Lecture 4: Vibrations and Free Energy

- Thermodynamics
- Vibrations: from molecules to crystals
- A 1 dimensional crystal
- The Harmonic Approximation
- The free energy.

Note:

In problem class 2 you compute the free energy of a gas of H_2 molecules

In this lecture we look at periodic crystals because of the relative simplicity – liquids are tricky !

TM lab. 1 – the free energy of MgO

What Can Atomic Vibrations Tell Us?

Atoms do not sit still at 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 …
- **The free energy**

The Free Energy (Problem Class 1)

Add up the Boltzman factor for every state of a system to get the partition function - Z

$$Z(T,N,V...) = \sum_{j=1}^{allstates} e^{-\varepsilon_j / k_B T}$$

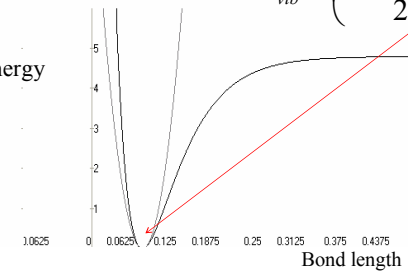
From *Z* you can compute properties, eg: the average energy.

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}_{N,V} = -\frac{\partial \ln(Z)}{\partial \beta}_{N,V}$$

H_2 : Problem Class 1

$$E_{vib} = \left(n + \frac{1}{2}\right)\hbar\omega$$

H_2 energy



Statistical Mechanics

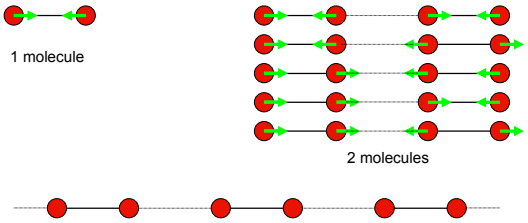
$$Z(T,N,V...) = \sum_{j=1}^{allstates} e^{-\varepsilon_j / k_B T}$$

Z provides the link from the molecular level to the macroscopic world.

In general it is very hard to compute *Z* because we don't know all of the energy levels – a vibrating crystal is an exception… as its (relatively) easy !

Atomic Vibrations in Periodic Systems

Example: 1D molecular crystal

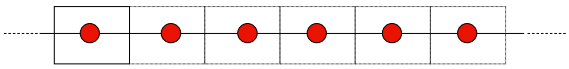


infinite crystal: continuum of vibrational modes

Counting the vibrations !

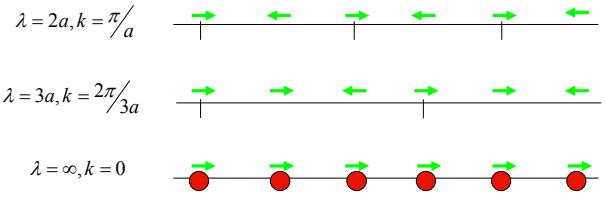
There are an infinite number of vibrations but we can count them all using a *very important trick*

The infinite crystal is made by repeating a *unit cell*



Vibrations have a "wavelength" - λ

equivalently, a *wavevector:* $k = 2\pi/\lambda$



In this case, as *k* increases the frequency of vibration, *w,* increases

Counting the vibrations…

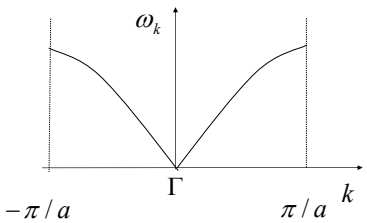
There is a *k* label for *every possible vibration* of the crystal.

You count vibrations by summing over *k.*

Note: the *k* label idea is very important in studies of crystals – you will see it again in the electronic band structures of semiconductors ☺.

The Dispersion Curve

In this case, as *k* increases the frequency of vibration, *w,* increases – typically w_k is plotted like this: a *dispersion curve*

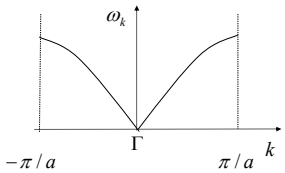


1D Monoatomic Chain

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

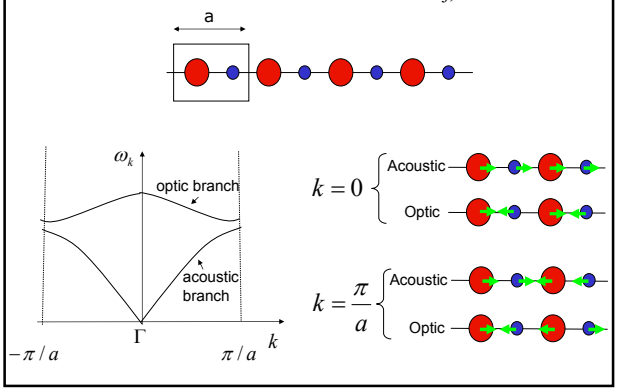
$k = \pi$/a : $\omega_{\pi/a} = \sqrt{\frac{4J}{M}}$

