Is the radial breathing mode really radial?

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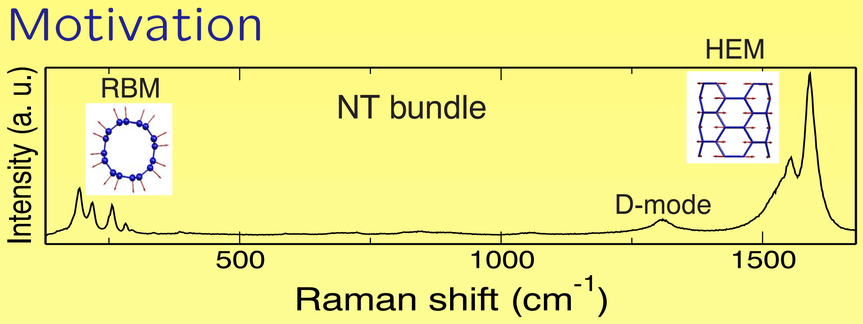
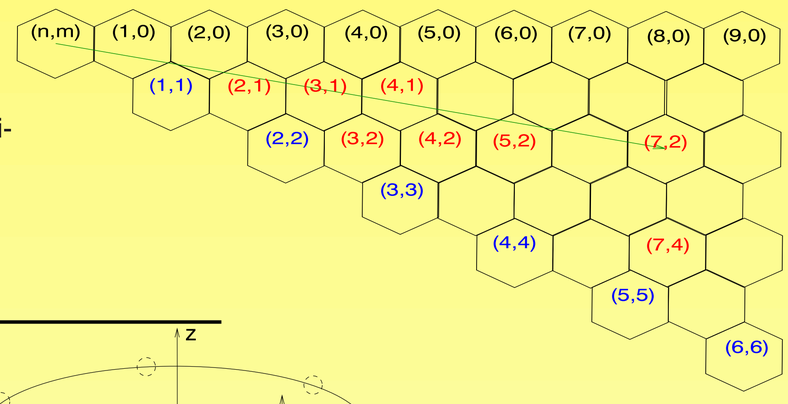
The diameter-dependent radial breathing mode (RBM) plays a key role in the characterization of carbon nanotubes. This mode is often *a priori* assumed to be radial. *Ab initio* calculations show small deviations from a purely radial displacement. Here we present an independent approach and a detailed analysis of the RBM. Small angular deviations result in large frequency differences due to a mixing of the RBM with the high energetic mode (HEM).

Motivation

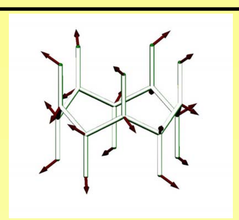


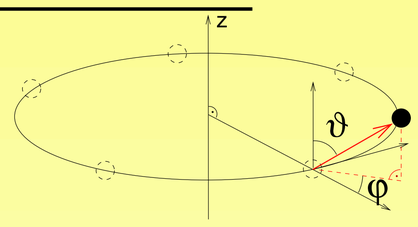
- $\omega_{\mathrm{RBM}} \propto 1/d$. In resonant Raman experiments chirality can be determined.
- RBM and HEM have A_1-symmetry



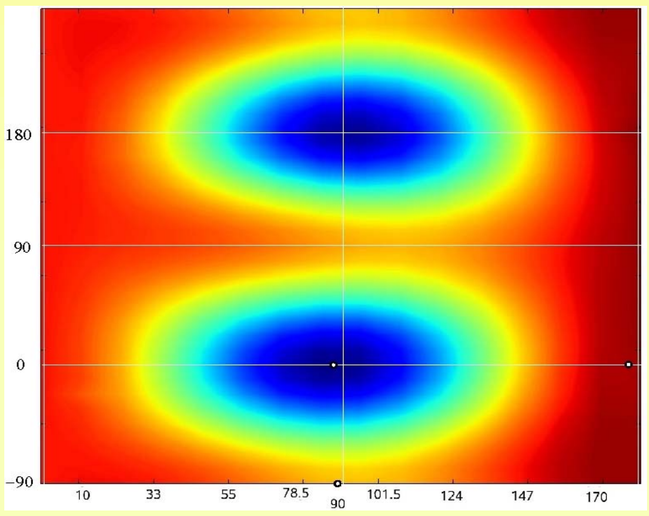
Method

- Displace one atom freely on a sphere with fixed radius.
- Apply the fully symmetric representation A_1 to obtain the displacements of all other atoms.
- Fully symmetric eigenmodes are in direction of extremal forces/total energy.

