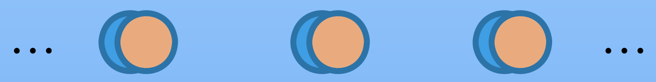
Lecture 4
Crystal Bonding
Intro to Phonons

- 1,2,3,∞
- Phonon = [Accoustic or Optic] Lattice Vibrations

  Accoustic Phonons are Goldstone Bosons for
  Breaking Translation Symmetry

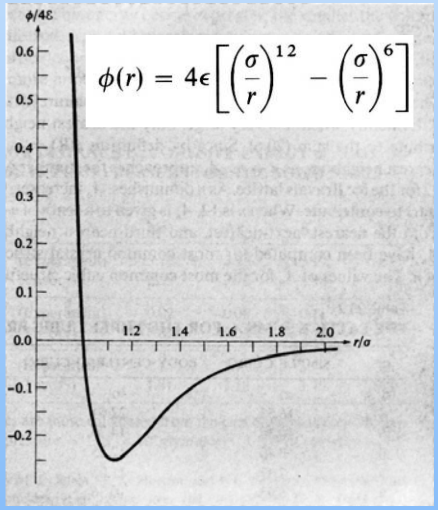


Classification of Solids

- "Molecular" Crystals

  Van der Waals attraction + Hard core repulsion

  Lennard-Jones "6-12" potential



- Ionic Crystals
- Covalent Crystals
- Metals
- Hydrogen-Bonded Solids

Crystal Bonding

- Measurement of bonding strength
  - *Cohesive energy*

    Energy to separate crystal into neutral free "atoms"
  - *Lattice energy* (ionic crystal)

    Energy to separate crystal into infinitely separated ions

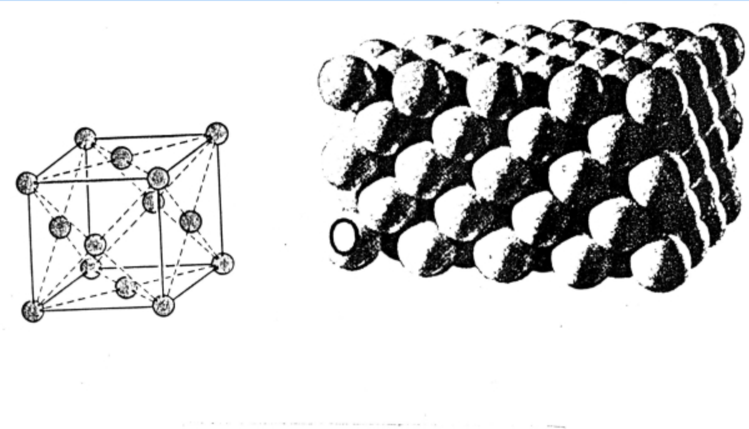
    (related to "*Madelung potential, energy, constant*")
- All due to electrons and protons and statistics

  (Property of many body ground state)

Crystal Bonding – van der Waals

Inert Gas Elements
He, Ne, Ar, Kr, Xe

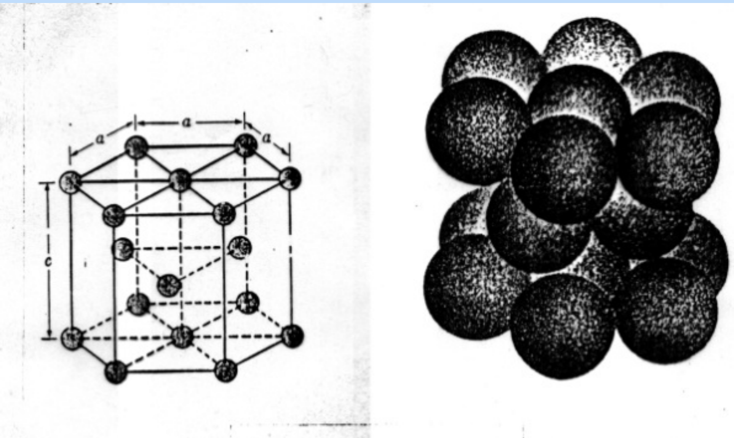
FCC (C<u>CP</u>)



