Phonon modes in graphene and carbon nanotubes

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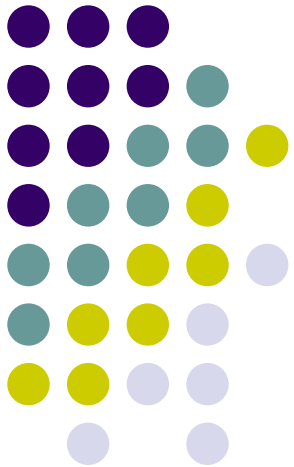
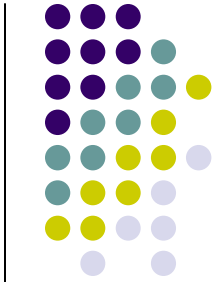
13.05.05

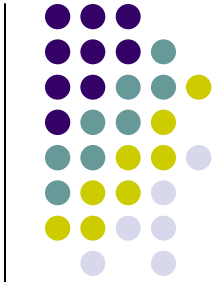


Outline



- Find an appropriate equation to describe the potential energy of graphene:
  - Keating-model
  - Mahan-model
  - Dresselhaus-Saito-model
- Calculate the phonon modes for graphene
- Make a comparison between this three models

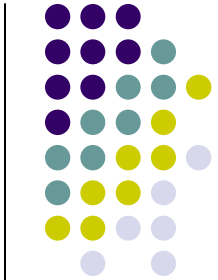
Perspectives: carbon nanotubes



- Is it possible to construct a spring and mass model for graphene and use the same forces to calculate the phonons in a carbon nanotube?
- We try to adapt the graphene models to carbon nanotubes and again compare the different results
- Main goal is to use appropriate force models for nanotubes which do obtain flexure modes at long wavelength

The Keating Model

P.N.Keating, Phys. Rev.**145**, 637 (1966)

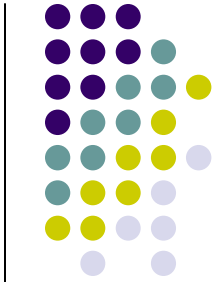


- Bond stretching

It denotes the change relative to the perfect lattice due to a bond length distorsion.
It gives a central two-body force acting between neighboring atoms.

$$V_s = \frac{k_s}{8d_0^2} \sum_{\langle ij \rangle} (\mathbf{x}_{ij} \cdot \mathbf{x}_{ij} - d_0^2)^2$$

$\mathbf{x}_{ij}$	vector from Atom *i* to Atom *j*
d_0	equilibrium bond length
k_s	taken from K.C.Hass, Phys. Rev. B **46**, 139 (1992)

