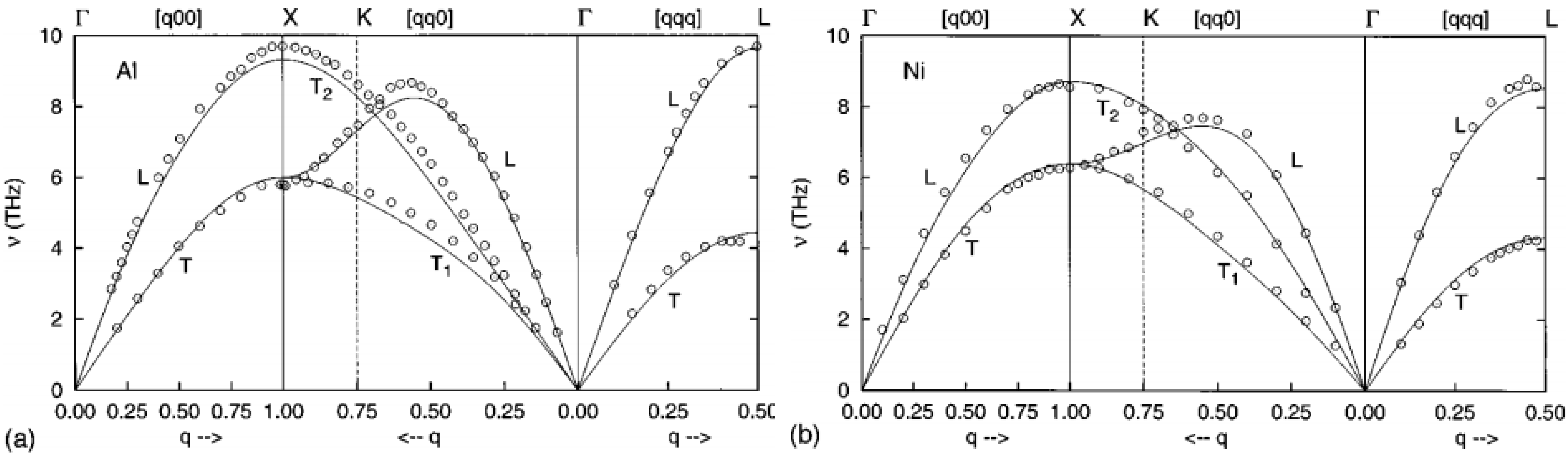
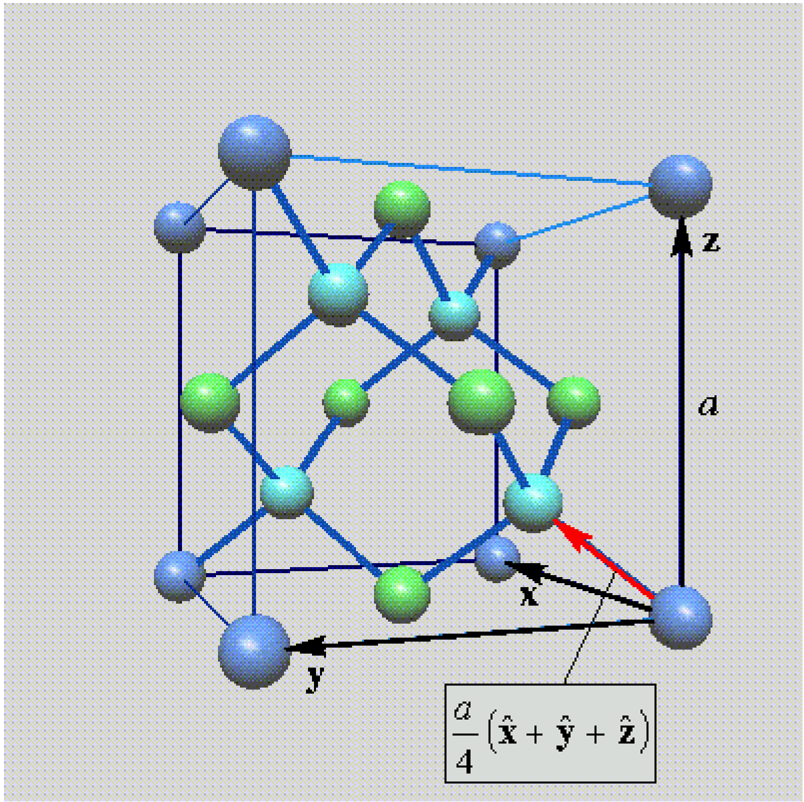


