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

Discussion for Lecture 19 – Chap. 4 (F & W)

Analysis of motion near equilibrium –

Normal Mode Analysis

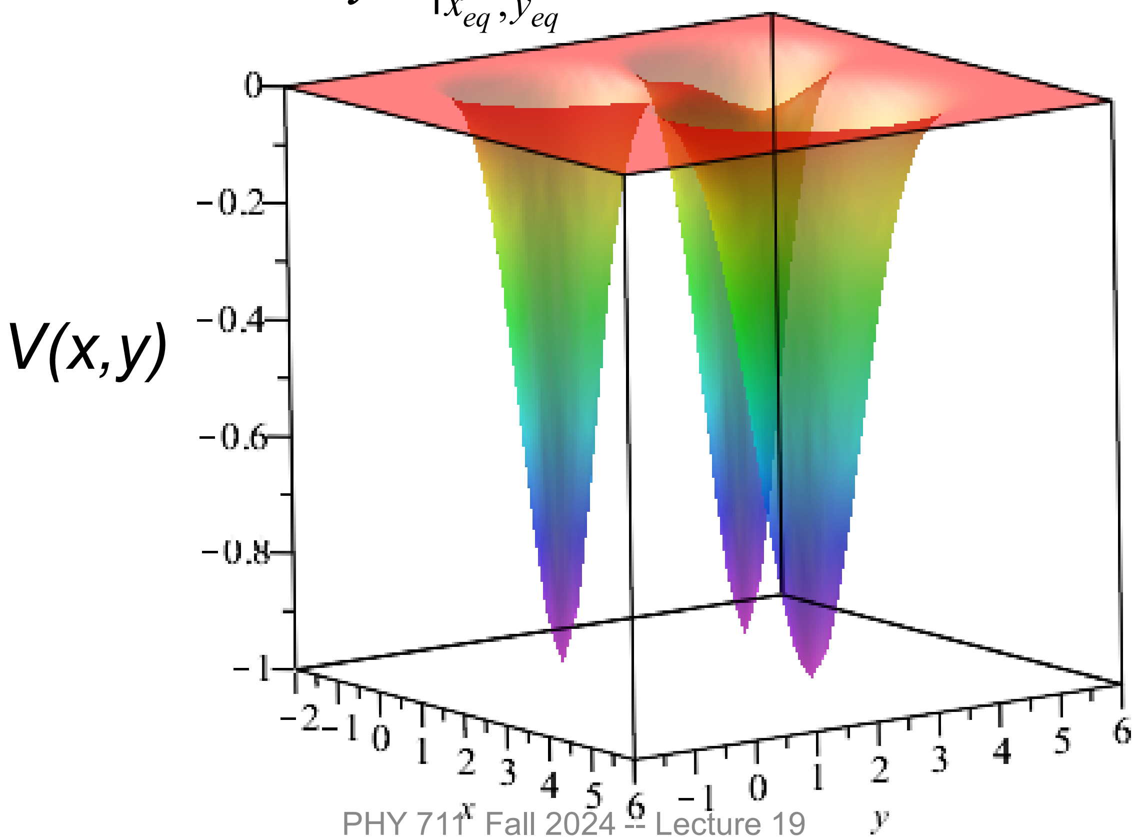
1. **Normal modes for finite 2 and 3 dimensional systems**
2. **Normal modes for extended systems**

11	Wed, 9/18/2024	Chap. 5	Dynamics of rigid bodies	#10
12	Fri, 9/20/2024	Chap. 5	Dynamics of rigid bodies	#11
13	Mon, 9/23/2024	Chap. 1	Scattering analysis	#12
14	Wed, 9/25/2024	Chap. 1	Scattering analysis	#13
15	Fri, 9/27/2024	Chap. 1	Scattering analysis	#14
16	Mon, 9/30/2024	Chap. 4	Small oscillations near equilibrium	
17	Wed, 10/2/2024	Chap. 1-6	Review	THE-10/3-9/24
18	Fri, 10/4/2024	Chap. 4	Normal mode analysis	THE-10/3-9/24
19	Mon, 10/7/2024	Chap. 4	Normal mode analysis in multiple dimensions	THE-10/3-9/24
20	Wed, 10/9/2024	Chap. 4&7	Normal modes of continuous strings	THE-10/3-9/24
21	Fri, 10/11/2024	Chap. 7	The wave and other partial differential equations	
22	Mon, 10/14/2024	Chap. 7	Sturm-Liouville equations	
23	Wed, 10/16/2024	Chap. 7	Sturm-Liouville equations	
	Fri, 10/18/2024	Fall Break		
24	Mon, 10/21/2024	Chap. 7	Laplace transforms and complex functions	

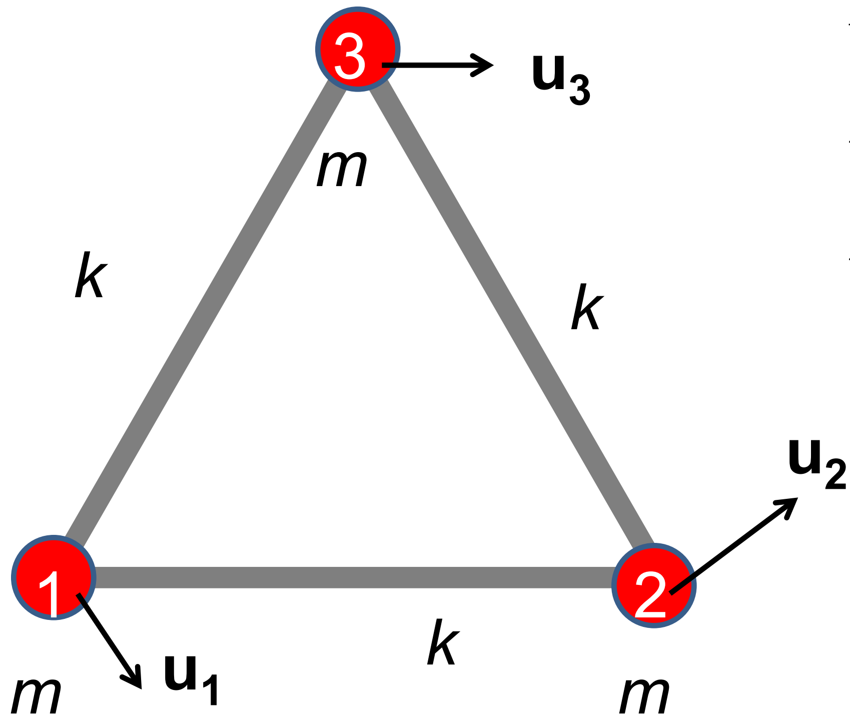
Now consider a potential system in 2 dimensions near its equilibrium point --