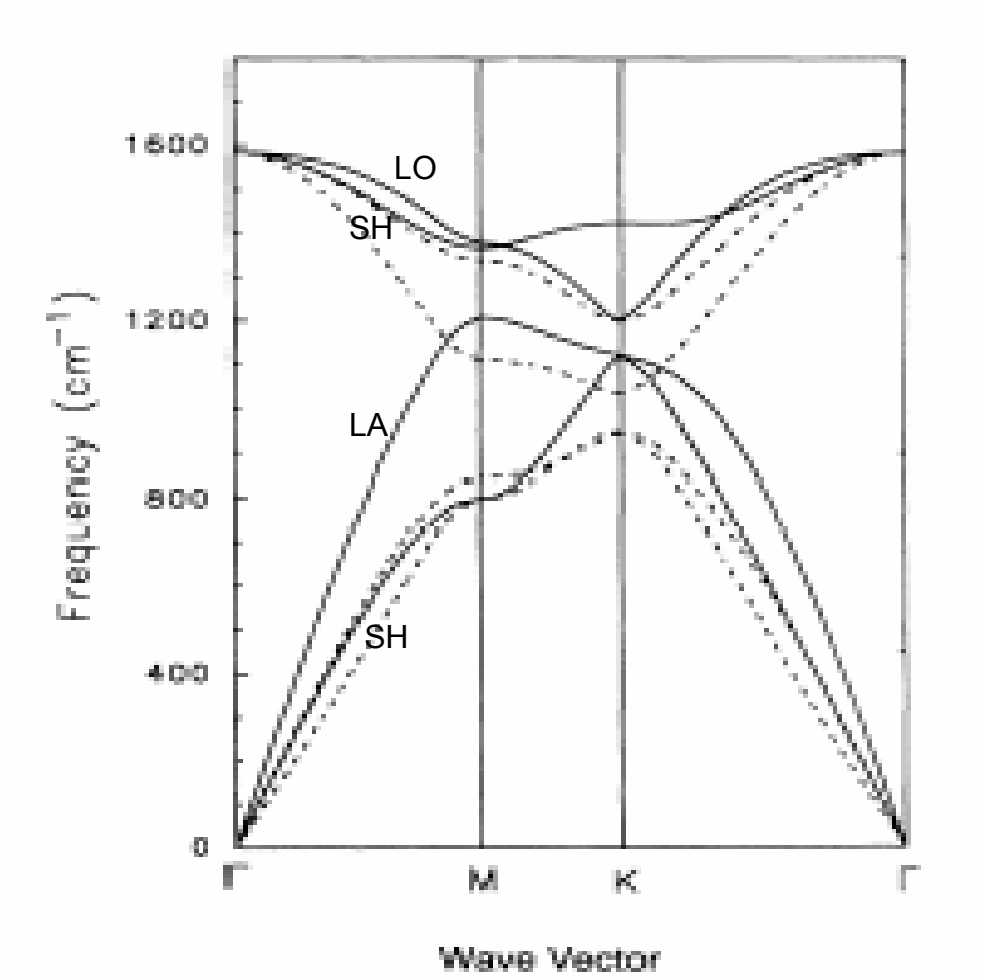


- Bond bending

It denotes the change in the scalar product between the two vectors connecting atom *j* with its neighbors *i* and *k.*
It is an angular potential, involving the angle θ between atoms *i*,*j* and *k*

$$V_s = \frac{k_b}{2d_0^2} \sum_{\langle ijk \rangle} (\mathbf{x}_{ji} \cdot \mathbf{x}_{jk} - d_0^2 \cos\theta_0)^2$$

$\mathbf{x}_{ij}$	vector from Atom *i* to Atom *j*
d_0	equilibrium bond length
$\theta_0 = 120°$	equilibrium bond angle



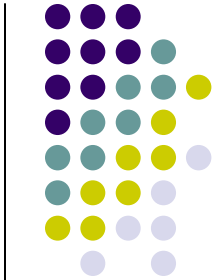
The model is constrained to give an optic mode Γ frequency of 1585 cm^{-1} and a SH (shear horizontal) mode at M of 800 cm^{-1}.

It doesn't reproduce the initial upward curvature of the LO branch (in-plane longitudinal optic) away from Γ that is seen in experimental data.

It gives no ZO, ZA (out-of plane) branches!!

The Mahan-model

G.D.Mahan, G.S.Jeon, Phys. Rev. B **70**, 075405 (2004)



- Bond stretching

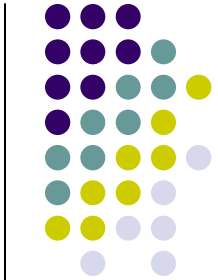
This potential is from stretching of directed bond length, and is applied to 1st and 2nd nearest neighbors

$$V_s = \frac{k_\alpha}{2} \sum_{\langle ij \rangle} \left| \hat{\boldsymbol{\delta}}_{ij} \cdot (\mathbf{u}_i - \mathbf{u}_j) \right|^2$$