Face Centered Cubic Lattice

Inert Gas Elements
He

H<u>CP</u>



Hexagonal Lattices

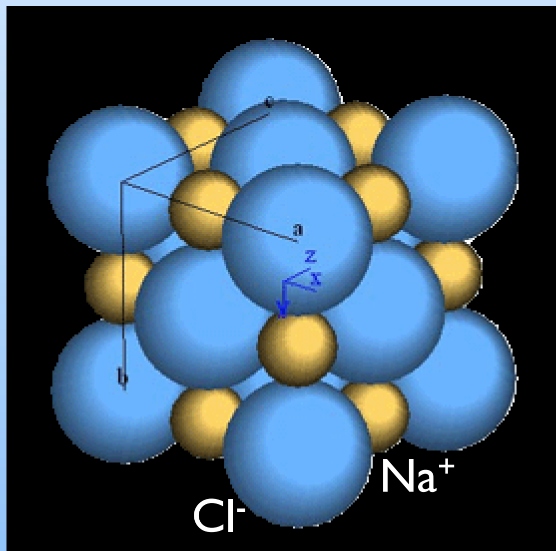
http://www.ae.iitm.ac.in/~sriram/as401/materials

Lattice/Crystal Sum of Lennard-Jones "6-12" potential accounts well for lattice constant, cohesive energy, bulk modulus etc. of heavy elements (cf. chap. 20 of A&M)

Crystal Bonding – Ionic Bonding

Long-Range Coulomb Interaction dominates over the vdW interaction.

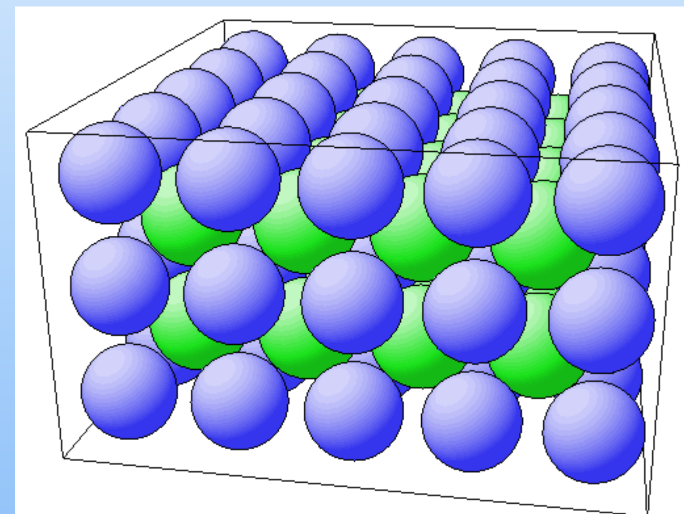
NaCl



http://www.matsci.ucdavis.edu/MatSciLT/ENG-45L/images/CaRIne.gif

Cl^- bigger than Na^+, by a factor of 2
Looks like close packing of bigger ions
fcc with two atom basis

CsCl



http://www.cmmp.ucl.ac.uk/~ijf/3c25/CsCl.gif

sc (simple cubic) with two atom basis

Madelung Energy, Constant

- $r_{ij} = p_{ij}\, r$
  (r = n.n. distance; i,j = ion position indices)
- **Madenlung Constant** $\alpha \equiv \Sigma'_j\, (\pm)/p_j$
  Σ'_j = sum over all ion positions, except the one in focus
  +(-) for opposite(equal) charge
- Energy per ion pair
  Madelung Energy + Repulsion

Table 20.4
THE MADELUNG CONSTANT α FOR SOME CUBIC CRYSTAL STRUCTURES

CRYSTAL STRUCTURE	MADELUNG CONSTANT α
Cesium chloride	1.7627
Sodium chloride	1.7476
Zincblende	1.6381

