INTRODUCTION
to the Computational Laboratory

Giuseppe Mallia
g.mallia@imperial.ac.uk

Imperial College London - Chemistry Department
Thomas Young Centre:
the London Centre for Theory and Simulation of Materials

AUTUM 2014

Outline

TIMETABLE and DEADLINE

Session	Start Date	End Date	Report Deadline
1	13/10/2014	17 / 10 / 2014	24 / 10 / 2014
2	27/10/2014	31 / 10 / 2014	07 / 11 / 2014
3	10/11/2014	14 / 11 / 2014	21 / 11 / 2014
4	24/11/2014	18 / 11 / 2014	05 / 12 / 2014
5	08/12/2014	12 / 12 / 2014	19 / 12 / 2014

TIMETABLE and DEADLINE

Session	Start Date	End Date	Report Deadline
1	13/10/2014	17 / 10 / 2014	24 / 10 / 2014
2	27/10/2014	31 / 10 / 2014	07 / 11 / 2014
3	10/11/2014	14 / 11 / 2014	21 / 11 / 2014
4	24/11/2014	18 / 11 / 2014	05 / 12 / 2014
5	08/12/2014	12 / 12 / 2014	19 / 12 / 2014

- Demonstrator

	Mon	Tue	Thur	Fri
1:00-4:00	☺	☺	☺	☺

DEADLINE:

when? **12:00am on next Friday**

where? Blackboard - bb.imperial.ac.uk

AIM:
The Thermal Expansion of MgO

- to predict how the material expands when heated;
- to calculate the thermal expansion coefficient: $\alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P$

AIM:
The Thermal Expansion of MgO

- to predict how the material expands when heated;
- to calculate the thermal expansion coefficient:
  $\alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P$
- **QUASI-HARMONIC APPROXIMATION** (LD)
  to compute vibrational energy levels of MgO;
  to understand the **phonon dispersion** of a material and the vibrational density of state;

AIM:
The Thermal Expansion of MgO

- to predict how the material expands when heated;
- to calculate the thermal expansion coefficient:
  $\alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P$
- **QUASI-HARMONIC APPROXIMATION** (LD)
  to compute vibrational energy levels of MgO;
  to understand the **phonon dispersion** of a material and the vibrational density of state;
- **MOLECULAR DYNAMICS** (MD)
  to simulate the vibrations as random motions of atoms inside a cell;

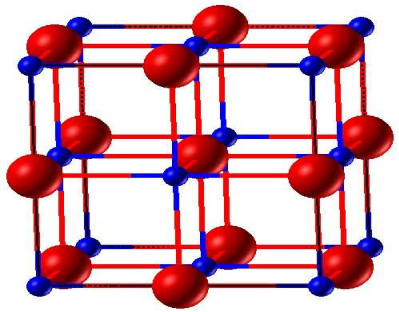
AIM:
The Thermal Expansion of MgO

- to predict how the material expands when heated;
- to calculate the thermal expansion coefficient:
  $\alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P$
- **QUASI-HARMONIC APPROXIMATION** (LD)
  to compute vibrational energy levels of MgO;
  to understand the **phonon dispersion** of a material and the vibrational density of state;
- **MOLECULAR DYNAMICS** (MD)
  to simulate the vibrations as random motions of atoms inside a cell;
- to compare QUASI-HARMONIC APPROXIMATION with MOLECULAR DYNAMICS results.

SYSTEMS: MgO crystal (fcc)

IDEAL, NON DEFECTIVE, PERIODIC SYSTEM IN 3D

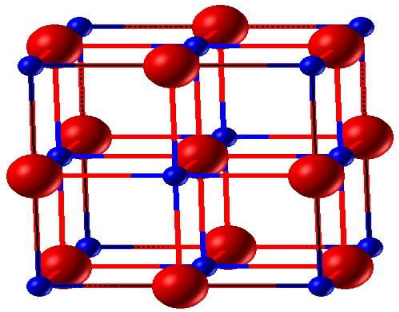
- CONVENTIONAL CELL
  $\mathbf{a}_c$=$\mathbf{b}_c$=$\mathbf{c}_c$; α_c, β_c, γ_c
  N_c: number of atoms
  V_c: volume

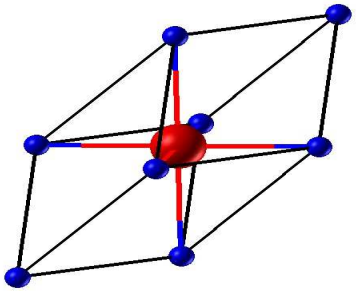


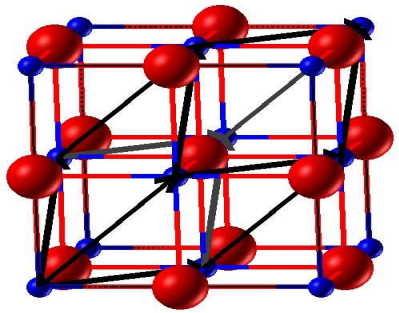
SYSTEMS: MgO crystal (fcc)

IDEAL, NON DEFECTIVE, PERIODIC SYSTEM IN 3D

- CONVENTIONAL CELL
  $\mathbf{a}_c$=$\mathbf{b}_c$=$\mathbf{c}_c$; α_c, β_c, γ_c
  N_c: number of atoms
  V_c: volume
- PRIMITIVE CELL
  $\mathbf{a}_p$=$\mathbf{b}_p$=$\mathbf{c}_p$; α_p, β_p, γ_p
  N_c: number of atoms
  V_p: volume