$\hat{\boldsymbol{\delta}}_{ij}$ unit vector from Atom *i* to Atom *j*

$\mathbf{u}_i$ displacement of Atom *i*

k_α constant; $\alpha = 1, 2$ for 1st and 2nd nearest neighbors



- Bond bending

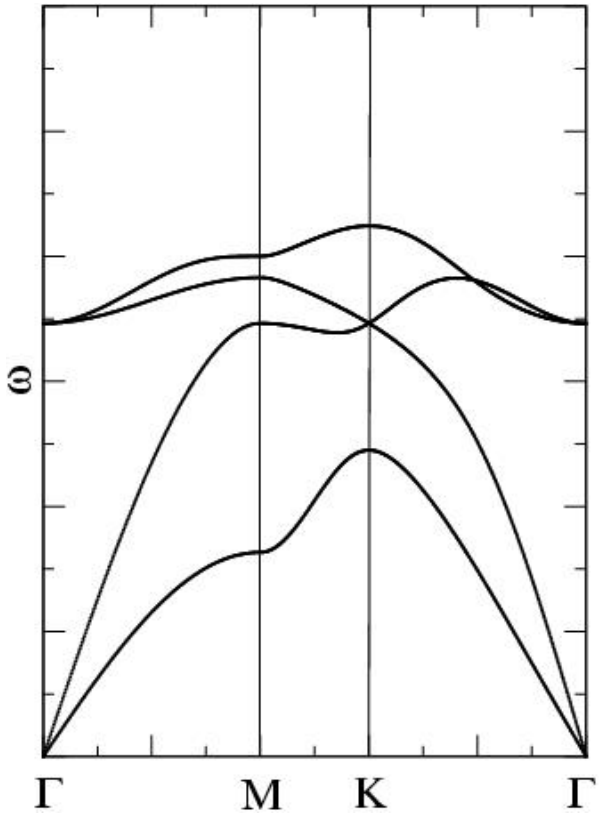
Bond bending forces are required to describe the out-of-plane vibrations

$$V_b = \frac{k_b}{2} \sum_j \left| \sum_{i=1}^{3} \hat{\mathbf{n}}_{ij} \cdot (\mathbf{u}_i - \mathbf{u}_j) \right|^2$$

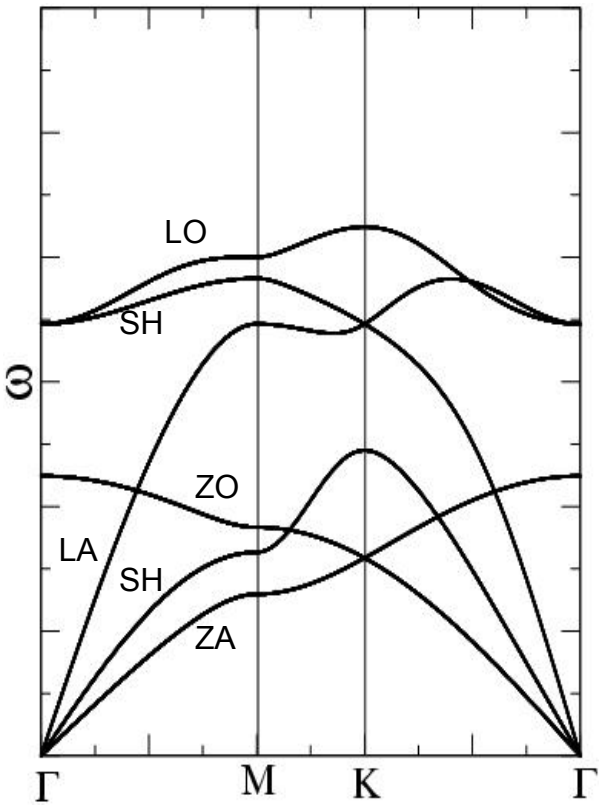
$\hat{\mathbf{n}}_{ij} = \hat{\mathbf{z}} \times \hat{\boldsymbol{\delta}}_{ij}$ normal vector (perpendicular to the graphene sheet) at the midpoint of the bond between atoms *i* and *j*