cf. Marder, Kittel

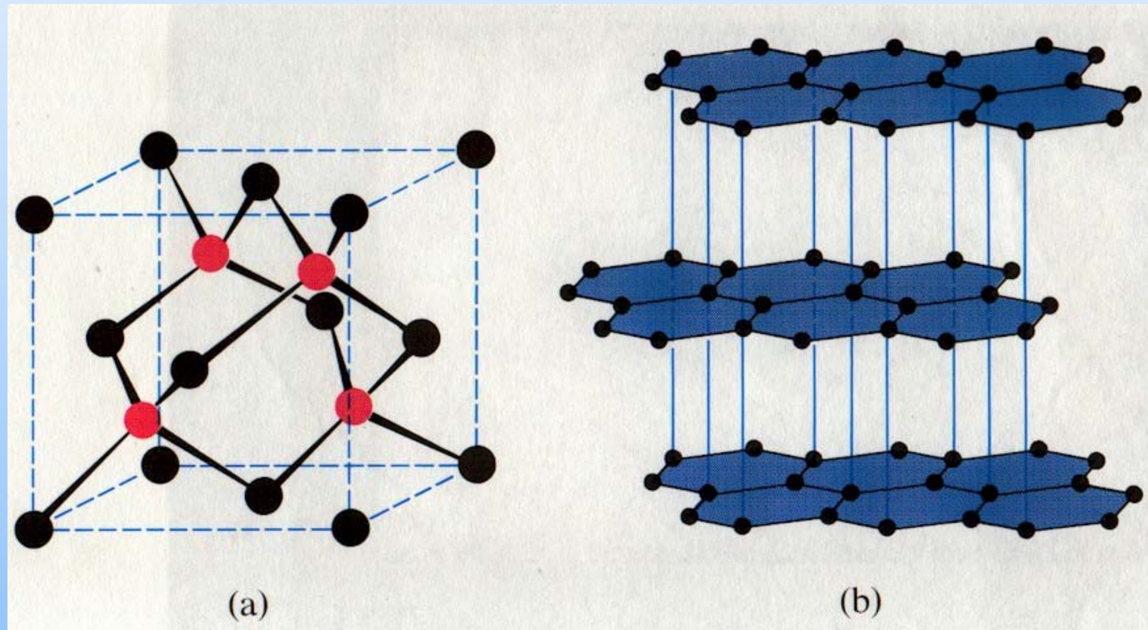
$$u(r) = -\frac{\alpha e^2}{r} + \frac{C}{r^m}$$

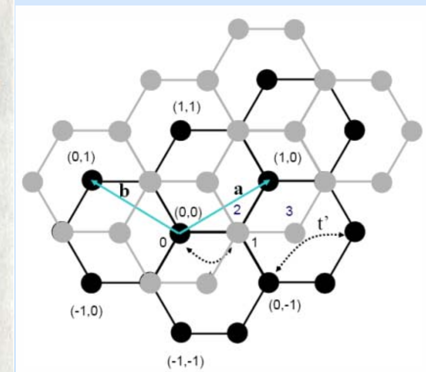
(consider e as Q, if necessary)

Fit to ground state properties like in molecular crystals:
lattice constant, compressibility, Bulk modulus, …

Crystal Bonding – Covalent Bonding

- Diamond
- Graphite





Top view
Gray=top
Black=next layer

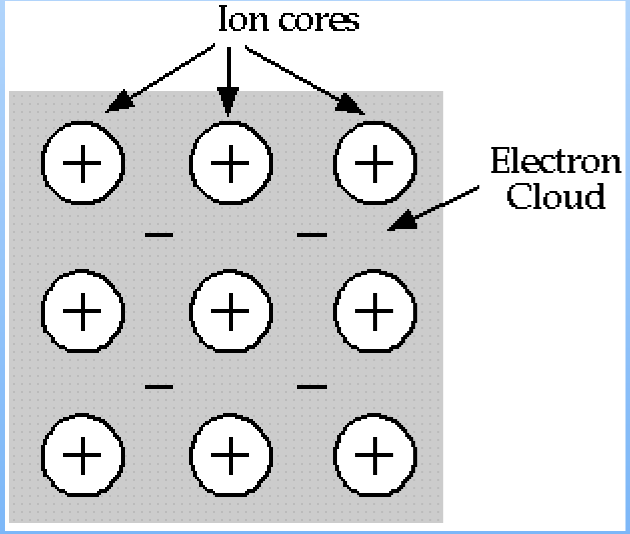
http://library.tedankara.k12.tr/chemistry/vol2/allotropy/h76.jpg

fcc with two atom basis
000 and ¼, ¼, ¼
ZnS, Si, Ge, GaAs
sp^3 bonding

Hexagonal with four atom basis
sp^2 bonding
Weak inter-plane bonding ("Van der Waals")
More stable than diamond!