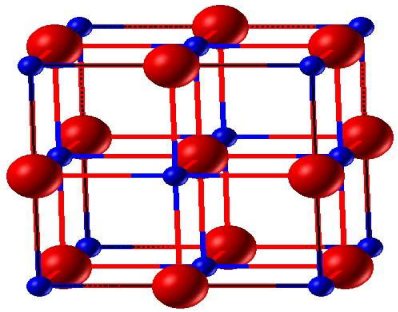


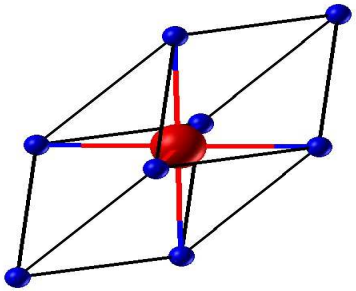


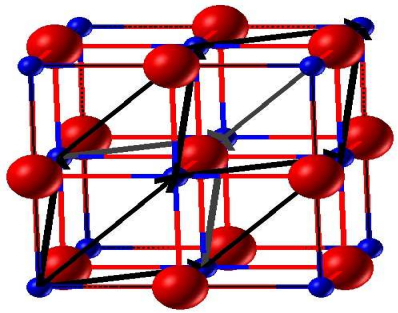
SYSTEMS: MgO crystal (fcc)

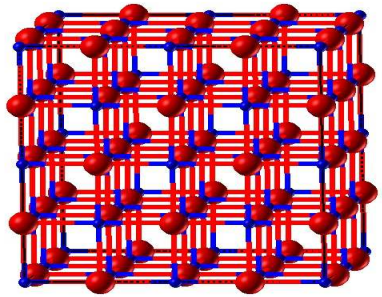
IDEAL, NON DEFECTIVE, PERIODIC SYSTEM IN 3D

- CONVENTIONAL CELL
  $\mathbf{a}_c$=$\mathbf{b}_c$=$\mathbf{c}_c$; α_c, β_c, γ_c
  N_c: number of atoms
  V_c: volume
- PRIMITIVE CELL
  $\mathbf{a}_p$=$\mathbf{b}_p$=$\mathbf{c}_p$; α_p, β_p, γ_p
  N_c: number of atoms
  V_p: volume
- SUPERCELL
  $\mathbf{a}_s$=$\mathbf{b}_s$=$\mathbf{c}_s$= 2 $\times$ $\mathbf{a}_c$
  α_s, β_s, γ_s
  N_s: number of atoms
  V_s: volume









SYSTEMS II: lattice parameter of MgO

What is the lattice parameter of MgO?

SYSTEMS II: lattice parameter of MgO

What is the lattice parameter of MgO?

CONVENTIONAL CELL

$\mathbf{a}_c = \mathbf{b}_c = \mathbf{c}_c$; α_c, β_c, γ_c

SYSTEMS II: lattice parameter of MgO

What is the lattice parameter of MgO?

CONVENTIONAL CELL

$\mathbf{a}_c = \mathbf{b}_c = \mathbf{c}_c$; α_c, β_c, γ_c

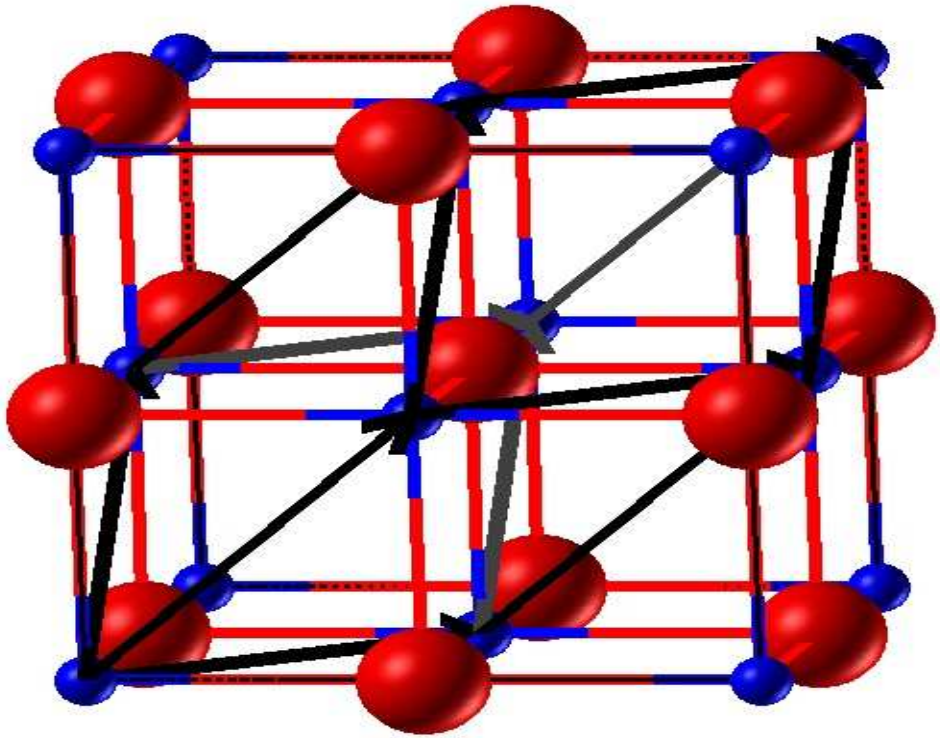
$\mathbf{a}_c$

SYSTEMS III

Is it possible to move
from the CONVENTIONAL CELL
to the PRIMITIVE CELL?