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



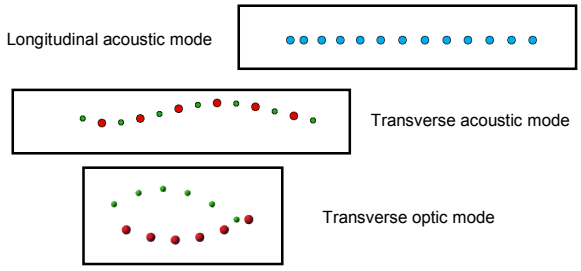
$\omega_k = \sqrt{\frac{4J}{M}}\left|\sin(ka/2)\right|$

1D Diatomic Chain – $w_{j,k}$



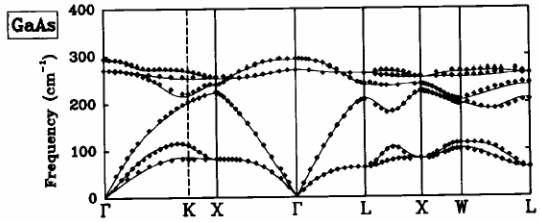
Longitudinal and Transverse Modes

So far everything was in 1 dimension but things can vibrate sideways too



Neutron Data for a crystal of GaAs

Two atoms per cell so 6 *vibrational bands* drawn here for some *k*-points : a *phonon band structure plot.*



The Vibrational Energy

If you sum over all of the vibrational bands *j* and all of the *k*-points you have summed over all vibrational energy levels and can compute, for example, the free energy of the crystal.

This is very similar to the calculation for H_2 in Problem Class 1 – we have simply learnt how to label and count the vibrations of the infinite solid.

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

Thermodynamics

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \sum_{k,j} k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp(\hbar\omega/k_B T)}{[\exp(\hbar\omega/k_B T)-1]^2}$$

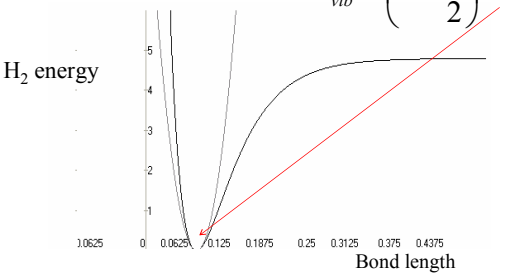
$$F = E_0 + \frac{1}{2}\sum_{k,j}\hbar\omega + k_B T\sum_{k,j}\ln\left[1-\exp(-\hbar\omega/k_B T)\right]$$

$$S = -\frac{\partial F}{\partial T}$$

Etc etc.. you can compute many things but remember: **this is all in the harmonic approx.**

H_2 : the harmonic approximation

$$E_{vib} = \left(n+\frac{1}{2}\right)\hbar\omega$$



Theoretical Methods Laboratory 1

The computer does much of the work !!

1. Calculate the phonons of MgO
2. Calculate the Free Energy sum by summing over *k*-points
3. Predict the structure of MgO at finite temperature by relaxing the geometry to minimise the free energy
4. Go beyond the harmonic approximation – *molecular dynamics*

Molecular Dynamics

Another way to average over all of the vibrational modes of a crystal without using the harmonic approximation…..

- Compute the forces on the atoms
- Accelerate the atoms using F=ma; a=F/m
- Move the atoms (ie: step in time)
- Repeat

ie: Reproduce nature in the computer !!

Molecular Dynamics II

MD simply simulates the motions of the atoms in the real material.

Much more expensive than summing over the harmonic frequencies but it does not rely on the harmonic approximation…

Theoretical Methods Lab 1 – you can do some MD too.

Summary

To compute the free energy of a material you can sum over its vibrational modes.

In a crystal this involves labelling all of the modes with k and then summing over k

An alternative is to let the computer vibrate the atoms and average over all of their motions (MD)

You will do both in TM Lab 1 ☺.