Crystal Bonding – Metallic "Bonding" and Hydrogen Bonding

- Metallic "Bonding": Electrons are released freely from atom and spend most of their time freely.
  Energy lowering can be viewed as "kinetic energy lowering."
  Na, Cu, Al, …



Electronic structure calculation over the whole crystal becomes <u>essential</u> for covalent crystals and metals.

- Hydrogen Bonding:
  DNA, Water (Ice)!

Born – von Karman Boundary Condition

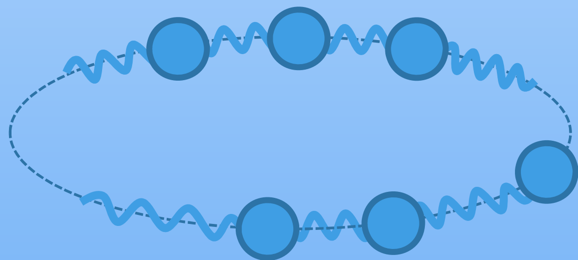
- Periodic Boundary Condition to describe the bulk property of crystals
- N unit cells are considered
  - In 1d, a crystal is a circle.
  - In 2d, a crystal is a torus.
  - In other dimensions, it is a hyper-torus.

Phonons – Quick Reminders of CM

- Let's recall some classical mechanics –
  coupled harmonic oscillator problem in one dimension (for simplicity, but without losing essence).
- For the following three cases, enumerate the total number of degrees of freedom. For the first case, sketch normal modes. For the low energy normal mode, find equivalent normal modes for the right two cases.

2 balls

3 balls

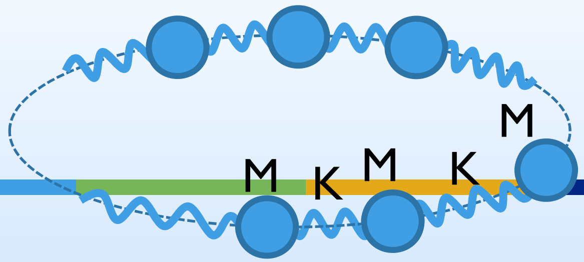


N balls on a ring/circle

Some more CM
Soft mode and stiff mode

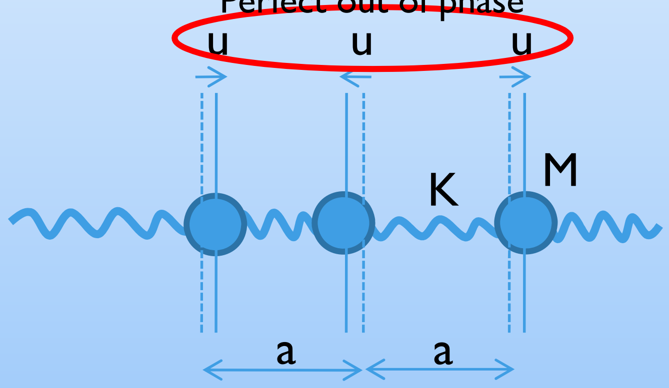
- Consider the "ring" problem

  which is model for 1d crystal (why?).

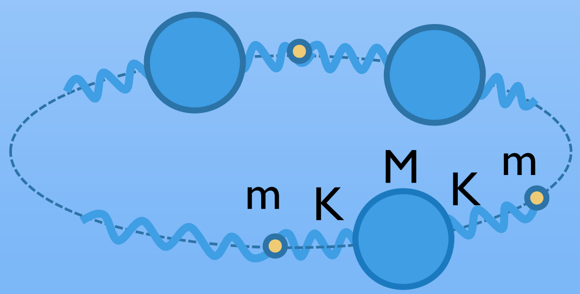


N balls on a circle

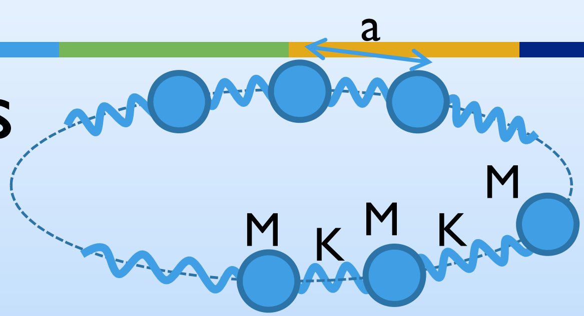
1) State the lowest ω mode and its k (wave vector).
2) Suppose the following mode was allowed.
   What is k? Obtain ω from
   Newton's eq. for u. Explain why this
   is the hardest or "stiffest" mode.
   (maximum frequency)



3) Now, consider two atoms
   per unit cell. Consider the limit M >> m.
   Discuss (k, ω) for the following three physical modes.
   (i) lowest energy mode,
   (ii) M's move perfectly out of phase
   and m just follows,
   (iii) m's move and M is fixed



Monatomic 1d harmonic crystal



N balls on a circle

- N balls – N normal modes
- By solving Newton's eq.