SYSTEMS III

Is it possible to move
from the CONVENTIONAL CELL
to the PRIMITIVE CELL?



VIBRATIONS

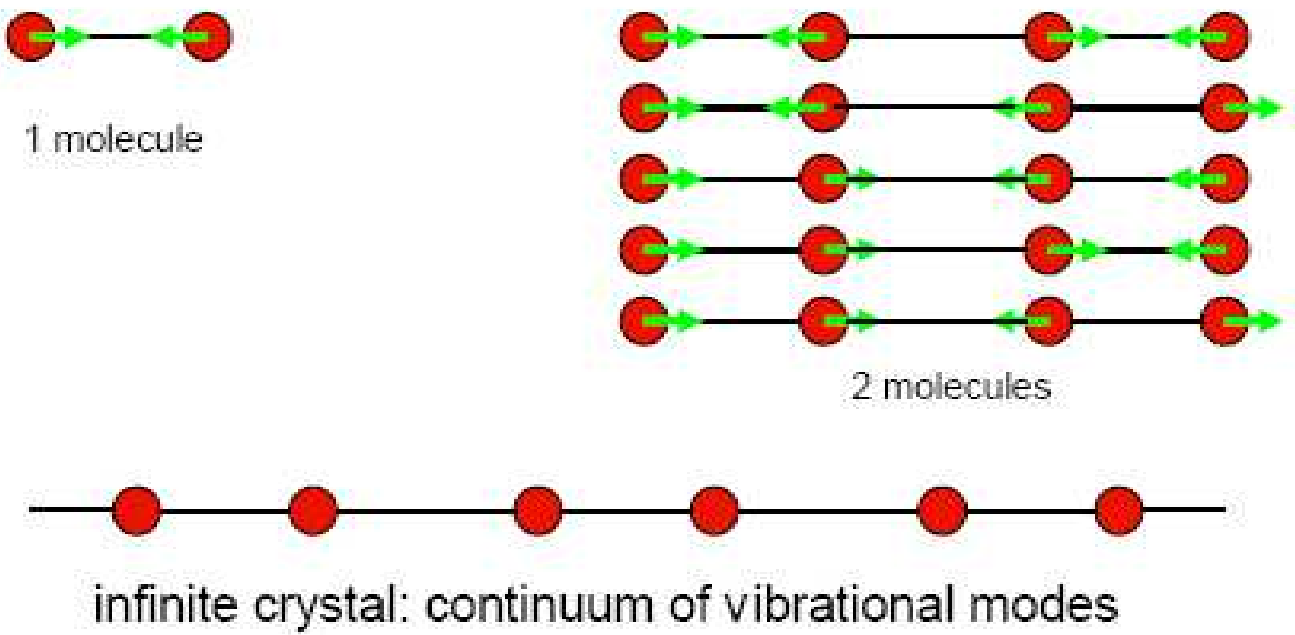
VIBRATIONS: WHY ARE THEY IMPORTANT? [1]

Atoms vibrate around their equilibrium positions.

- thermal properties: heat capacity, expansion
- phase transitions, including melting
- transport: thermal conductivity, sound
- electrical properties, e.g., superconductivity
- dielectric phenomena at low frequencies

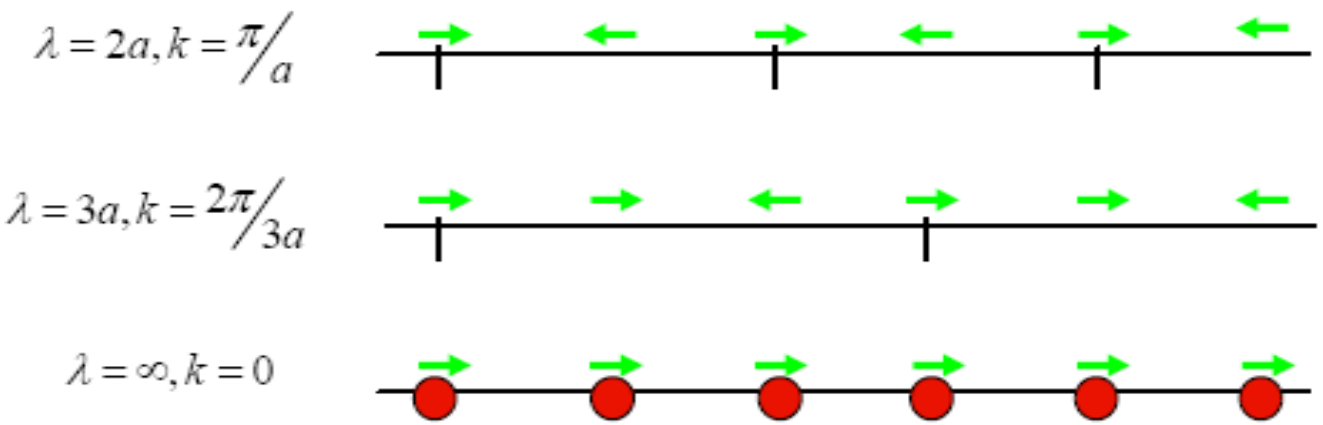
[1] From Prof N. M. Harrison's Lectrure Notes: Vibrations in crystals