$\mathbf{u}_i$ displacements of the first neighbors of atom *j*

Bond stretching



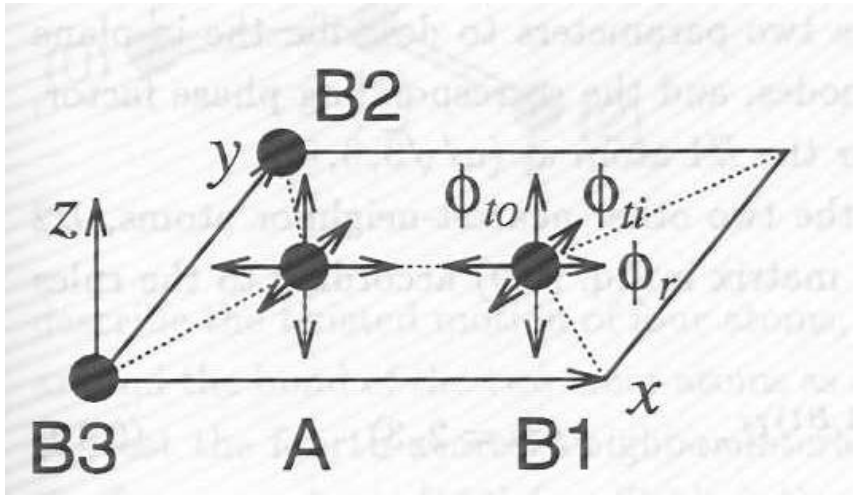
Bond stretching and bond bending



Dresselhaus-Saito model

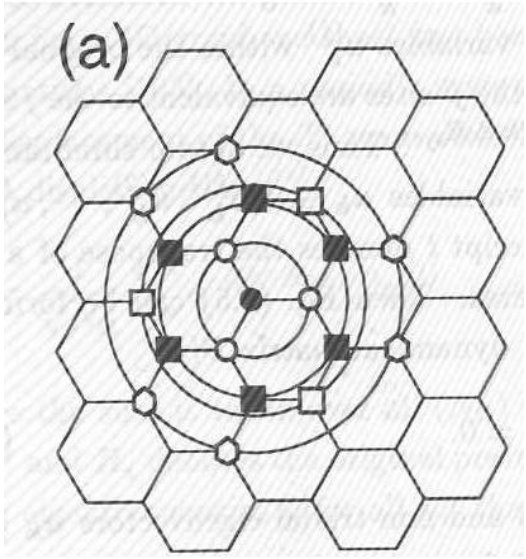
R.Saito,G.Dresselhaus, M.S.Dresselhaus, *Physical properties of carbon nanotubes* (Imperical college Press, London,1998)

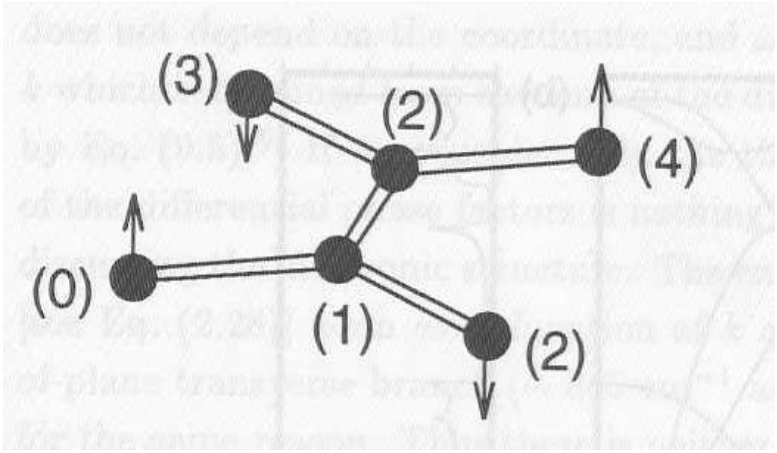
- It starts considering the force constants between atoms A and its nearest neighbors B1, B2 and B3.