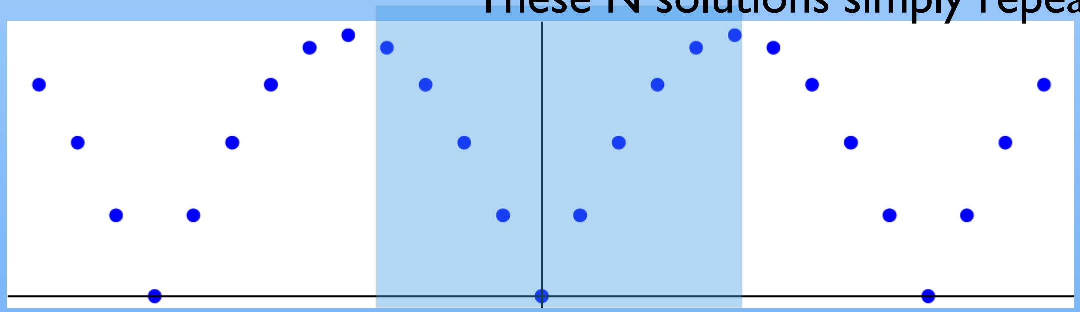
$$M\,\frac{d^2u_i}{dt^2} = -K\,[(u_i - u_{i-1}) + (u_i - u_{i+1})]$$

with a travelling wave form

$$u_n = A\exp[i(kx_n - \omega t)] = A\exp[i(kna - \omega t)]$$

one finds all N normal modes (eq. 2.9).

These N solutions simply repeat.



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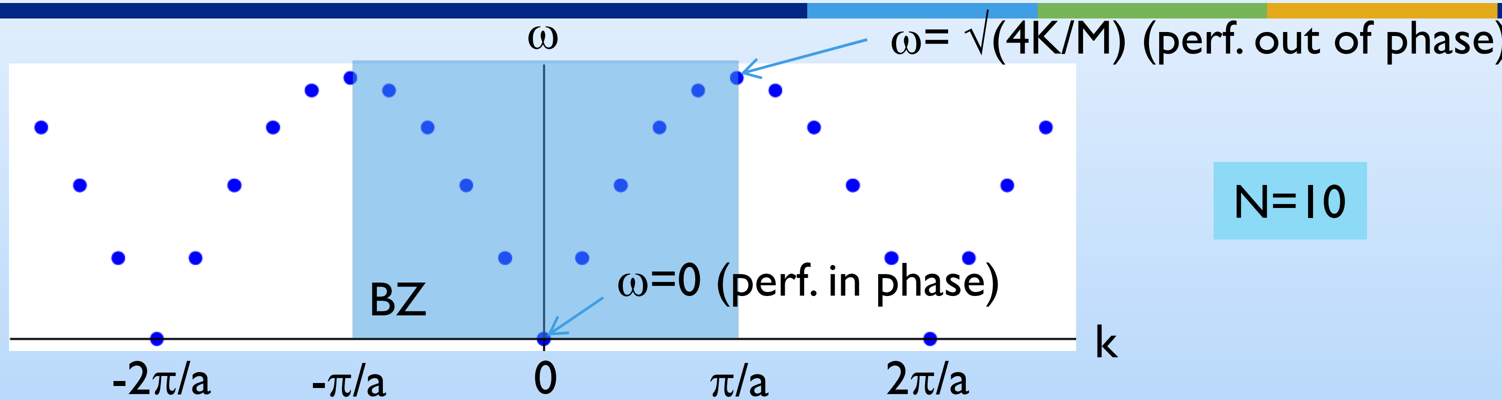
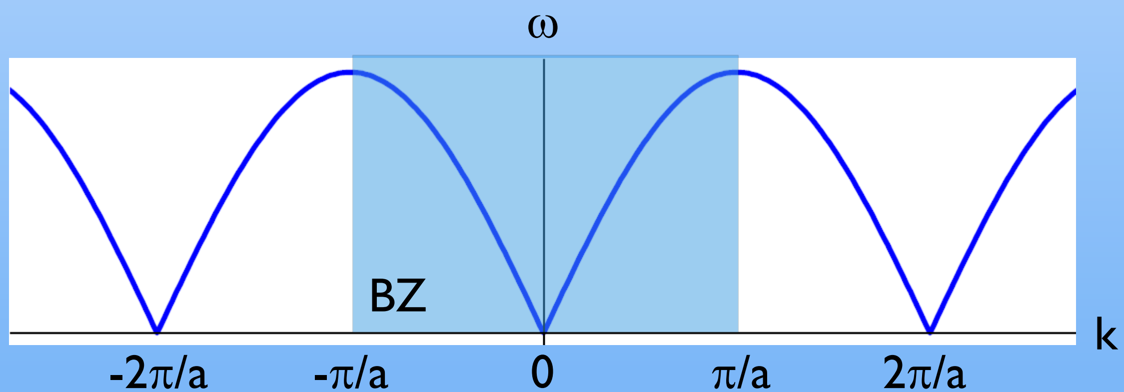