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

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



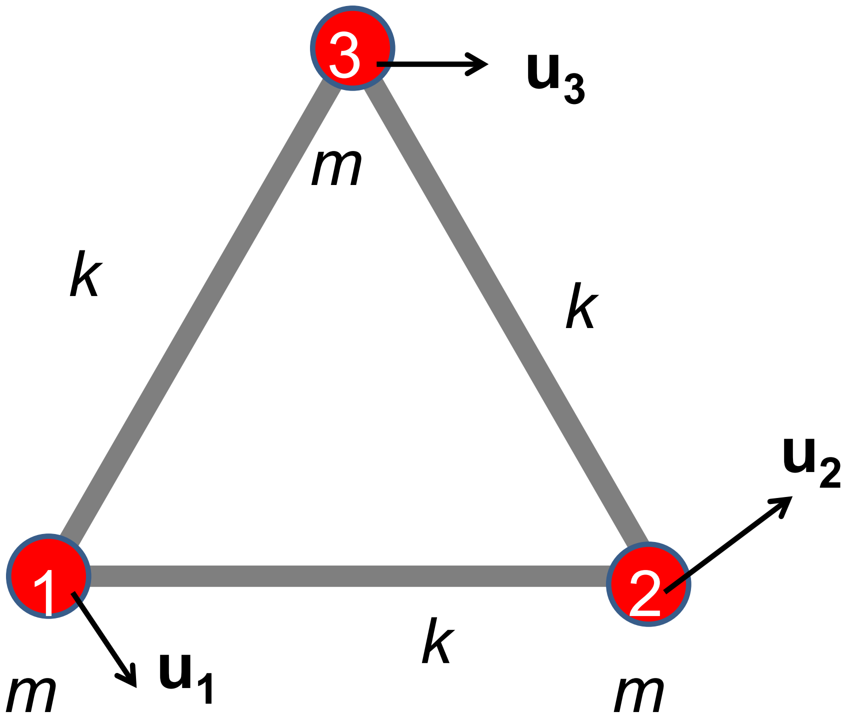
Example – normal modes of a system with the symmetry of an equilateral triangle



Degrees of freedom for 2-dimensional motion:

$$2N = 6$$

Some details for this case of the equilateral triangle --

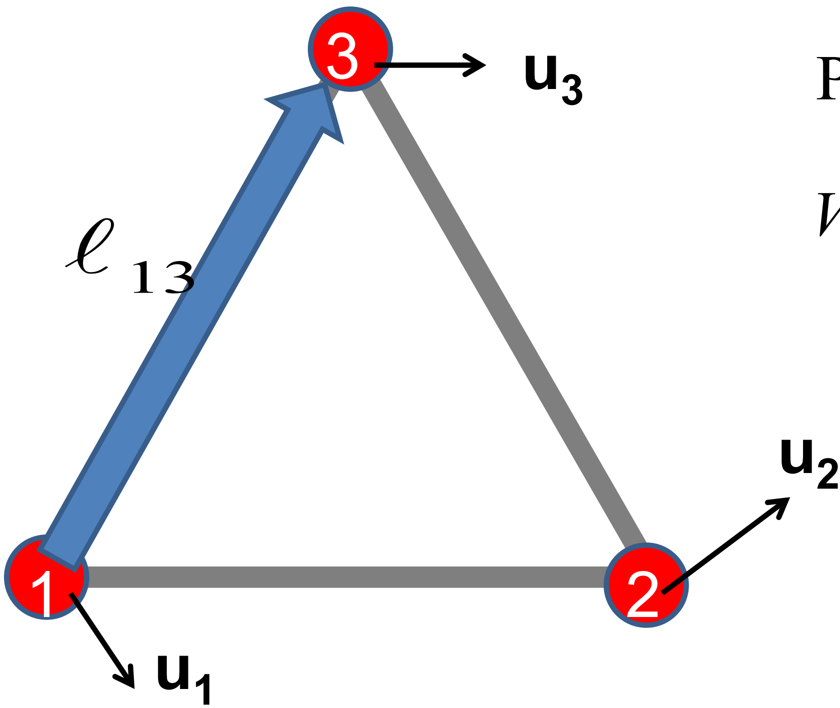


$$\ell_{12} = \left|\ell_{12}\right| \hat{\mathbf{x}}$$

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

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

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:

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

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

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

Some details for spring 13:

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

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

negligible

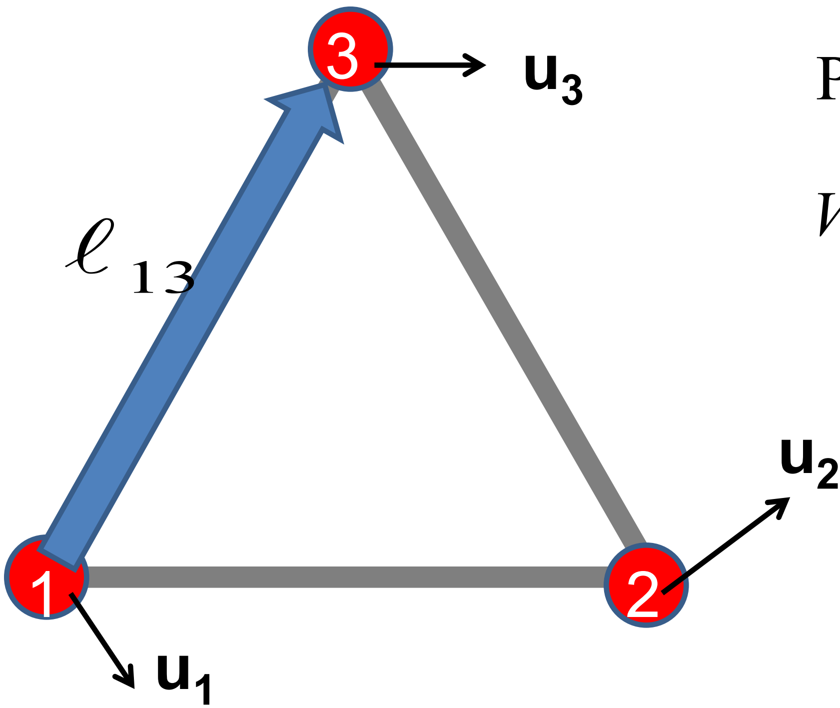
Assume $\left|\mathbf{u}_{13}\right| \ll \left|\boldsymbol{\ell}_{13}\right|$

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

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

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

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

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

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

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

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

Equations of motion:

$$m\ddot{u}_{x1} = -\frac{\partial V}{\partial u_{x1}} \quad m\ddot{u}_{y1} = -\frac{\partial V}{\partial u_{y1}} \quad m\ddot{u}_{z1} = -\frac{\partial V}{\partial u_{z1}}$$

$$m\ddot{u}_{x2} = -\frac{\partial V}{\partial u_{x2}} \quad m\ddot{u}_{y2} = -\frac{\partial V}{\partial u_{y2}} \quad m\ddot{u}_{z2} = -\frac{\partial V}{\partial u_{z2}}$$

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

$$V \approx \frac{1}{2}k\left(u_{x2} - u_{x1}\right)^2 + \frac{1}{2}k\left(\frac{1}{2}\left(u_{x3} - u_{x1}\right) + \frac{\sqrt{3}}{2}\left(u_{y3} - u_{y1}\right)\right)^2$$

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

$$-\frac{\partial V}{\partial u_{x1}} \approx -k\left(u_{x2} - u_{x1}\right) - \frac{1}{2}k\left(\frac{1}{2}\left(u_{x3} - u_{x1}\right) + \frac{\sqrt{3}}{2}\left(u_{y3} - u_{y1}\right)\right)$$

Equations of motion:

$$m\ddot{u}_{x1} = -\frac{\partial V}{\partial u_{x1}} \quad m\ddot{u}_{y1} = -\frac{\partial V}{\partial u_{y1}} \quad m\ddot{u}_{z1} = -\frac{\partial V}{\partial u_{z1}}$$

$$m\ddot{u}_{x2} = -\frac{\partial V}{\partial u_{x2}} \quad m\ddot{u}_{y2} = -\frac{\partial V}{\partial u_{y2}} \quad m\ddot{u}_{z2} = -\frac{\partial V}{\partial u_{z2}}$$

Assume harmonic time dependence --

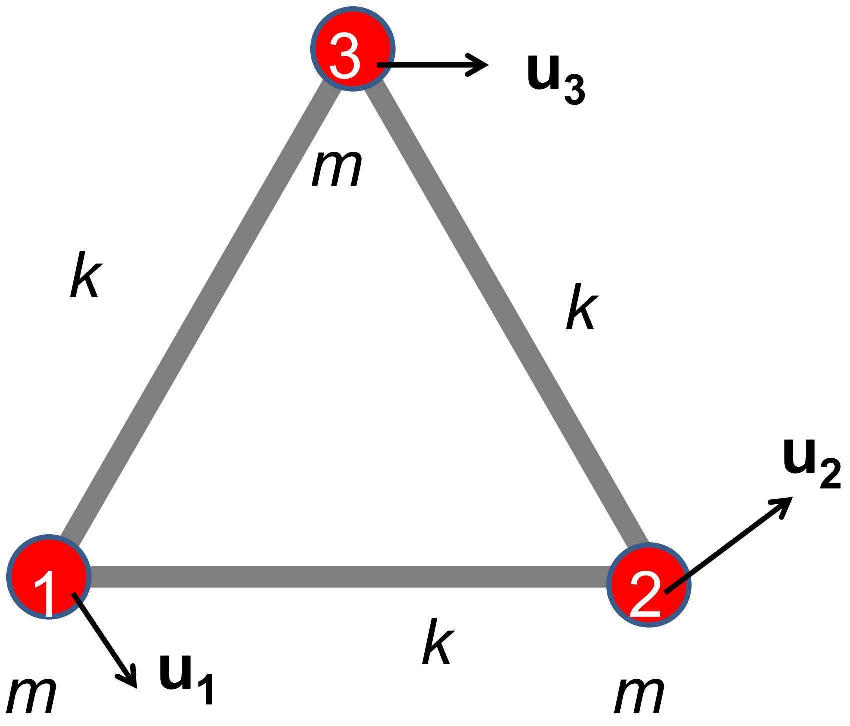
$$u_{x1}(t) \to u_{x1} e^{-i\omega_\alpha t}$$