VIBRATIONS: FROM A FINITE SYSTEM TO AN INFINITE SYSTEM [1]



[1] From Prof N. M. Harrison's Lectrure Notes: Vibrations in crystals

VIBRATIONS: WAVELENGTH - WAVEVECTOR [1]



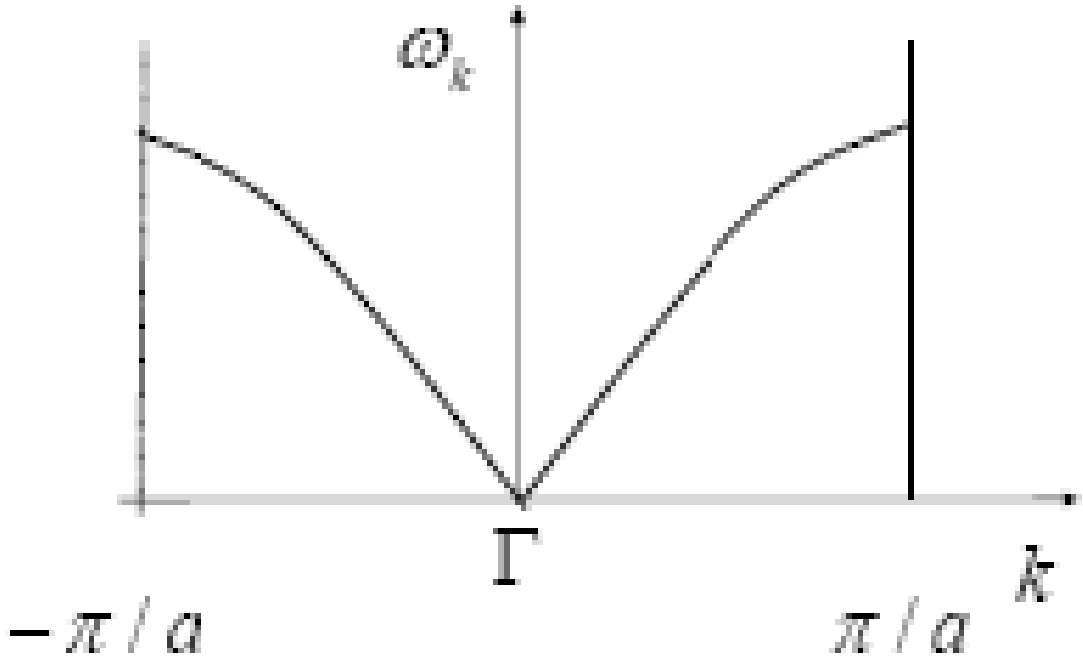
$$k = \frac{2\pi}{\lambda}$$

In this case, as k increases, the energy of vibration increases and the frequency too.

[1] From Prof N. M. Harrison's Lectrure Notes: Vibrations in crystals

VIBRATIONS: PHONON DISPERSION [1]

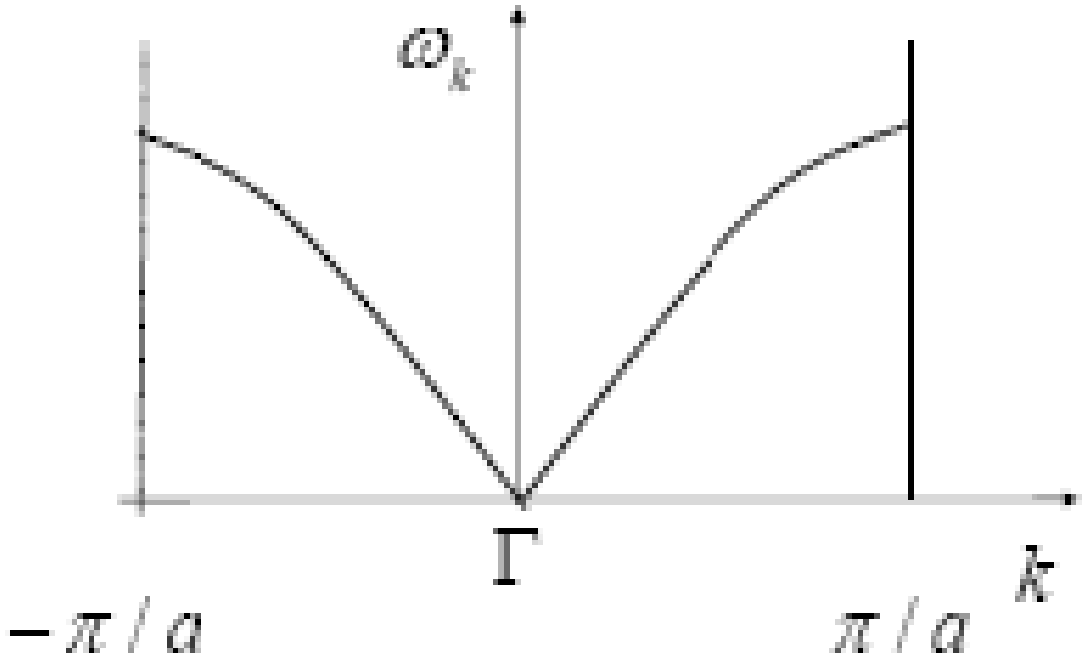
VIBRATIONAL FREQUENCY ω AS A FUNCTION OF k