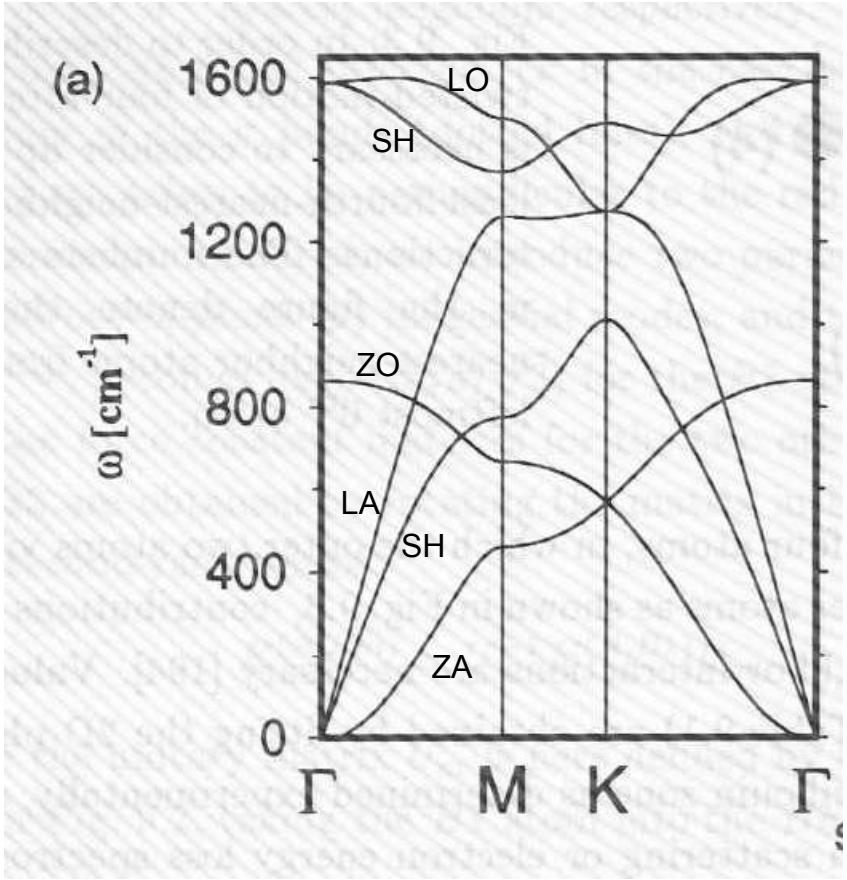
Here Φ_r, Φ_{ti} and Φ_{to} represent forces in the radial (bond stretching), in-plane and out-of-plane tangential (bond bending) directions, respectively.

- In this case the interaction between two nearest neighbor atoms is not sufficient to reproduce the experimental results, and its necessary to consider contributions from long-distance forces.
  To describe the twisted motion of four atoms, that vibrate like shown in the figure, contributions up to at least the 4th nearest neighbor interactions are necessary.





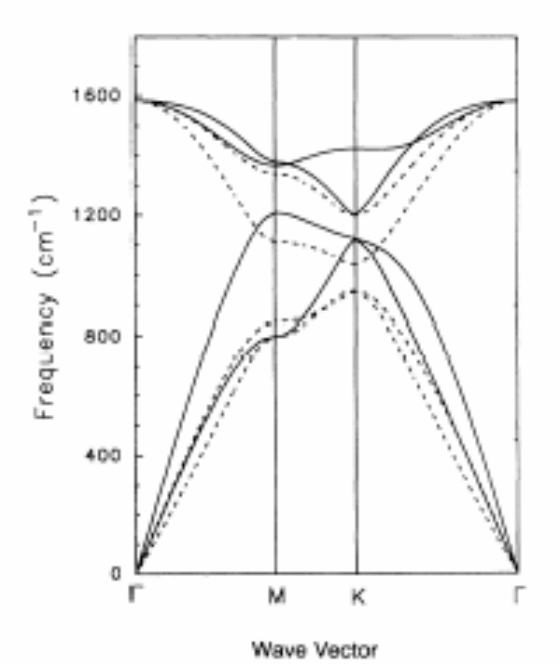
Values for the force constants are obtained by fitting the 2D phonon dispersion relations as determined experimentally (inelastic neutron scattering, electron energy loss spectroscopy)