$$\ddot{u}_{x1}(t) \to -\omega_\alpha^2 u_{x1} e^{-i\omega_\alpha t}$$

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

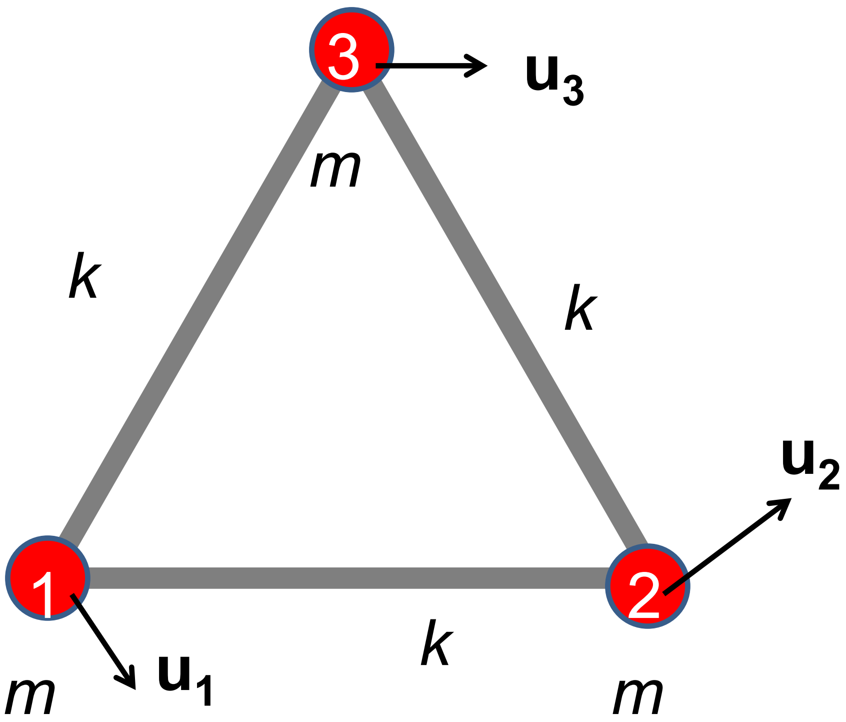
$$\frac{k}{m}\begin{bmatrix} \frac{5}{4} & -1 & -\frac{1}{4} & \frac{1}{4}\sqrt{3} & 0 & -\frac{1}{4}\sqrt{3} \\ -1 & \frac{5}{4} & -\frac{1}{4} & 0 & -\frac{1}{4}\sqrt{3} & \frac{1}{4}\sqrt{3} \\ -\frac{1}{4} & -\frac{1}{4} & \frac{1}{2} & -\frac{1}{4}\sqrt{3} & \frac{1}{4}\sqrt{3} & 0 \\ \frac{1}{4}\sqrt{3}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

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 :

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

so that

$$U\left(\left\{\mathbf{R}^a\right\}\right) \approx U_0 + \frac{1}{2}\sum_{a,b,j,k} u^a_j D^{ab}_{jk} u^b_k$$

$$L\left(\left\{u^a_j, \dot{u}^a_j\right\}\right) = \frac{1}{2}\sum_{a,j} m_a \left(\dot{u}^a_j\right)^2 - U_0 - \frac{1}{2}\sum_{a,b,j,k} u^a_j D^{ab}_{jk} u^b_k$$

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

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 --

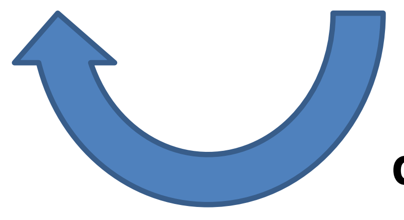
Equilibrium positions: $\mathbf{R}_0^a = \boldsymbol{\tau}^a + \mathbf{T}$

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

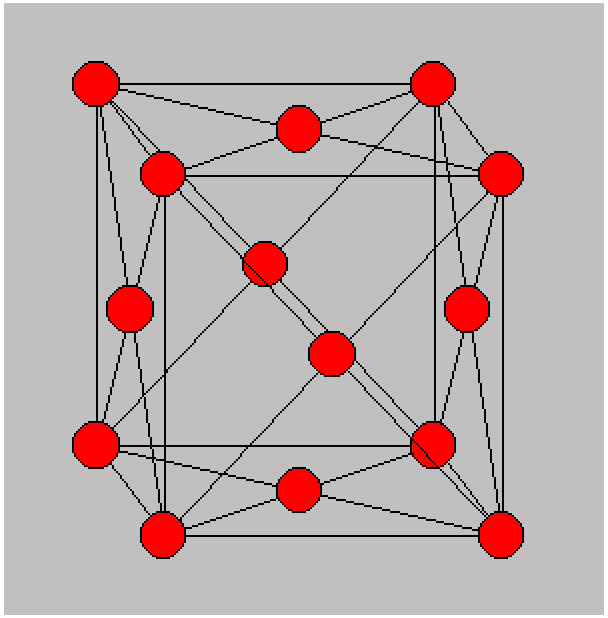
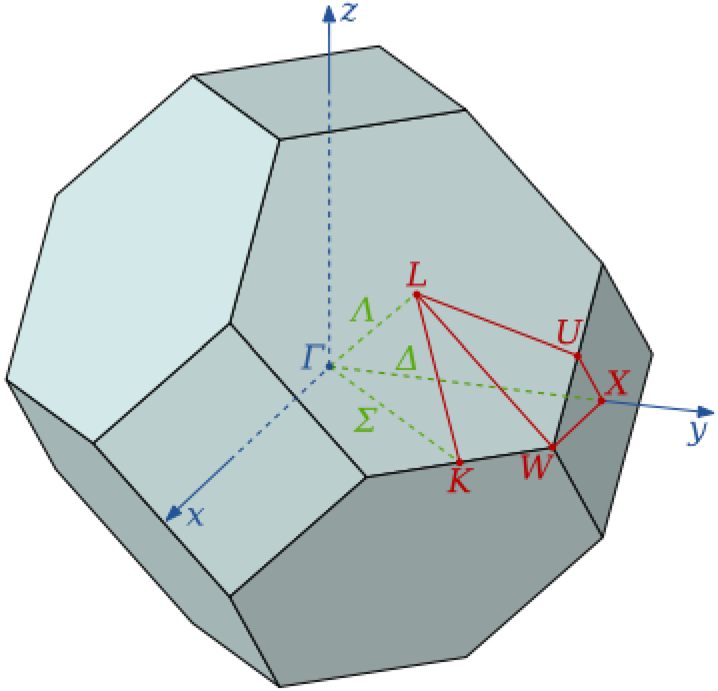