FIG. 2. Comparison of phonon-dispersion curves for Al (a) and Ni (b) predicted by the present EAM potentials, with the experimental values measured by neutron diffraction at 80 K (Al) and 298 K (Ni) (Ref. 33 for Al and Ref. 34 for Ni). The phonon frequencies at point *X* were included in the fitting database with low weight.

Note that for each q, there are 3 frequencies.

Lattice vibrations for 3-dimensional lattice

Example: diamond lattice



Ref: http://phycomp.technion.ac.il/~nika/diamond_structure.html

B. P. Pandy and B. Dayal, J. Phys. C. Solid State Phys. **6** 2943 (1973)

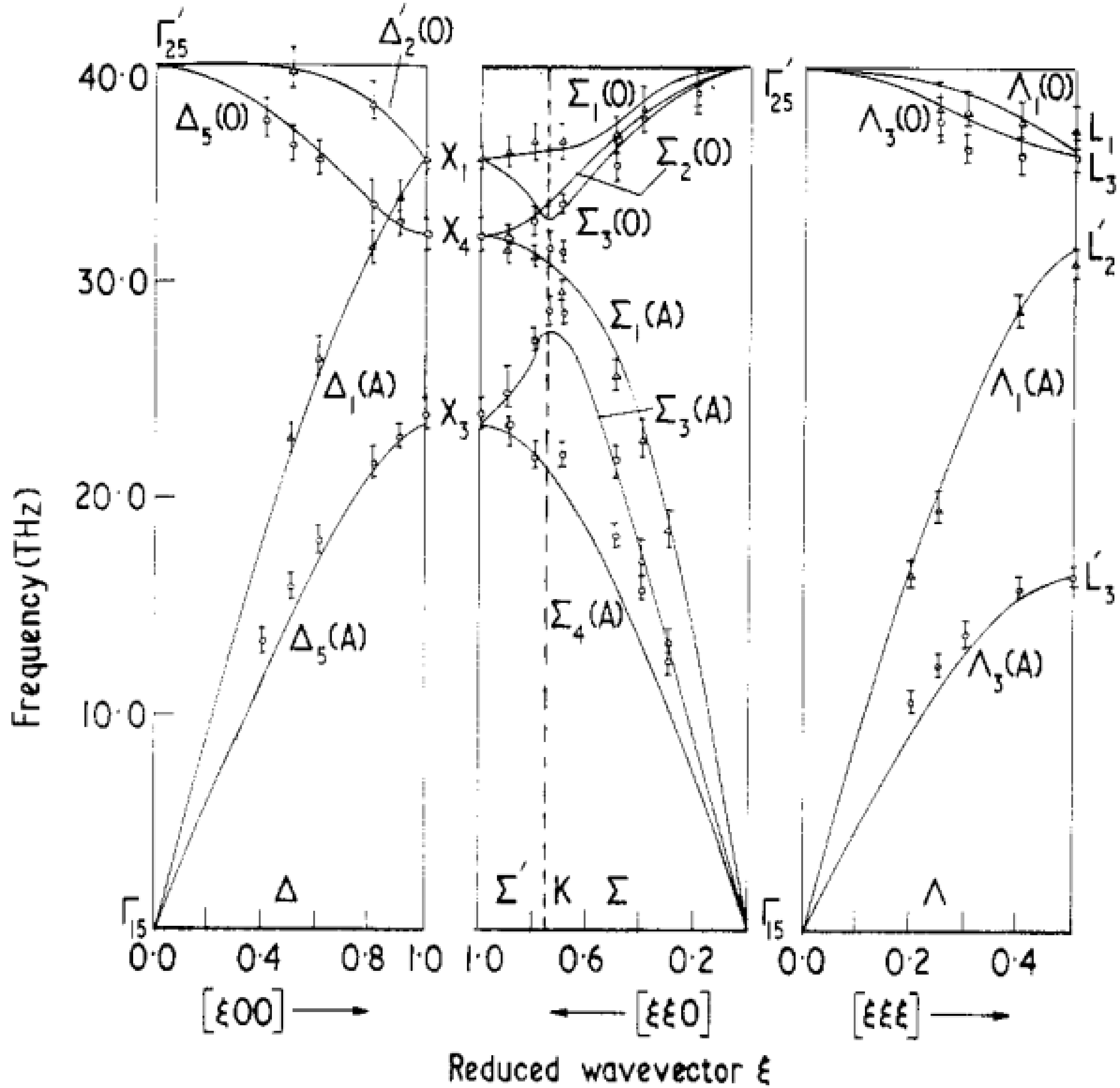


Figure 2. Phonon dispersion curves of diamond. Experimental points