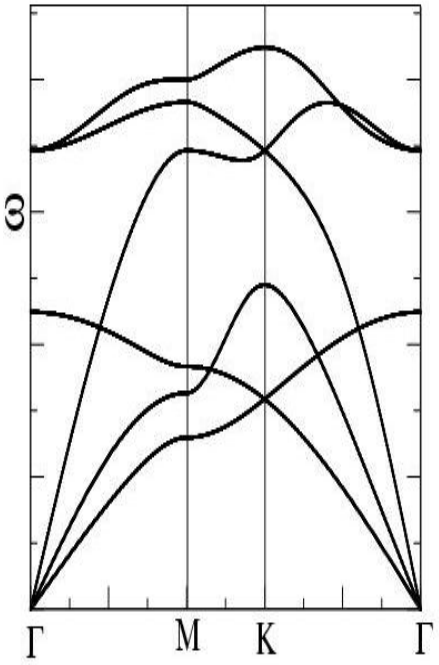
With this model we obtain two out-of-plane modes (ZO, ZA) !
The out-of-plane acoustic branch (ZA) shows a k^2 energy dispersion relation around the G point, while the other two in-plane acoustic branches show a linear k dependence, as is normally seen for acoustic modes.

Phonon modes in graphene

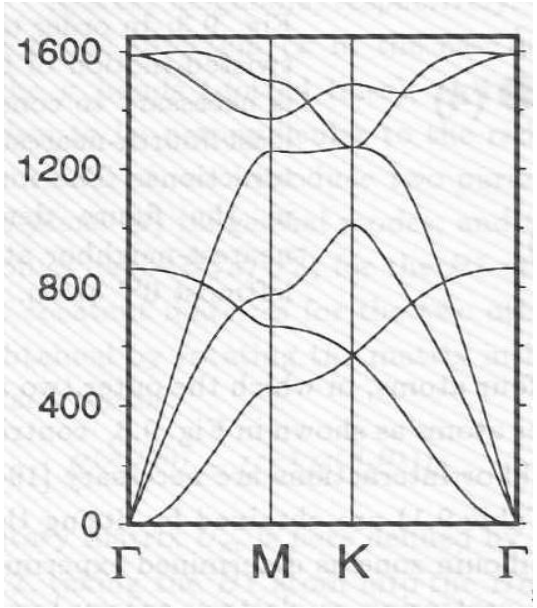
Keating



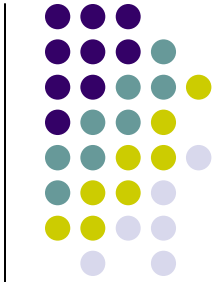
Mahan



Dresselhaus-Saito



Carbon nanotubes



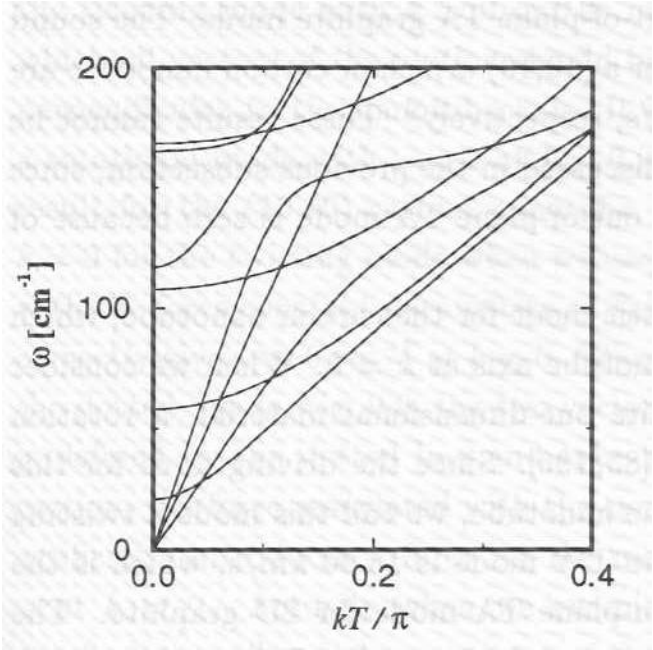
- Next step is to applicate the graphene models to carbon nanotubes and, if required, to change and adapt them
- We will find out that it is not possible to construct a model for a graphene sheet and use the same forces to calculate the phonons in nanotubes
- We will see that the Mahan model obtains flexure modes and works better for carbon nanotubes than for graphene