Diagram of q-space $\nu(q)$



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

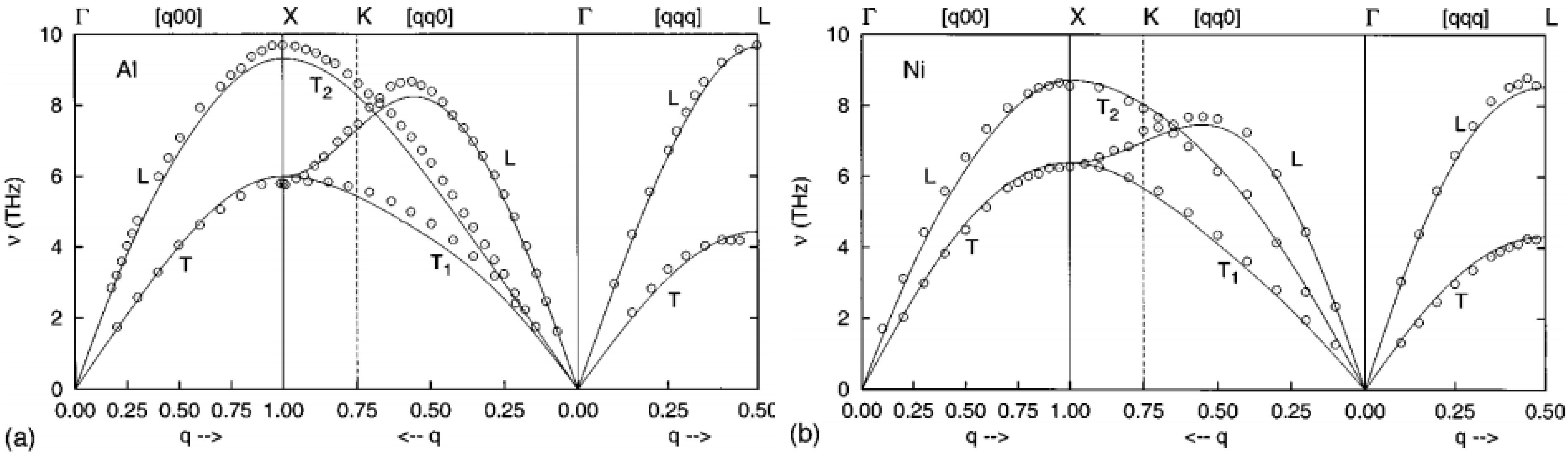
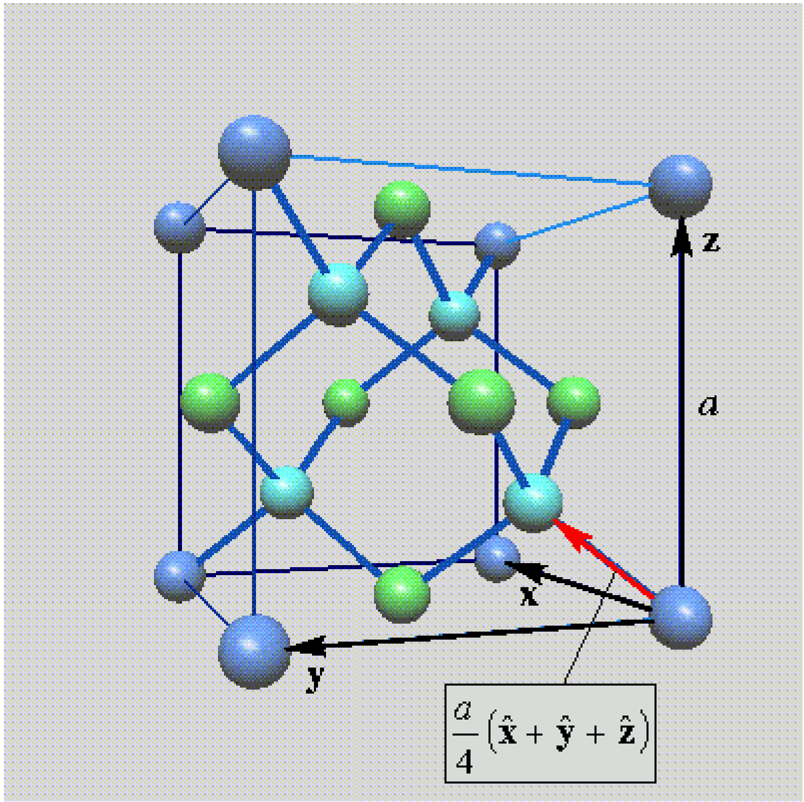


FIG. 2. Comparison of phonon-dispersion curves for Al (a) and Ni (b) predicted by the present EAM potentials, with the experimental values measured by neutron diffraction at 80 K (Al) and 298 K (Ni) (Ref. 33 for Al and Ref. 34 for Ni). The phonon frequencies at point *X* were included in the fitting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