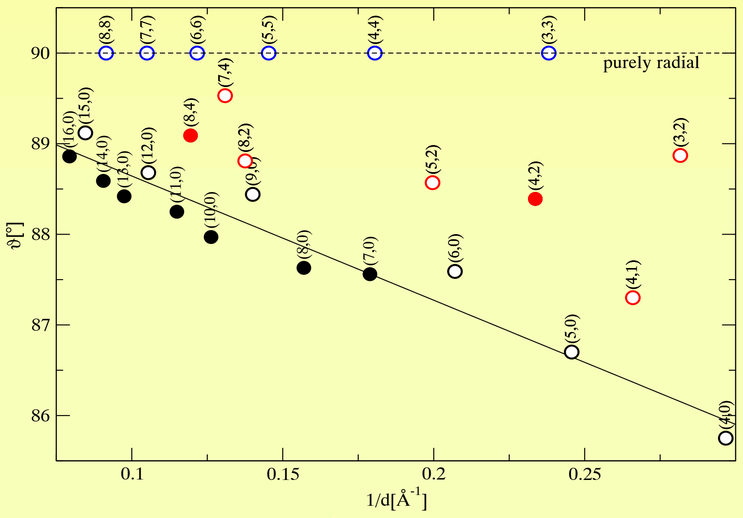




Eigenvectors



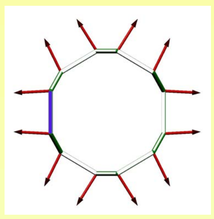
Contour plot of the total energy as a function of ϑ and φ for a (4,1) nanotube. Circles indicate the directions of the fully symmetric phonon modes obtained with a force constants calculation.



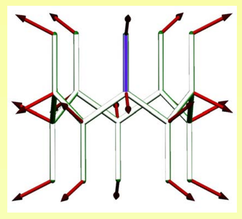
Armchair: As expected from group theory: mirror plane $\perp$ $z \Rightarrow \vartheta$ is 90°.($\varphi \neq 0°$)

Zigzag: Line shows a linear fit for zigzag (n,0) tubes.Metallic tubes (open symbol) show smaller deviations from 90°. (mirror plane $\parallel z \Rightarrow \varphi = 0°$)

Chiral: no mirror planes $\Rightarrow \vartheta \neq 90°$ and $\varphi \neq 0°$



(3,3)



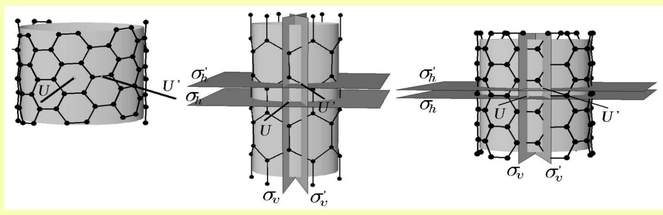
(5,0)

The angles φ and ϑ are exaggerated for clarity.

(3,3): Displ. vector is bent towards the blue bond

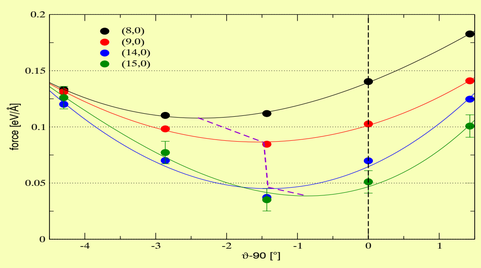
(5,5): Displ. vector is bent away from the blue bond.