Method of Dresselhaus-Saito

- The method consist in solving the 3dim-carbon nanotube dynamical matrix directly using the same force constant parameters as in graphene, but taking into account the effect of curvature

R.Saito, G.Dresselhaus, M.S. Dresselhaus, *Physical properties of carbon nanotubes* (Imperical college Press, London,1998)

(10,10) CNT

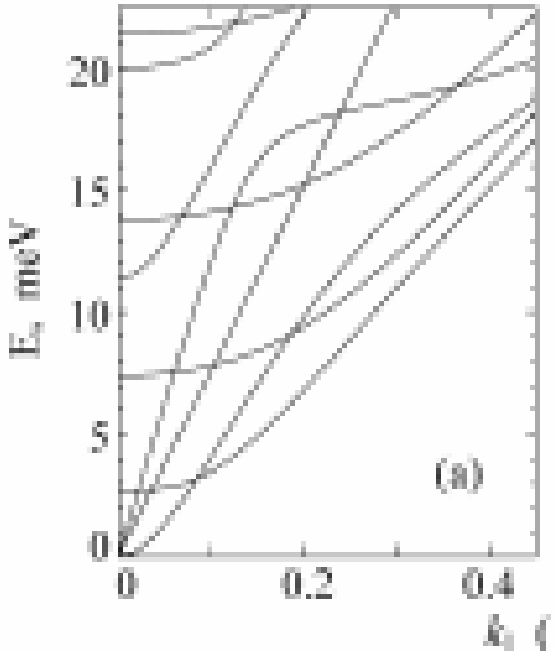


Keating model applied to nanotubes

- In order to obtain flexure modes with the Keating model, the harmonic potential energy, expressed as a function of variations of bond lengths and various angles, requires ten elastic parameters!

Y.N.Gartstein, Phys. Lett. A **327**, 83 (2004)

(10,10) CNT

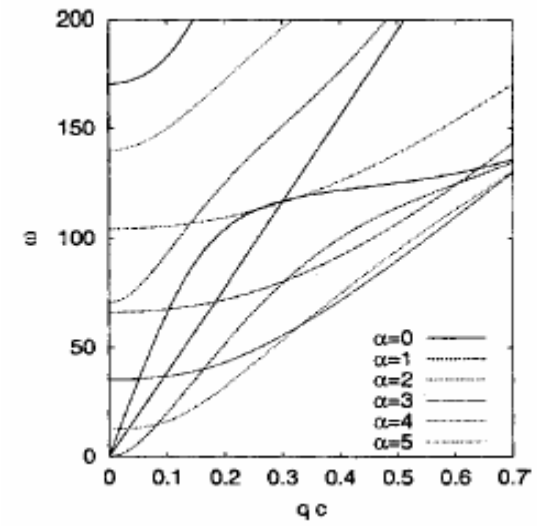


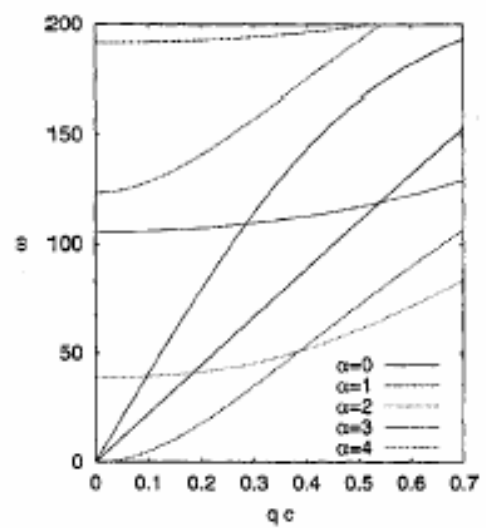
Mahan model applied to nanotubes

- Mahans bond stretching and bond bending potentials seen before are optimized for nanotubes