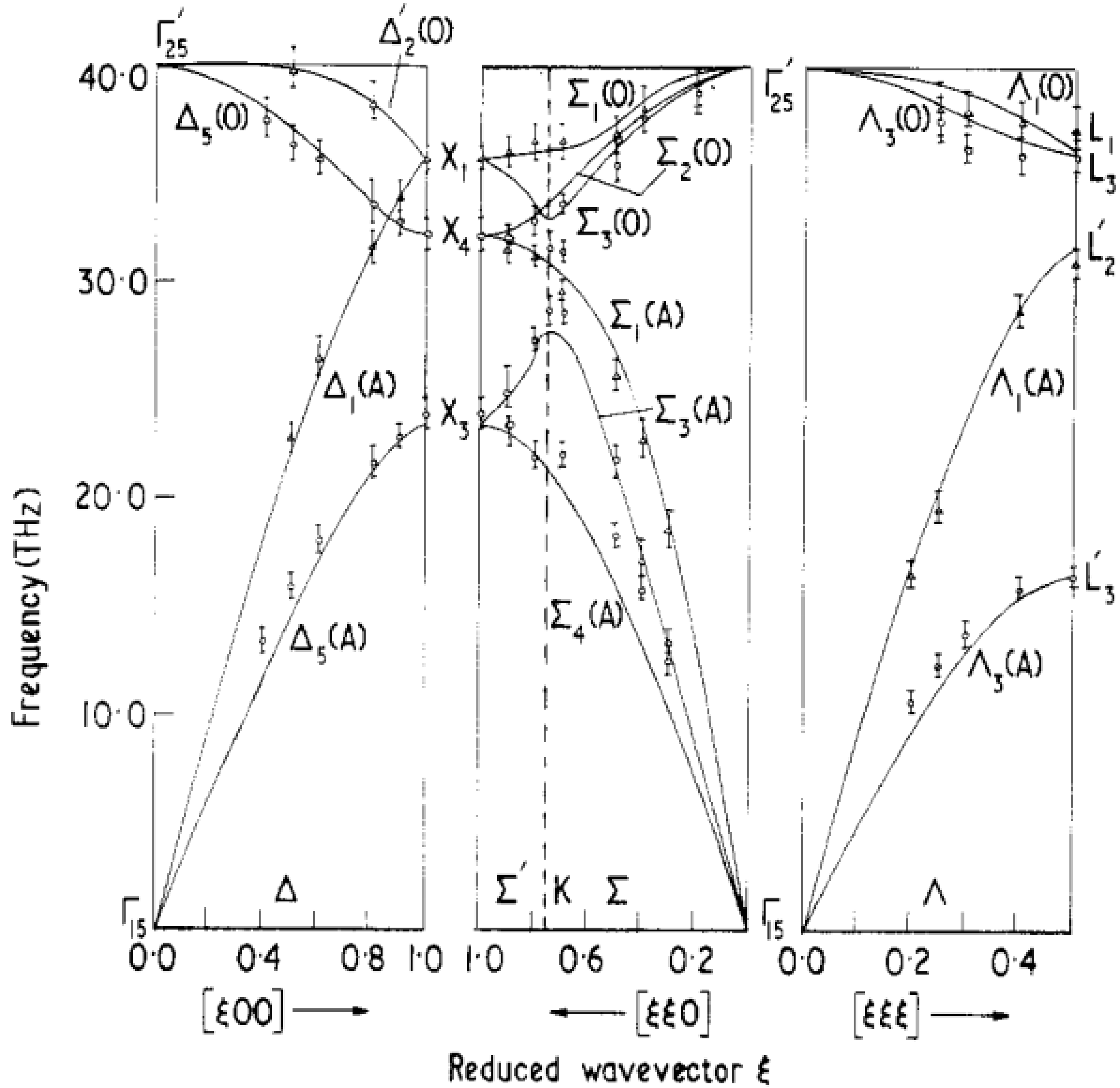


Figure 2. Phonon dispersion curves of diamond. Experimental points
et al (1965, 1967). △ and ○ represent the longitudinal and transverse m

Examples of phonon spectra of two forms of boron nitride

Cubic structure

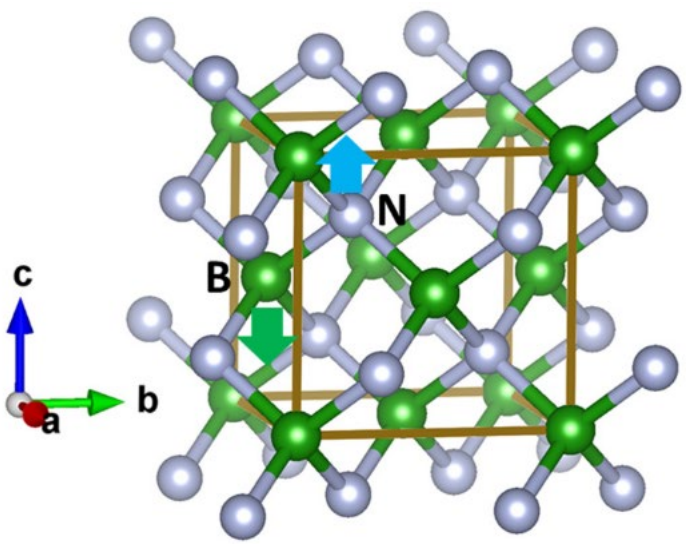


Figure 3. Ball and stick drawing of conventional unit cell of cubic BN (space group $F\bar{4}3m$ [44]) indicating one B and one N site within a primitive cell. The arrows indicate the vibrational directions of the atoms for one of the three degenerate optical modes at $\mathbf{q} = 0$ ($\mathbf{\Gamma}$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