N=10

- k period = $2\pi/a$, N solutions in one period (i.e. complete)
- k step = $2\pi/(Na) = 2\pi/L$ (L=length of crystal=circumference of ring)
- $\omega = vk$ for small k, with $v = a\sqrt{K/M}$ (sound velocity)



N=∞

The momentum quantum in crystal (Very Important!)

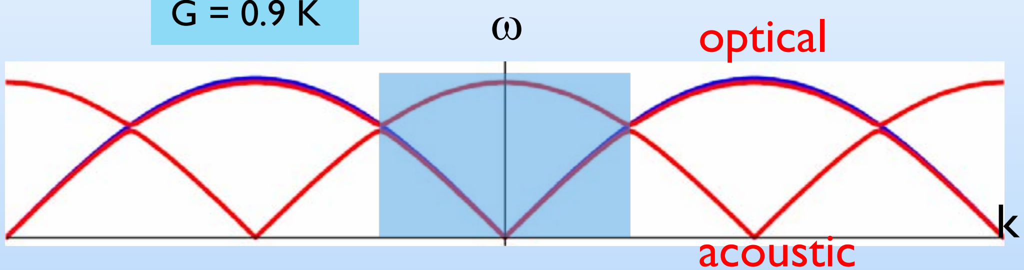
- Let's use "Bravais Lattice" to mean primitive from now on, unless noted otherwise. By the same token, "unit cell" means "primitive unit cell."
- "Lattice" usually means either "Bravais Lattice" or "Crystal Lattice" (i.e. crystal itself) – context is a big part of language!

- If the crystal consists of N unit cells in position space, then there are N distinct k points per unit cell in momentum space. This is true for <u>all</u> waves (= particles) in crystal <u>independent</u> of all other details (number of atoms in the basis, the nature of wave and so on). E.g. In 1d, the quantum of k is $2\pi/L = 2\pi/(Na)$.

Diatomic 1d harmonic crystal

Change spring constant at every other bond from K to G

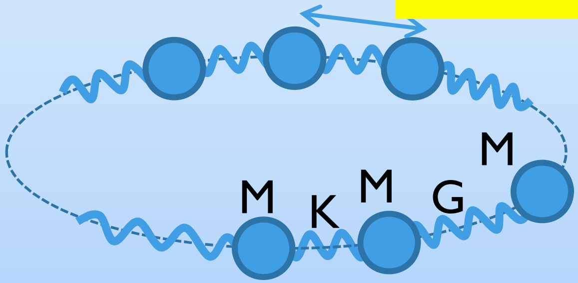
G = 0.9 K



Blue: before

Red: after change

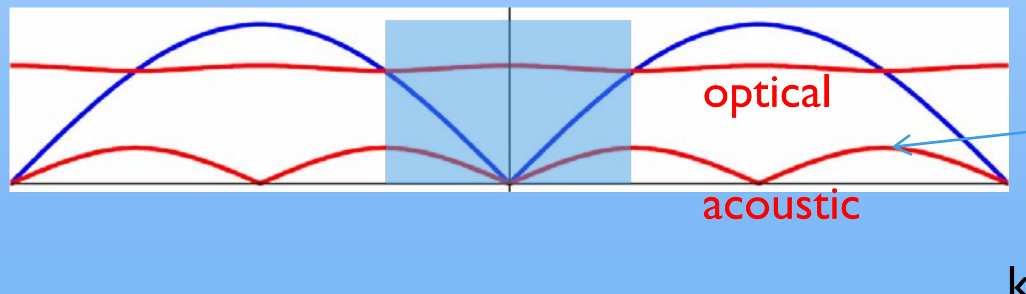
Differs from A&M !



