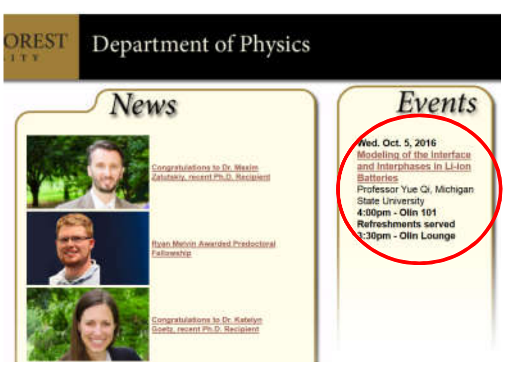
PHY 711 Classical Mechanics and Mathematical Methods
11-11:50 AM MWF Olin 107
(shifted to 9-9:50 AM for 10/4/2016)

Plan for Lecture 14:

Continue reading Chapter 4

1. Normal modes for extended one-dimensional systems
2. Normal modes for 2 and 3 dimensional systems

3	Wed, 9/07/2016	Chap. 1	Scattering theory	#3	9/9/2016
4	Fri, 9/09/2016	Chap. 1 & 2	Scattering theory and rotations	#4	9/12/2016
5	Mon, 9/12/2016	Chap. 3	Calculus of variations	#5	9/14/2016
6	Wed, 9/14/2016	Chap. 3	Calculus of variations	#6	9/16/2016
7	Fri, 9/16/2016	Chap. 3	Lagrangian mechanics	#7	9/19/2016
8	Mon, 9/19/2016	Chap. 3 and 6	Lagrangian mechanics and constraints	#8	9/21/2016
9	Wed, 9/21/2016	Chap. 3 and 6	Constants of the motion	#9	9/23/2016
10	Fri, 9/23/2016	Chap. 3 and 6	Hamiltonian and canonical equations of motion	#10	9/26/2016
11	Mon, 9/26/2016	Chap. 3 and 6	Phase space	#11	9/28/2016
12	Wed, 9/28/2016	Chap. 6	Canonical transformations	#12	9/30/2016
13	Fri, 9/30/2016	Chap. 4	Small oscillations	#13	10/04/2016
14	Tue, 10/04/2016	Chap. 4	Normal modes	#14	10/07/2016
15	Wed, 10/05/2016	Chap. 7	Wave motion in one dimension	#15	10/07/2016
16	Fri, 10/07/2016	Chap. 7			
17	Mon, 10/10/2016	Chap. 7		Take-home exam	
18	Wed, 10/12/2016			Take-home exam	
19	Fri, 10/14/2016			Take-home exam	
20	Mon, 10/17/2016			Exam due	
21	Wed, 10/19/2016				
	Fri, 10/21/2016		Fall break -- no class		
22	Mon, 10/24/2016				



WFU Physics Colloquium

TITLE: Modeling of the Interface and Interphases in Li-ion Batteries

SPEAKER: Professor Yue Qi,

Department of Chemical Engineering and Materials Science
Michigan State University
East Lansing, Michigan

TIME: Wednesday October 5, 2016 at 4:00 PM

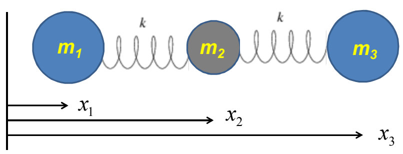
PLACE: Room 101 Olin Physical Laboratory

Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

ABSTRACT

One of the most significant challenges for current and future lithium ion batteries is the smart structure design at the nanoscale and the control of electron and ion transport at the electrode/electrolyte interface. This issue is further complicated by the existence of ultrathin solid electrolyte interphase (SEI) covering the electrode, forming a complex heterogeneous electrode/SEI/electrolyte interface. Based on joint multi-scale modeling and experimental results, we point out that the well-known two-layer structure of SEI also exhibits two different Li^+ ion transport mechanisms. The SEI has a porous (organic) outer layer permeable to both Li^+ and anions (dissolved in electrolyte), and a dense (inorganic) inner layer facilitate only Li^+ transport. This model suggests a strategy to deconvolute the