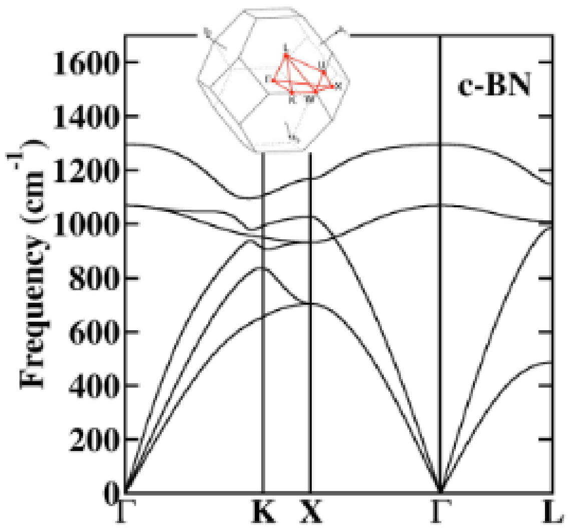


Figure 1. Phonon dispersion curves ($\omega^{\nu}(\mathbf{q})$) for cubic BN. The inset Brillouin zone diagram was reprinted from Setyawan *et al* [7], copyright (2010), with permission from Elsevier.

Examples of phonon spectra of two forms of boron nitride

Hexagonal structure

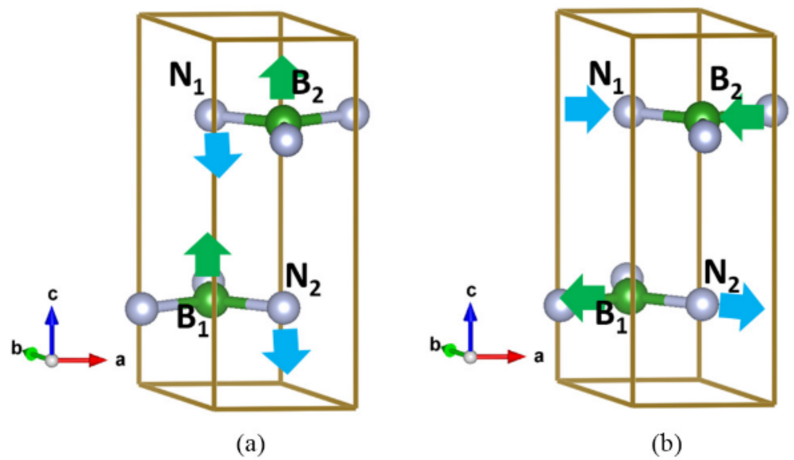


Figure 5. Ball and stick drawing of unit cell of hexagonal BN (space group $P6_3/mmc$ [44]) indicating the four B and N sites. The arrows indicate the vibrational directions of the atoms for $\mathbf{q} = 0$ (Γ point) mode # 7 (a) and for mode # 11 (b).

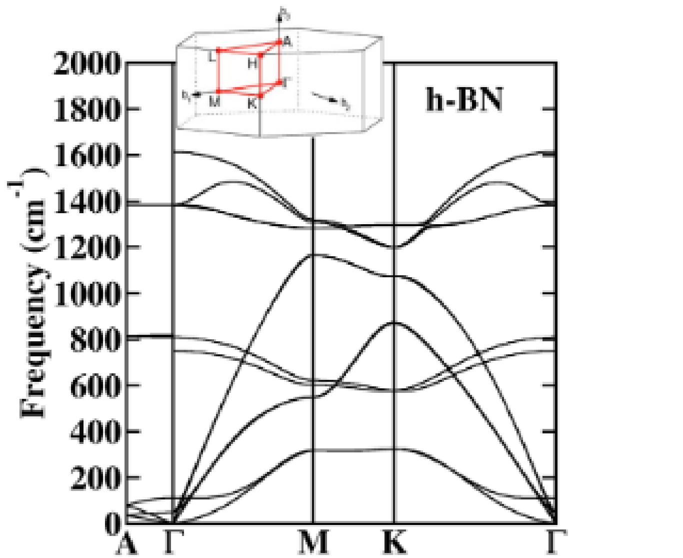


Figure 2. Phonon dispersion curves ($\omega^{\nu}(\mathbf{q})$) for hexagonal BN. The inset Brillouin zone diagram was reprinted from Setyawan *et al* [7], copyright (2010), with permission from Elsevier.

Helmholz free energy for vibrational energy at temperature T:

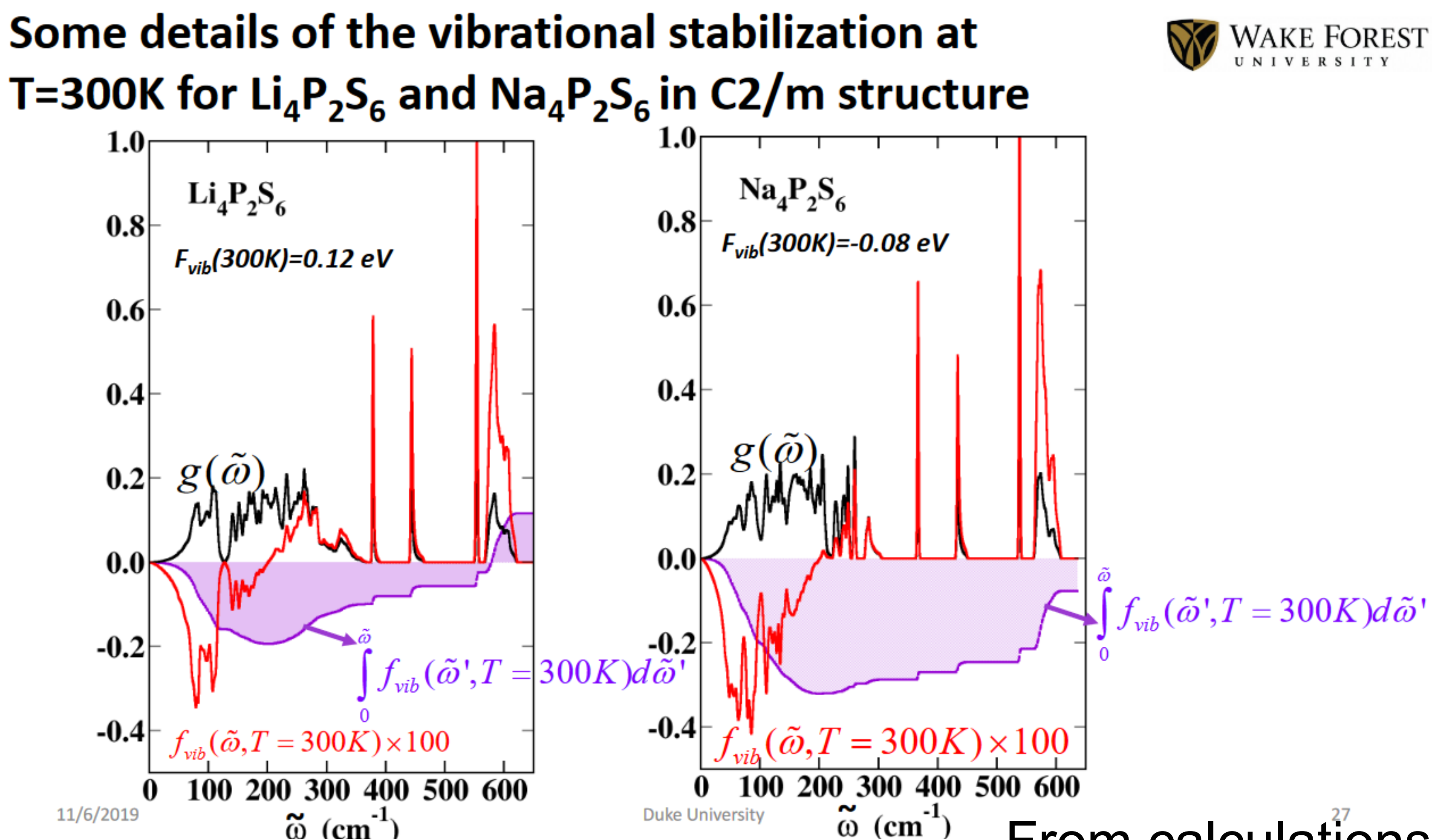
$$F_{\text{vib}}(T) = \int_0^{\infty} d\omega \, f_{\text{vib}}(\omega, T),$$

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

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 --

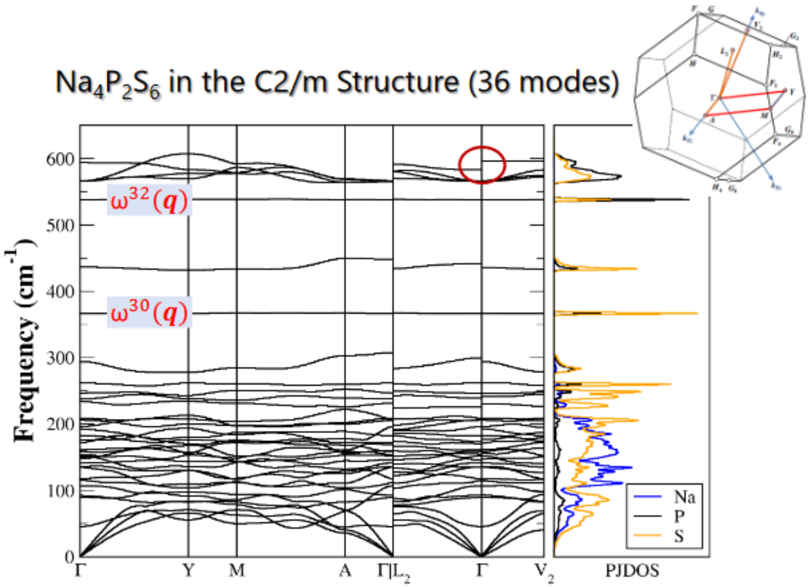


From calculations by Yan Li

Simulation of structural stability patterns -- continued

WAKE FOREST UNIVERSITY

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



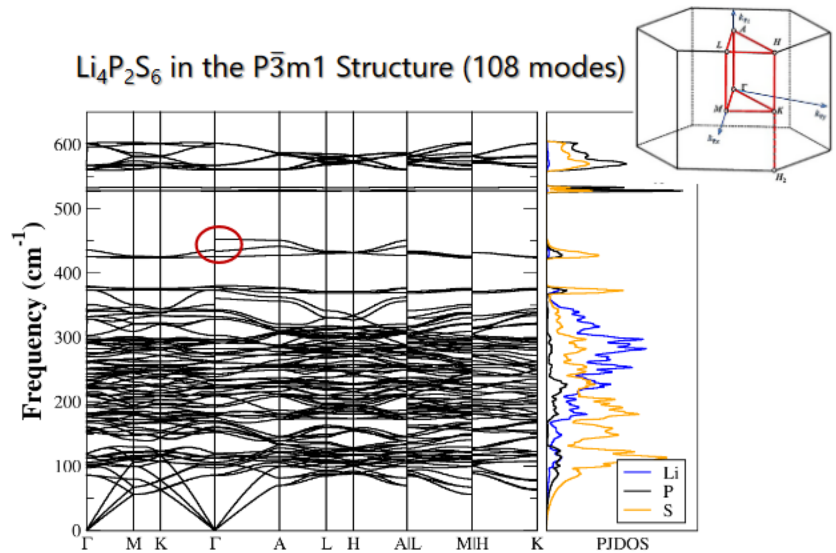
Na$^+$ 0~300 cm^{-1}

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

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



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

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

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 phonon

From calculations by Yan Li