[1] From Prof N. M. Harrison's Lectrure Notes: Vibrations in crystals

VIBRATIONS: PHONON DISPERSION [1]

VIBRATIONAL FREQUENCY ω AS A FUNCTION OF k



SIMILARLY, ELECTRONIC BAND STRUCTURE OF THE HYDROGEN POLYMER

[1] From Prof N. M. Harrison's Lectrure Notes: Vibrations in crystals

VIBRATIONS: PHONON?

electron: WAVE or PARTICLE

radiation: WAVE or PARTICLE

VIBRATIONS: PHONON?

electron: WAVE or PARTICLE

radiation: WAVE or PARTICLE **(photon)**

VIBRATIONS: PHONON?

electron: WAVE or PARTICLE

radiation: WAVE or PARTICLE **(photon)**

vibration: WAVE or PARTICLE

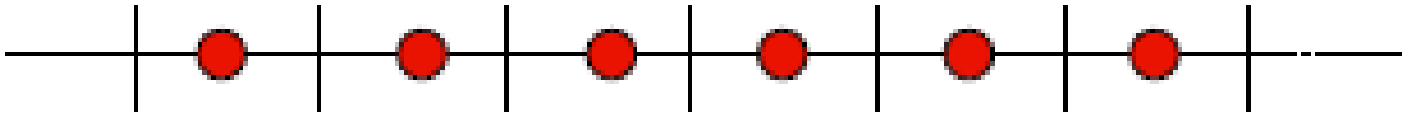
VIBRATIONS: PHONON?

electron: WAVE or PARTICLE

radiation: WAVE or PARTICLE **(photon)**

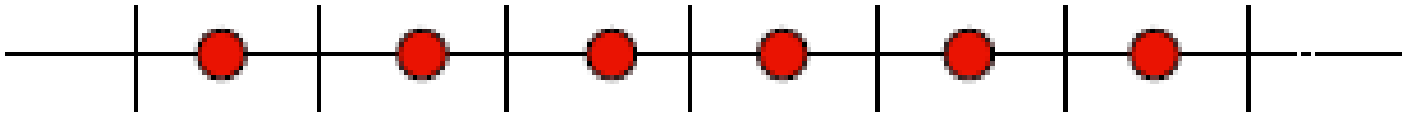
vibration: WAVE or PARTICLE **(phonon)**

VIBRATIONS: 1D MONOATOMIC CHAIN (OR POLYMER) [1]

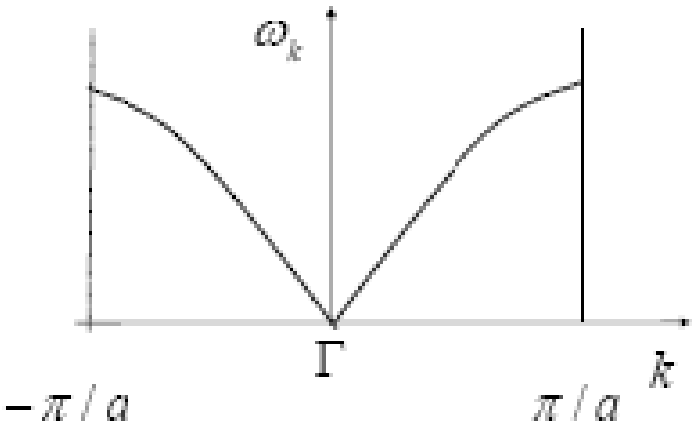


INFINITE NUMBER OF VIBRATIONS $\rightarrow$ **BRANCH**

VIBRATIONS: 1D MONOATOMIC CHAIN (OR POLYMER) [1]

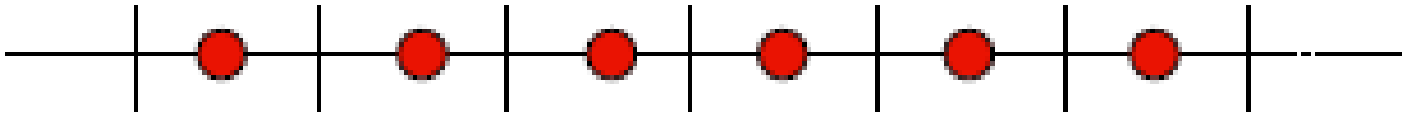


INFINITE NUMBER OF VIBRATIONS $\rightarrow$ **BRANCH**

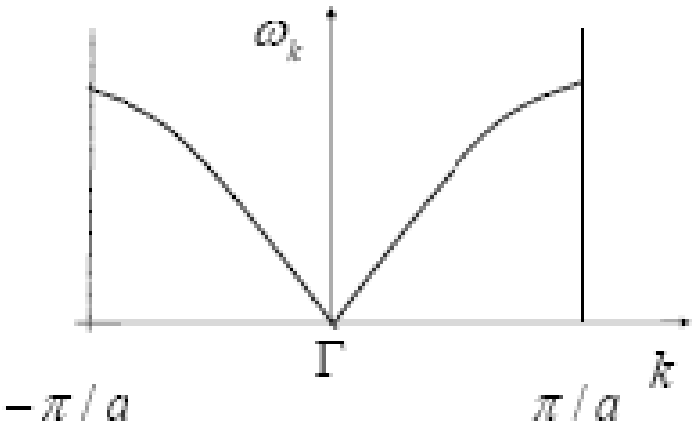


$$\omega_k = \sqrt{\frac{4J}{M}}|sin(ka/2)|$$

VIBRATIONS: 1D MONOATOMIC CHAIN (OR POLYMER) [1]