Example – linear molecule



$$L = \frac{1}{2} m_1 \dot{x}_1^2 + \frac{1}{2} m_2 \dot{x}_2^2 + \frac{1}{2} m_3 \dot{x}_3^2$$
$$- \frac{1}{2} k (x_2 - x_1 - \ell_{12})^2 - \frac{1}{2} k (x_3 - x_2 - \ell_{23})^2$$

Let: $x_1 \to x_1 - x_1^0 \quad x_2 \to x_2 - x_1^0 - \ell_{12} \quad x_3 \to x_3 - x_1^0 - \ell_{12} - \ell_{23}$

$$L = \frac{1}{2} m_1 \dot{x}_1^2 + \frac{1}{2} m_2 \dot{x}_2^2 + \frac{1}{2} m_3 \dot{x}_3^2 - \frac{1}{2} k (x_2 - x_1)^2 - \frac{1}{2} k (x_3 - x_2)^2$$

Coupled equations of motion :

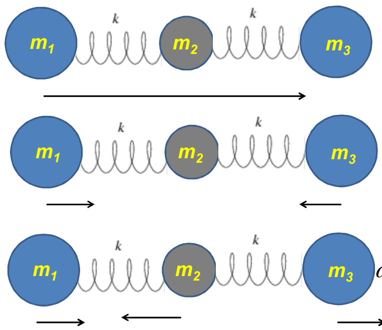
$$m_1 \ddot{x}_1 = k(x_2 - x_1)$$
$$m_2 \ddot{x}_2 = -k(x_2 - x_1) + k(x_3 - x_2) = k(x_1 - 2x_2 + x_3)$$
$$m_3 \ddot{x}_3 = -k(x_3 - x_2)$$

Let $x_i(t) = X_i^\alpha e^{-i\omega_\alpha t}$

$$-\omega_\alpha^2 m_1 X_1^\alpha = k(X_2^\alpha - X_1^\alpha)$$
$$-\omega_\alpha^2 m_2 X_2^\alpha = k(X_1^\alpha - 2X_2^\alpha + X_3^\alpha)$$
$$-\omega_\alpha^2 m_3 X_3^\alpha = -k(X_3^\alpha - X_2^\alpha)$$

For $m_1 = m_3 \equiv m_O$

and $m_2 \equiv m_C$

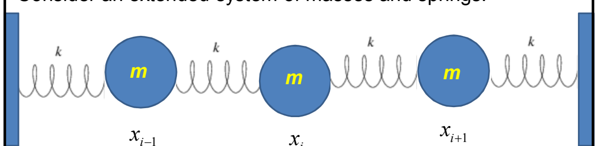


$\omega_1 = 0$

$\omega_2 = \sqrt{\frac{k}{m_O}}$

$\omega_3 = \sqrt{\frac{k}{m_O} + \frac{2k}{m_C}}$

Consider an extended system of masses and springs:



x_{i-1} x_i x_{i+1}

Note: each mass coordinate is measured relative to its equilibrium position x_i^0

$$L = T - V = \frac{1}{2} m \sum_{i=1}^{N} \dot{x}_i^2 - \frac{1}{2} k \sum_{i=0}^{N} \left(x_{i+1} - x_i \right)^2$$

Note: In fact, we have N masses; x_0 and x_{N+1} will be treated using boundary conditions.

$$L = T - V = \frac{1}{2} m \sum_{i=1}^{N} \dot{x}_i^2 - \frac{1}{2} k \sum_{i=0}^{N} \left(x_{i+1} - x_i \right)^2$$

$x_0 \equiv 0$ and $x_{N+1} \equiv 0$

From Euler - Lagrange equations:

$m\ddot{x}_1 = k(x_2 - 2x_1)$

$m\ddot{x}_2 = k(x_3 - 2x_2 + x_1)$

....

$m\ddot{x}_i = k(x_{i+1} - 2x_i + x_{i-1})$

....