- Real space periodicity doubles, and so k space periodicity halves.
- k spacing ($2\pi/L$) is unchanged.
- Number of branches doubles (2 – acoustic and optical – now).
- Total number of modes = total number of atoms = unchanged (only because of our underlying assumption here)

- Acoustic branch: $\omega \to 0$ as $k \to 0$
- Optical branch: others

G = 0.1 K

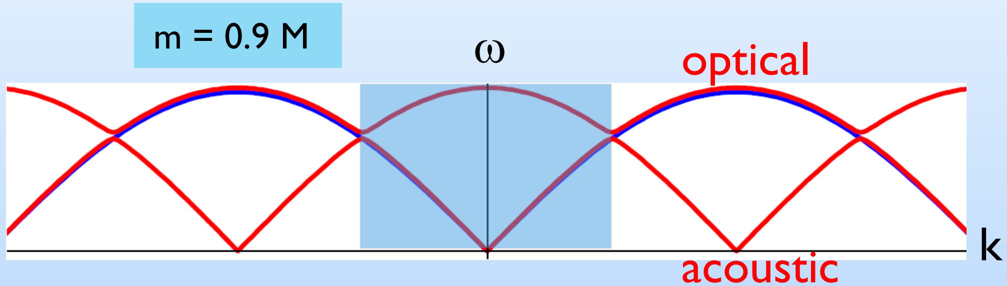


$\omega \approx \sqrt{(2K/M)}$

$\omega = \sqrt{(2G/M)}$

Diatomic 1d harmonic crystal

Change mass at every other atom from M to m



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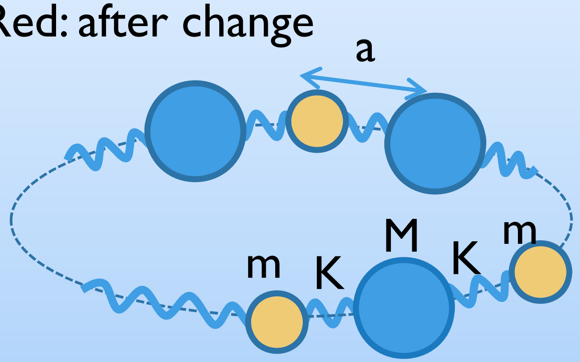

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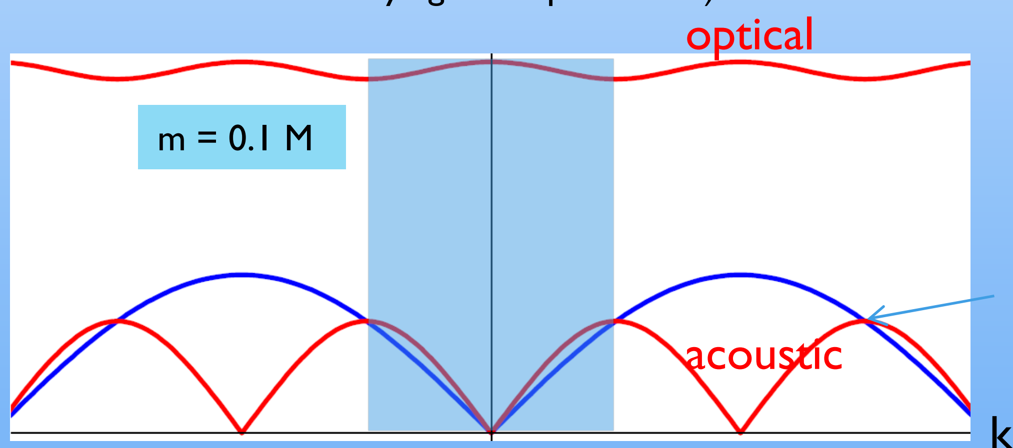

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