INFINITE NUMBER OF VIBRATIONS → **BRANCH**



$$\omega_k = \sqrt{\frac{4J}{M}}|sin(ka/2)|$$

$k = 0$ (Γ point) : $\omega_{k=0} = 0$

$k = \pi/a$: $\omega_{\pi/a} = \sqrt{\frac{4J}{M}}$

$k = \pi/2a$: $\omega_{\pi/2a} = \sqrt{\frac{2J}{M}}$

VIBRATIONS: DIRECT AND RECIPROCAL SPACE

1 PERIODIC DIRECTION IN THE DIRECT SPACE!

$$\mathbf{a}$$

1 PERIODIC DIRECTION IN THE RECIPROCAL SPACE!

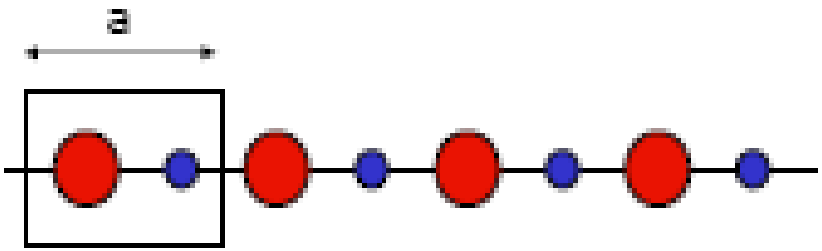
$$\mathbf{a}^* = \frac{2\pi}{\mathbf{a}}$$

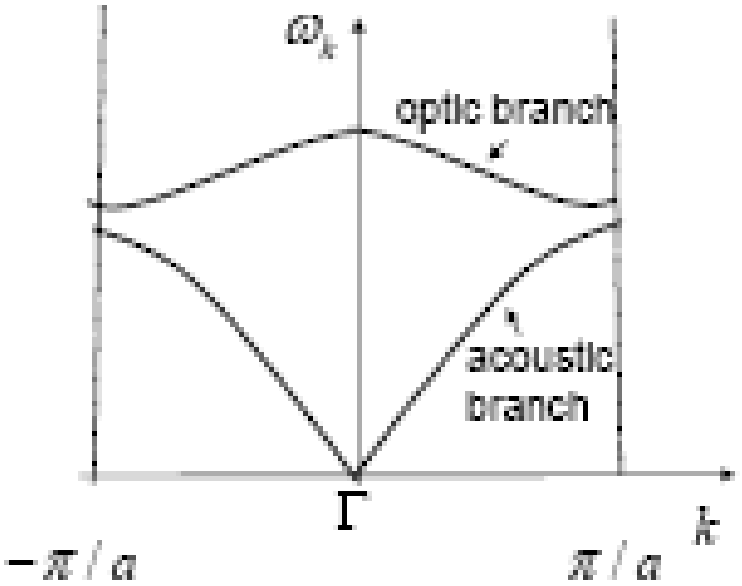
VIBRATIONS: 1D DIATOMIC CHAIN

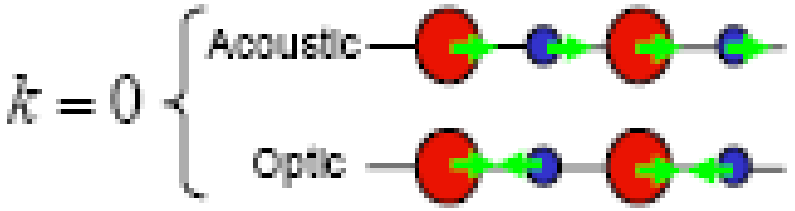
(SIMILARLY TO THE POLYMER WITH H_2 PER CELL)

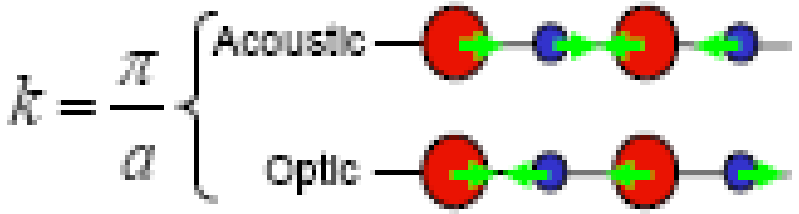
FOLDING PROCESS!!!

VIBRATIONS: 1D HETERO DIATOMIC CHAIN [1]









[1] From Prof N. M. Harrison's Lectrure Notes: Vibrations in crystals

VIBRATIONS: OPTIC AND ACOUSTIC MODES

OPTIC:

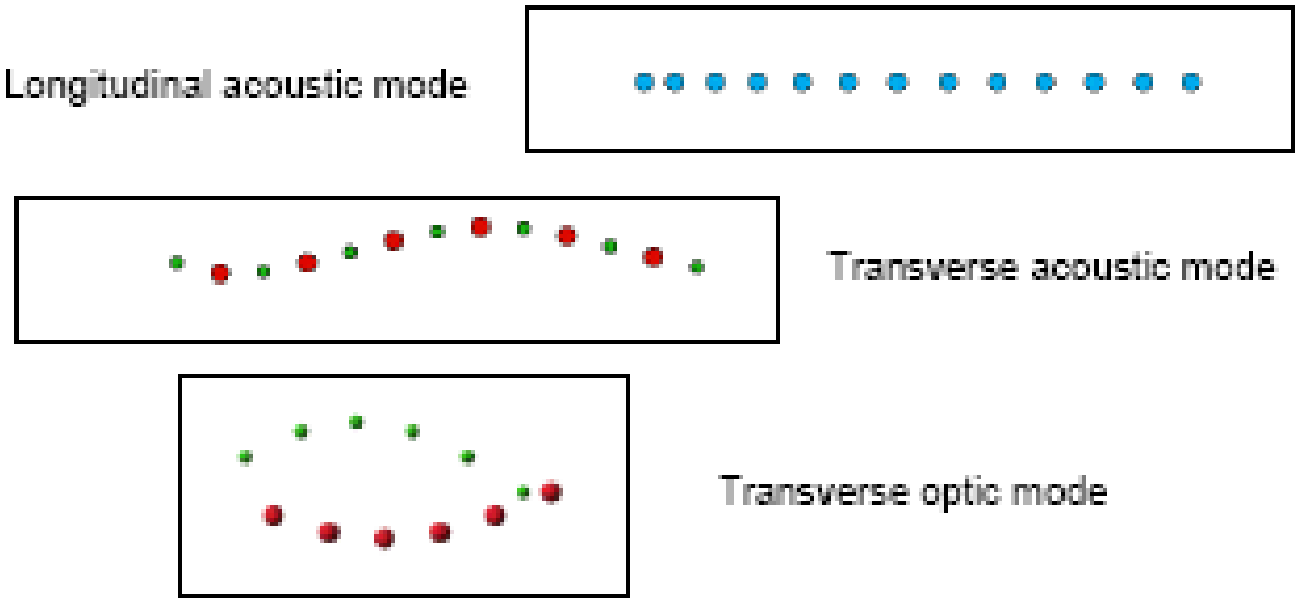
1) has a frequency that is in the vicinity of the optical region of the electromagnentic spectrum

2) the atomic motions associated are the same as the response to an oscillating electromagnentic field

ACOUSTIC:

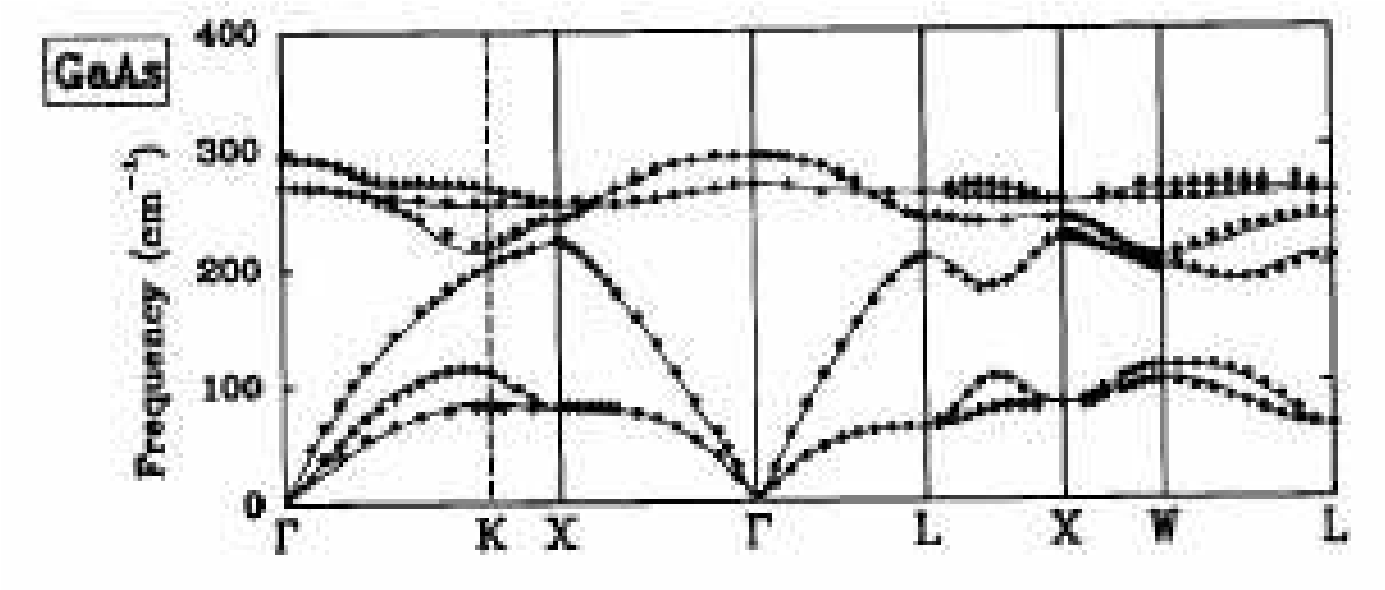
1) has acoustic frequency

VIBRATIONS: LONGITUDINAL AND TRANSVERSE MODES [1]



[1] From Prof N. M. Harrison's Lectrure Notes: Vibrations in crystals

VIBRATIONS: 3D HETERO DIATOMIC CRYSTAL [1]



Neutron data for GaAs

[1] From Prof N. M. Harrison's Lectrure Notes: Vibrations in crystals

HOW?

COMPUTATIONAL EXPERIMENT / SIMULATION

- program
- input

Environment:
the choice of the Operating System $\rightarrow$ **linux**

Interface:
DLV = package for the visualisation of materials structures and properties.