- It gives four low frequency modes at long wavelengths:
  - A longitudinal acoustic ($\omega_L = v_l q$)
  - A torsional mode ($\omega_T = v_t q$)
  - Two flexure modes ($\omega_F = vRq^2$)

(10,10) CNT



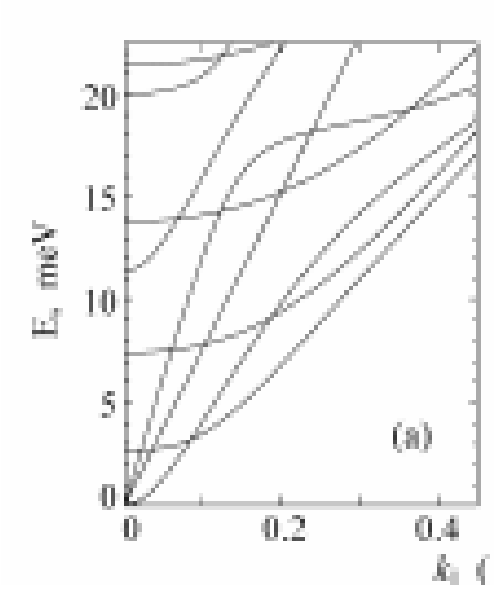


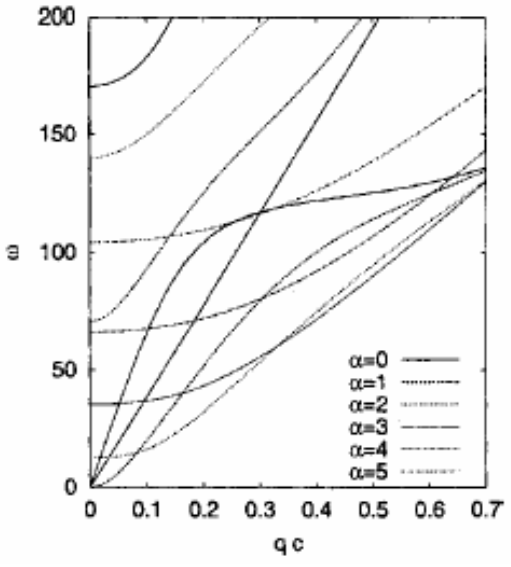
(10,0) CNT

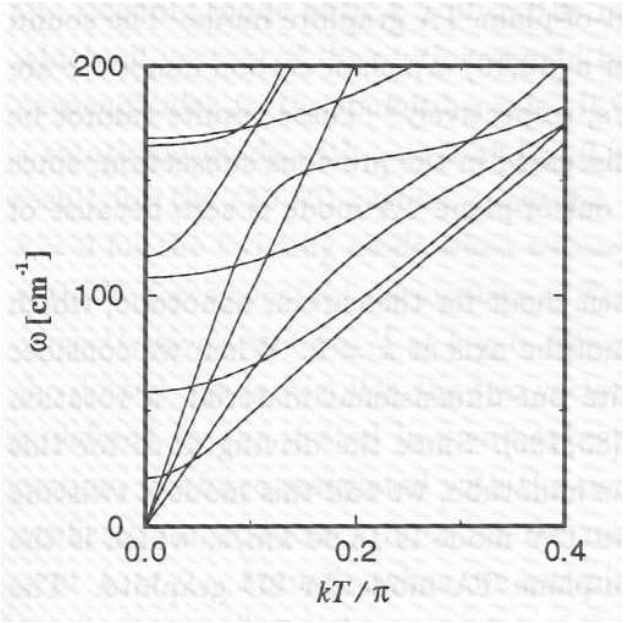
G.D.Mahan, G.S.Jeon, Phys. Rev. B **70**, 075405 (2004)

Phonon modes in carbon nanotubes

(10,10) CNT







Gartstein
(Keating model)

Mahan

Dresselhaus-Saito