et al (1965, 1967). △ and ○ represent the longitudinal and transverse m

Examples of phonon spectra of two forms of boron nitride

Cubic structure

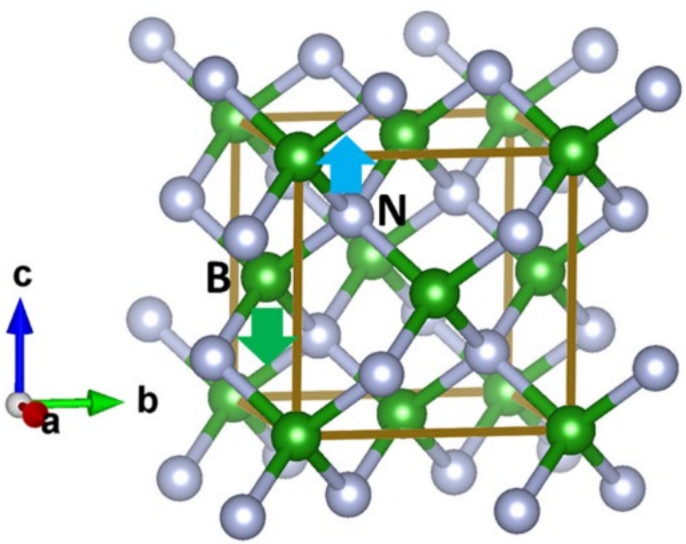


Figure 3. Ball and stick drawing of conventional unit cell of cubic BN (space group $F\bar{4}3m$ [44]) indicating one B and one N site within a primitive cell. The arrows indicate the vibrational directions of the atoms for one of the three degenerate optical modes at $\mathbf{q} = 0$ (Γ point).

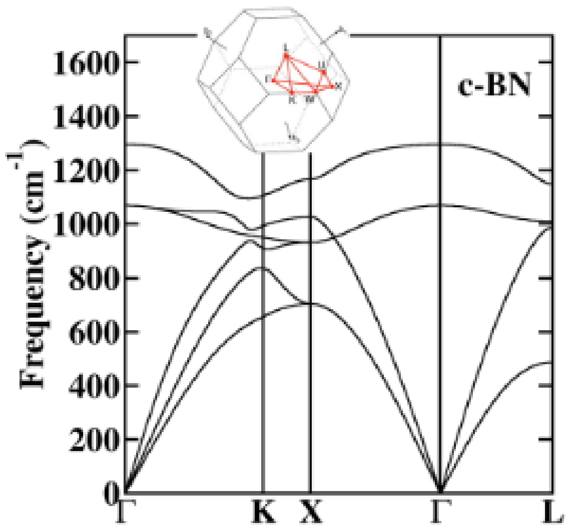


Figure 1. Phonon dispersion curves ($\omega^{\nu}(\mathbf{q})$) for cubic BN. The inset Brillouin zone diagram was reprinted from Setyawan *et al* [7], copyright (2010), with permission from Elsevier.