SIMULATION TYPES

- CLASSICAL SIMULATION

  Newton law $\rightarrow$ GULP
- QUANTUM-MECHANICAL SIMULATION

  Schroedinger equation $\rightarrow$ CRYSTAL

Systems under investigation

Properties

Accuracy

Computational time

Resources

CLASSICAL SIMULATION

INTERATOMIC POTENTIAL

- coulombic interaction
- short term repusilve contribution
- Morse-like potential

QUASI-HARMONIC APPROXIMATION [1]

HELMHOLTZ FREE ENERGY

$$F = E_0 + \frac{1}{2}\sum_{k,j}\hbar\omega_{j,k} + k_B T \sum_{k,j}\ln\left[1-\exp(-\hbar\omega_{j,k}/k_B T)\right]$$

[1] From Prof N. M. Harrison's Lectrure Notes: Vibrations in crystals

QUASI-HARMONIC APPROXIMATION I

HELMHOLTZ FREE ENERGY

$$F = E - TS$$

$$F = F(T, V)$$

MOLECULAR DYNAMICS [1]

Initial configuration and initial velocities:
the initial configuration will be that of ideal MgO
the velocities will be random but scaled to produce roughly the target temperature.

- Compute the forces on the atoms (F).
- Compute the accelerations a=F/m
- Update the velocities: Vnew = Vold + a * dt
- Update the positions of the atoms: Rnew = Rold + Vnew * dt
- Repeat until average properties like E and T settle down
- Once settled measure some properties.

[1] From Prof N. M. Harrison's Lectrure Notes: Vibrations in crystals

GEOMETRY OPTIMIZATION I

What does it mean?

GEOMETRY OPTIMIZATION I

What does it mean?

Minimization of the energy as a function of the atomic position

(x_i, y_i, z_i, with $i = 1, N$,
and N is the number of atoms)

and of the lattice parameters

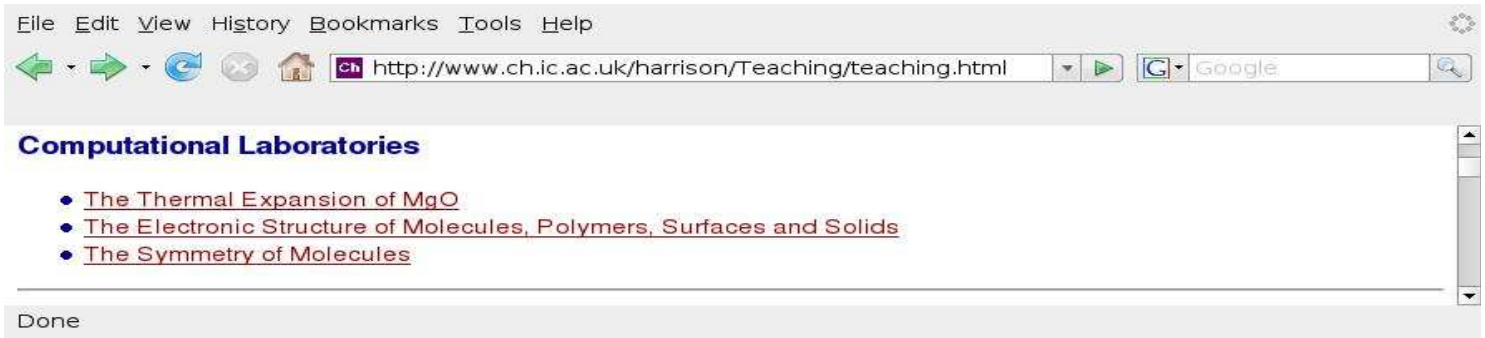
(**a**,**b**,**c**,α,β,γ)

GEOMETRY OPTIMIZATION II

How many variables for MgO?

FIRST STEP

1. Restart the PCs that are running Windows;
2. Once you have a black screen with the following line:
   > **boot:**
   Type linux
   > **boot: linux**
   Press Enter
3. Use your login and passwd as in Window
4. Open firefox: the web browser
5. http://www.ch.ic.ac.uk/harrison/Teaching/teaching.html



HOW TO WRITE A REPORT I
by Giulia C. De Fusco

Introduction

- the system
- the methodology (theory in use)
- the aims of the exercise
- the tools in use (programs)

Body of the text

- write it like a scientific paper (well-articulated sentences, NOT a list of two-word answers)
- analyse *critically* obtained data and given answers
- round numerical answers to a specific number of decimal places (i.e. 4)
- add literature/web citations whenever a comparison with experimental data is required
- add explicitely every formula used one to obtain results
- check spelling

HOW TO WRITE A REPORT II
by Giulia C. De Fusco

Pictures

- max 20
- reasonably sized (NOT one-page sized pictures, but still readable)
- white background (follow the instructions given on the website clicking on the link 'How to save a picture for your report')
- described in caption or in the text

Graphs

- add labels and units
- add a *critical* comment whenever required (NOT a merely descriptive comment)

HOW TO WRITE A REPORT III
by Giulia C. De Fusco

Tables

- add labels and units
- round numerical answers to a specific number of decimal places (i.e. 4)
- repeat heading if the table cannot fit in a single page

Conclusions

- give a general description of your calculations and your main findings
- outline the differences between the methods in use and the results obtained
- analyse critically these differences

THANK YOU!!!