$m\ddot{x}_N = k(x_{N-1} - 2x_N)$

From Euler - Lagrange equations :

$$m\ddot{x}_j = k\left(x_{j+1} - 2x_j + x_{j-1}\right) \qquad \text{with } x_0 = 0 = x_{N+1}$$

Try : $x_j(t) = Ae^{-i\omega t + iqaj}$

$$-\omega^2 Ae^{-i\omega t+iqaj} = \frac{k}{m}\left(e^{iqa} - 2 + e^{-iqa}\right)Ae^{-i\omega t+iqaj}$$

$$-\omega^2 = \frac{k}{m}\left(2\cos(qa) - 2\right)$$

$$\Rightarrow \omega^2 = \frac{4k}{m}\sin^2\left(\frac{qa}{2}\right)$$

From Euler - Lagrange equations - - continued :

$$m\ddot{x}_j = k\left(x_{j+1} - 2x_j + x_{j-1}\right) \qquad \text{with } x_0 = 0 = x_{N+1}$$

Try : $x_j(t) = Ae^{-i\omega t + iqaj}$ $\quad \Rightarrow \omega^2 = \frac{4k}{m}\sin^2\left(\frac{qa}{2}\right)$

Note that : $x_j(t) = Be^{-i\omega t - iqaj}$ $\quad \Rightarrow \omega^2 = \frac{4k}{m}\sin^2\left(\frac{qa}{2}\right)$

General solution :

$$x_j(t) = \Re\left(Ae^{-i\omega t+iqaj} + Be^{-i\omega t-iqaj}\right)$$

Impose boundary conditions :

$$x_0(t) = \Re\left(Ae^{-i\omega t} + Be^{-i\omega t}\right) = 0$$

$$x_{N+1}(t) = \Re\left(Ae^{-i\omega t+iqa(N+1)} + Be^{-i\omega t-iqa(N+1)}\right) = 0$$

Impose boundary conditions - - continued :

$$x_0(t) = \Re\left(Ae^{-i\omega t} + Be^{-i\omega t}\right) = 0$$

$$x_{N+1}(t) = \Re\left(Ae^{-i\omega t+iqa(N+1)} + Be^{-i\omega t-iqa(N+1)}\right) = 0$$

$\Rightarrow B = \text{-}A$

$$x_{N+1}(t) = \Re\left(Ae^{-i\omega t}\left(e^{iqa(N+1)} - e^{-iqa(N+1)}\right)\right) = 0$$

$$\Rightarrow \sin\left(qa(N+1)\right) = 0$$

$$\Rightarrow qa(N+1) = \nu\pi \quad \text{where } \nu = 0,1,2\cdots$$

$$qa = \frac{\nu\pi}{N+1}$$

Recap -- solution for integer parameter ν

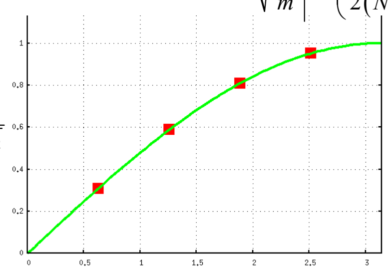
$$x_j(t) = \Re\left(2iAe^{-i\omega_\nu t}\sin\left(\frac{\nu\pi j}{N+1}\right)\right)$$

$$\omega_\nu{}^2 = \frac{4k}{m}\sin^2\left(\frac{\nu\pi}{2(N+1)}\right)$$

Note that non-trivial, unique values are

$$\nu = 1, 2, \cdots N$$

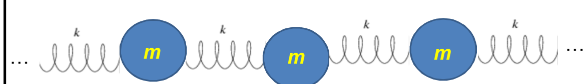
Example for *N=4*: $\omega_\nu = \sqrt{\frac{4k}{m}}\left|\sin\left(\frac{\nu\pi}{2(N+1)}\right)\right|$



Note that solution form remains correct for *N*→∞

$$\omega(qa) = \sqrt{4k/m}\left|\sin(qa)\right|$$

For extended chain without boundaries:



From Euler-Lagrange equations:

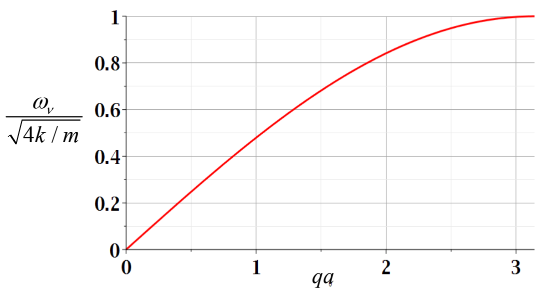
$$m\ddot{x}_j = k\left(x_{j+1} - 2x_j + x_{j-1}\right) \qquad \text{for all } x_j$$

Try: $x_j(t) = Ae^{-i\omega t + iqaj}$

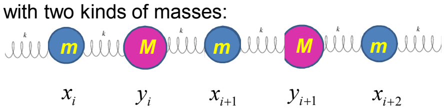
$$-\omega^2 Ae^{-i\omega t+iqaj} = \frac{k}{m}\left(e^{iqa} - 2 + e^{-iqa}\right)Ae^{-i\omega t+iqaj}$$

$$-\omega^2 = \frac{k}{m}\left(2\cos(qa) - 2\right)$$

$$\Rightarrow \omega^2 = \frac{4k}{m}\sin^2\left(\frac{qa}{2}\right) \qquad \text{distinct values for } 0 \le qa \le \pi$$



Consider an infinite system of masses and springs now with two kinds of masses:



Note: each mass coordinate is measured relative to its equilibrium position $x_i^0, y_i^0, \cdots$

$$L = T - V$$
$$= \frac{1}{2} m \sum_{i=0}^{\infty} \dot{x}_i^2 + \frac{1}{2} M \sum_{i=0}^{\infty} \dot{y}_i^2 - \frac{1}{2} k \sum_{i=0}^{\infty} (x_{i+1} - y_i)^2 - \frac{1}{2} k \sum_{i=0}^{\infty} (y_i - x_i)^2$$

$$L = T - V$$
$$= \frac{1}{2} m \sum_{i=0}^{\infty} \dot{x}_i^2 + \frac{1}{2} M \sum_{i=0}^{\infty} \dot{y}_i^2 - \frac{1}{2} k \sum_{i=0}^{\infty} (x_{i+1} - y_i)^2 - \frac{1}{2} k \sum_{i=0}^{\infty} (y_i - x_i)^2$$

Euler - Lagrange equations:

$$m\ddot{x}_j = k\left(y_{j-1} - 2x_j + y_j\right)$$
$$M\ddot{y}_j = k\left(x_j - 2y_j + x_{j+1}\right)$$

Trial solution:

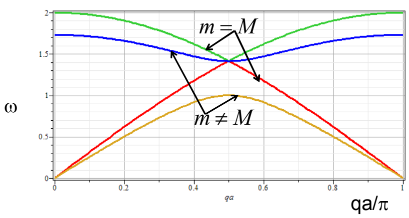
$$x_j(t) = Ae^{-i\omega t + i2qaj}$$
$$y_j(t) = Be^{-i\omega t + i2qaj}$$

$$\begin{pmatrix} m\omega^2 - 2k & k\left(e^{-i2qa} + 1\right) \\ k\left(e^{i2qa} + 1\right) & M\omega^2 - 2k \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = 0$$

$$\begin{pmatrix} m\omega^2 - 2k & k\left(e^{-i2qa}+1\right) \\ k\left(e^{i2qa}+1\right) & M\omega^2 - 2k \end{pmatrix}\begin{pmatrix} A \\ B \end{pmatrix} = 0$$

Solutions :

$$\omega_\pm^{\ 2} = \frac{k}{m} + \frac{k}{M} \pm k\sqrt{\frac{1}{m^2} + \frac{1}{M^2} + \frac{2\cos(2qa)}{mM}}$$



Eigenvectors:

For $qa = 0$:

$$\omega_- = 0 \qquad \omega_+ = \sqrt{\frac{2k}{m} + \frac{2k}{M}}$$

$$\begin{pmatrix} A \\ B \end{pmatrix}_- = N\begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \begin{pmatrix} A \\ B \end{pmatrix}_+ = N\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

For $qa = \frac{\pi}{2}$:

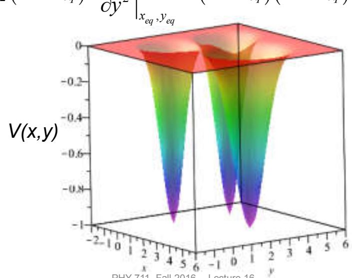
$$\omega_- = \sqrt{\frac{2k}{M}} \qquad \omega_+ = \sqrt{\frac{2k}{m}}$$

$$\begin{pmatrix} A \\ B \end{pmatrix}_- = N\begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \begin{pmatrix} A \\ B \end{pmatrix}_+ = N\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

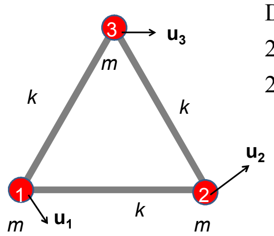
Potential in 2 and more dimensions

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

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

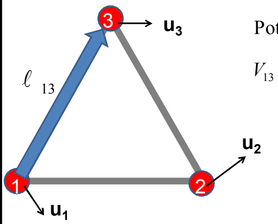


Example – normal modes of a system with the symmetry of an equilateral triangle



Degrees of freedom for 2-dimensional motion:
$2N = 6$

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

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

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

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

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

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

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

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

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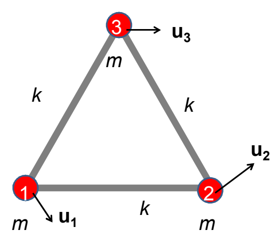
Example – normal modes of a system with the symmetry of an equilateral triangle -- continued



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

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3-dimensional periodic lattices

Example – face-centered-cubic unit cell (Al or Ni)

Diagram of atom positions

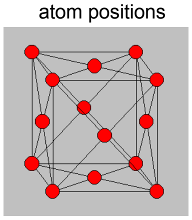
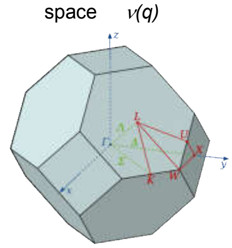


Diagram of q-space $\nu(q)$



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

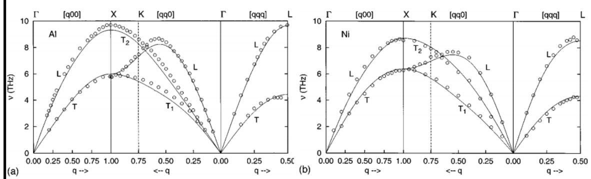
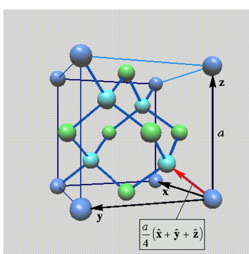


FIG. 2. Comparison of phonon-dispersion curves for Al (a) and Ni (b) predicted by the present EAM potentials, with the experimental values measured by neutron diffraction at 80 K (Al) and 298 K (Ni) (Ref. 33 for Al and Ref. 34 for Ni). The phonon frequencies at point *X* were included in the fitting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

Lattice vibrations for 3-dimensional lattice

Example: diamond lattice



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

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

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

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

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

Equations of motion:

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

Solution form:

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

Details: $\mathbf{R}_0^a = \boldsymbol{\tau}^a + \mathbf{T}$ where $\boldsymbol{\tau}^a$ denotes unique sites and $\mathbf{T}$ denotes replicas

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" $\omega(\mathbf{q})$

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

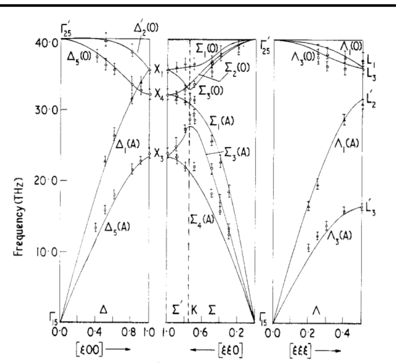


Figure 2. Phonon dispersion curves of diamond. Experimental points *et al* (1965, 1967). △ and ○ represent the longitudinal and transverse m