Symmetry operations



RBM frequency

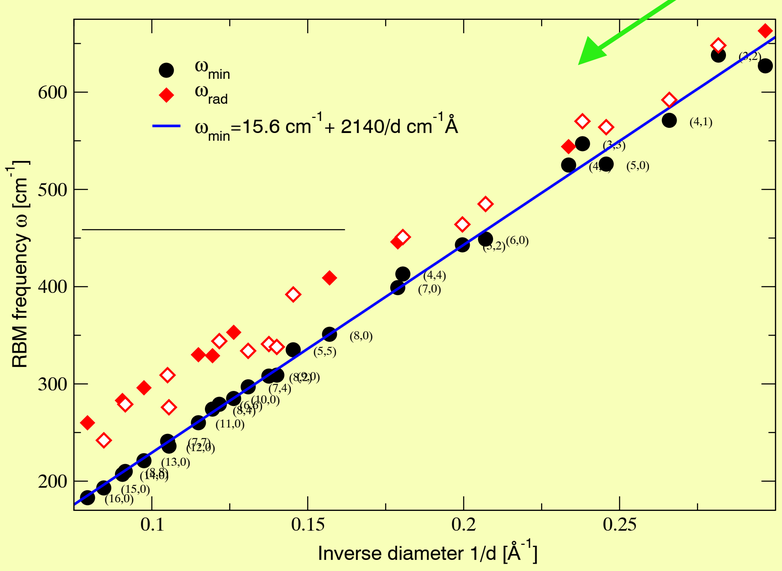
Force per atom over ϑ.



We calculate the RBMfrequencies:

ω_{rad}: pure radial displacement

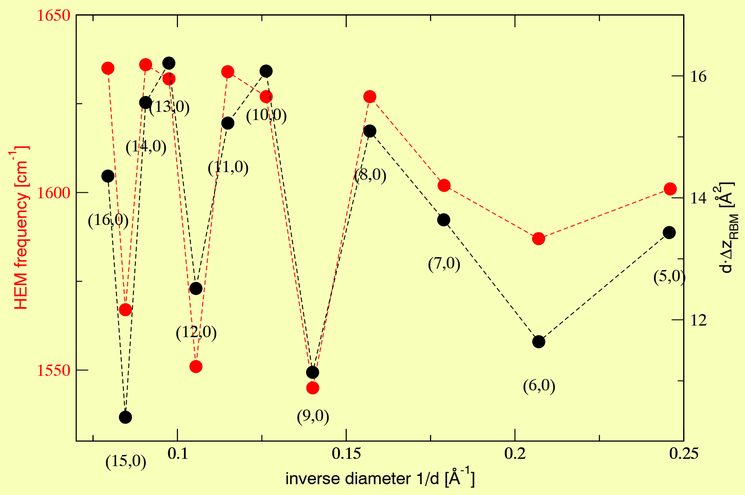
ω_{min}: taking the HEM-RBM mixing into account



- Excellent agreement with experimental fit: $\omega_{\mathrm{RBM}} = 18\ \mathrm{cm}^{-1} + 2150/d\ \mathrm{cm}^{-1}\text{Å}.^3$
- For larger tubes the deviation of ω_{rad} from ω_{min} increases

  $\Rightarrow$ the widely used pure radial displ. oversimplifies the problem and leads to wrong frequencies.
- Pure radial displ. leads to a wrong, chirality-dependent frequency.
- Semiconducting tubes (closed) show stronger deviations than metallic tubes (open).

RBM-HEM coupling



HEM frequencies and non-radial polarizations of the RBM are strongly correlated. The HEM frequency for metallic tubes is smaller due to electron-phonon coupling.

The strong effect of the HEM on the RBM can be understood in the harmonic approximation: $k \propto \omega^2$

- $\omega_{\mathrm{HEM}}/\omega_{\mathrm{RBM}} = 6 \Longrightarrow k_{\mathrm{HEM}}/k_{\mathrm{RBM}} = 6^2 = 64$
- $\tan 1° \approx 1/57$

Conclusions

- The RBM shows small non-radial component.
- When taking the HEM-RBM mixing into account the chirality dependence diminishes dramatically.
- RBM-HEM mixing of metallic tubes tends to be smaller. This is a result of the electron-phonon coupling of the HEM and a mixing of the HEM with the RBM
- Excellent agreement with experiment.

References

[1] *Reich, Thomsen, and Maultzsch, Carbon nanotubes, basic concepts and physical properties, WILEY-VCH (2004)*

[2] All calculations were performed with the SIESTA code
P. Ordejón et al., PRB **53**, *R10 441 (1996)*
J Soler et al., J. Phys. Condens. Mat. **14**,*2745 (2002)*

[3] J. Maultzsch *et al. Phys. Rev. B* **72**, 205438 (2005)

[4] M. Mohr *et al.* in preparation (2006)

[5] M. Damnjanović *et al. J. Phys.: Cond. Mat.* **16**, L505 (2003)

[6] O. Dubay and G. Kresse *Phys. Rev. B* **67**, 035401 (2003)

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