Examples of phonon spectra of two forms of boron nitride

Hexagonal structure

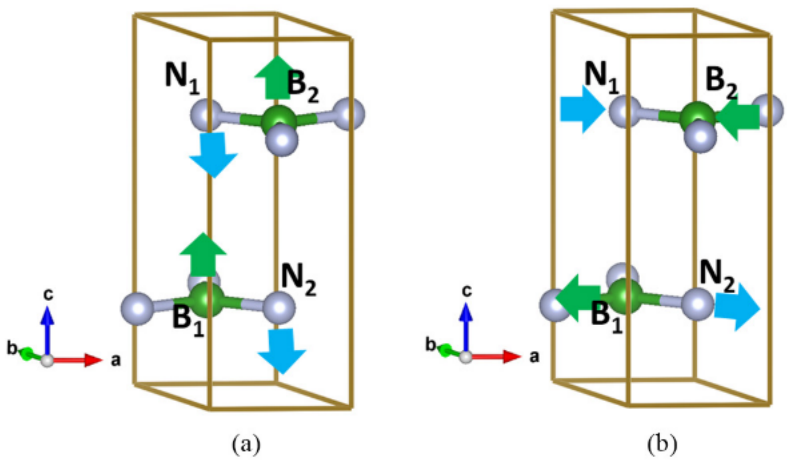


Figure 5. Ball and stick drawing of unit cell of hexagonal BN (space group *P*6_3/*mmc* [44]) indicating the four B and N sites. The arrows indicate the vibrational directions of the atoms for $\mathbf{q} = 0$ (Γ point) mode # 7 (a) and for mode # 11 (b).

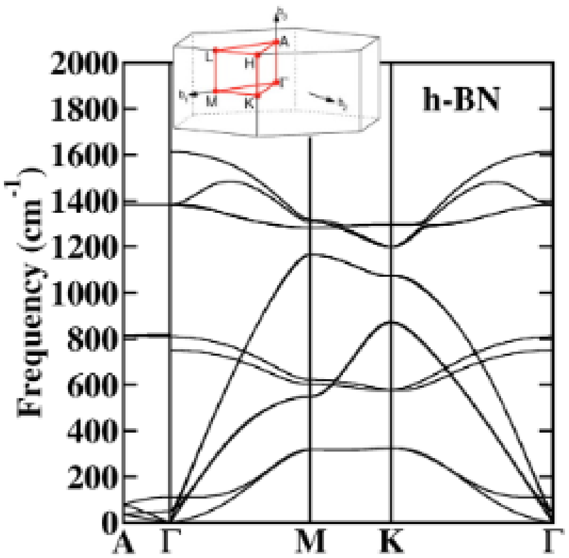


Figure 2. Phonon dispersion curves ($\omega^{\nu}(\mathbf{q})$) for hexagonal BN. The inset Brillouin zone diagram was reprinted from Setyawan *et al* [7], copyright (2010), with permission from Elsevier.

Helmholz free energy for vibrational energy at temperature T:

$$F_{\text{vib}}(T) = \int_0^\infty d\omega \, f_{\text{vib}}(\omega, T),$$

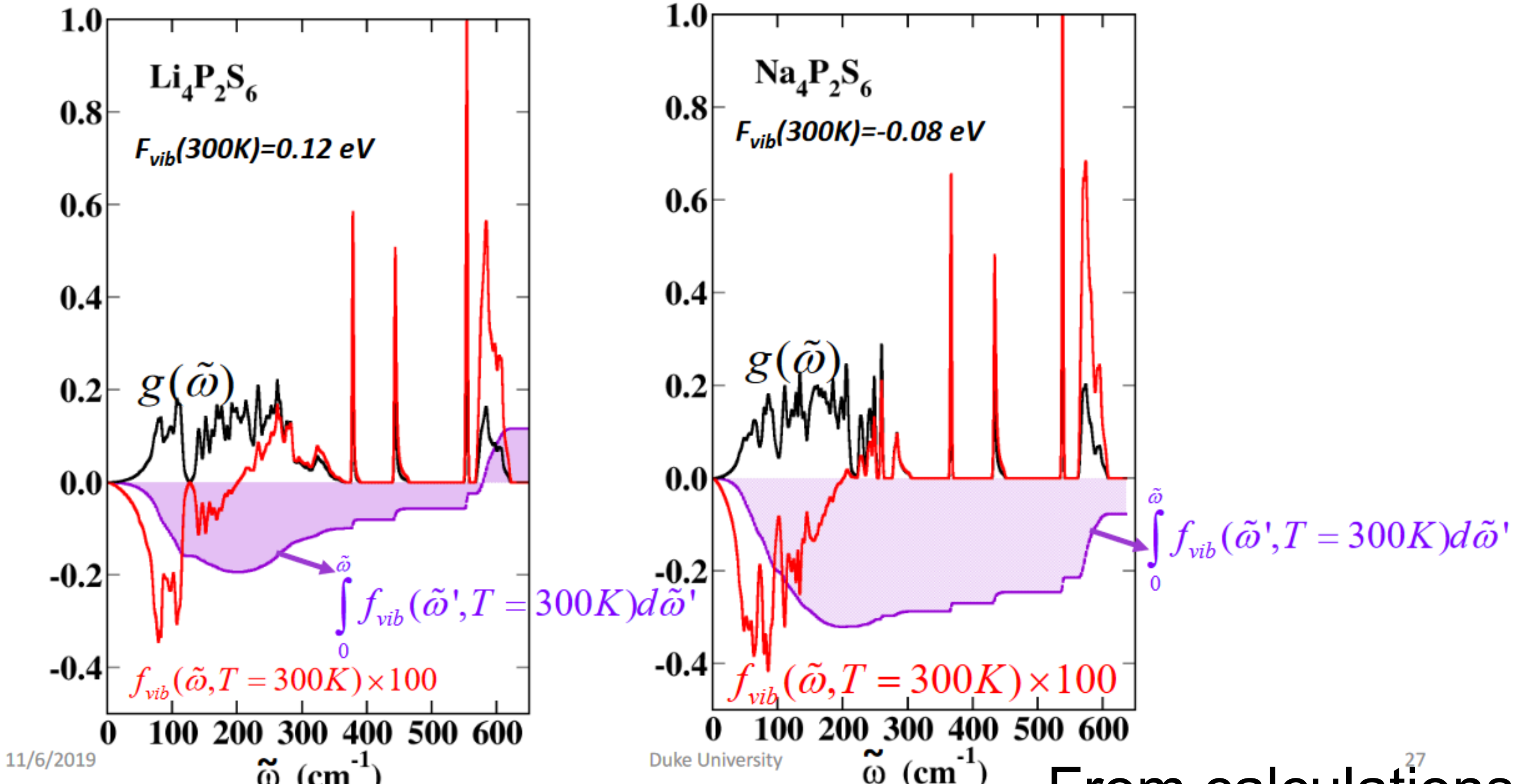
$$f_{\text{vib}}(\omega, T) = k_B T \ \ln\left[2 \ \sinh\left(\frac{\hbar\omega}{2k_B T}\right)\right] g(\omega).$$

Phonon density of states:

$$g(\omega) = \frac{V}{(2\pi)^3} \int d^3q \sum_{\nu=1}^{3N} \delta(\omega - \omega_\nu(\mathbf{q})),$$

An example of phonon analysis for two similar materials --

Some details of the vibrational stabilization at T=300K for $Li_4P_2S_6$ and $Na_4P_2S_6$ in C2/m structure



From calculations by Yan Li

Simulation of structural stability patterns -- continued

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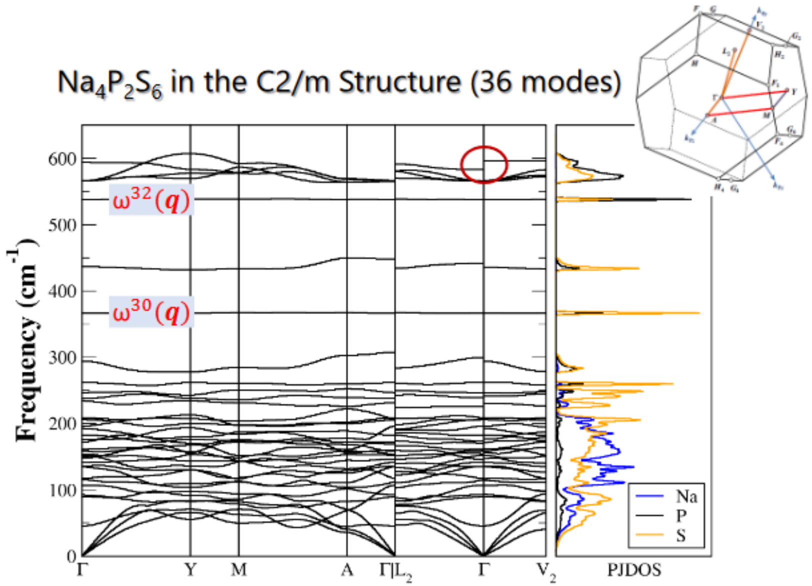
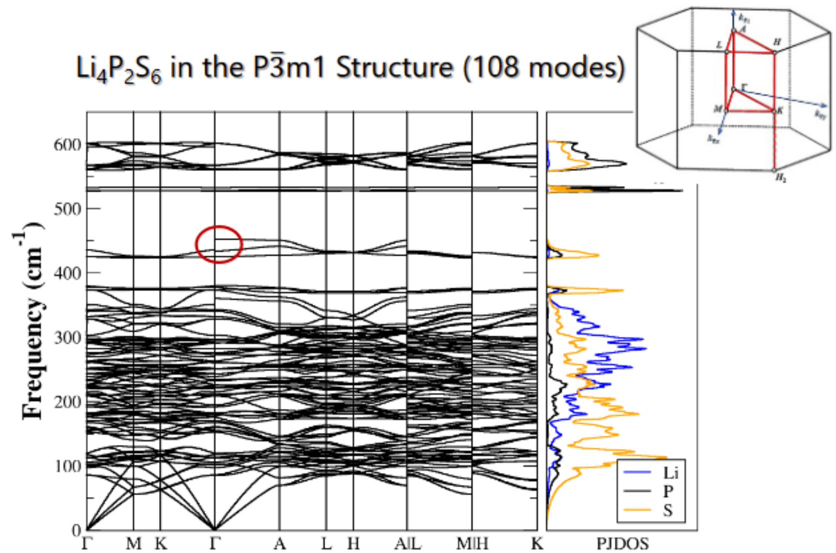
$Na_4P_2S_6$ in the C2/m Structure (36 modes)



Na$^+$ 0~300 cm^{-1}

$(P_2S_6)^{4-}$ 300~600 cm^{-1}

$Li_4P_2S_6$ in the P$\bar{3}$m1 Structure (108 modes)



Li$^+$ 0~370 cm^{-1}

$(P_2S_6)^{4-}$ 370~600 cm^{-1}

[1]Suggested path: Hinuma et al., *Comp. Mat. Sci.* **128**, 140-184 (2017)
[2]Li et al., *J. Phys. Condens. Matter,* **32,** 055402 (2020)

PJDOS: $g^a(\omega) \equiv \frac{V}{(2\pi)^3}\int d^3q \sum_{\nu=1}^{3N}(\delta(\omega-\omega_\nu(\mathbf{q}))W_a^\nu(\mathbf{q}))$

Discontinuous branches at Γ: coupling between photon and photon[2]

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From calculations by Yan Li