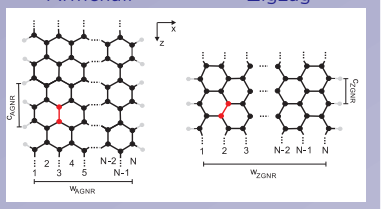
Vibrational properties of graphene nanoribbons by first-principles calculations

Roland Gillen, Marcel Mohr, Janina Maultzsch and Christian Thomsen
Institut für Festkörperphysik, Technische Universität Berlin, Germany

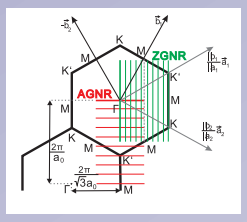
We investigated the vibrational properties of graphene nanoribbons (GNRs) by means of first-principles calculations on the basis of density functional theory. We find that the phonon modes of GNRs with armchair and zigzag type edges can be interpreted as fundamental oscillations and their overtones. These show a characteristic dependence on the nanoribbon width. Furthermore, we demonstrate that a mapping of the calculated Γ-point phonon frequencies of nanoribbons onto the phonon dispersion of graphene corresponds to an "unfolding" of nanoribbons' Brillouin zone onto that of graphene.

Structure



Structure of a N-AGNR (armchair GNR) and a N-ZGNR (zigzag GNR). In each case one dimer is emphasized in red. The corresponding ribbon widths are $w_{AGNR} = \frac{1}{2}(N-1)a_0$ and $w_{ZGNR} = \frac{\sqrt{3}}{2}(N-1)a_0$ (with a_0=lattice constant of graphene).

Reciprocal space

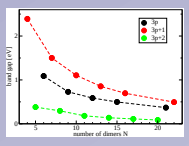


Brillouin zones of graphene, armchair (10-AGNR) and zig-zag (10-ZGNR) nanoribbons. $\vec{a}_1$ and $\vec{a}_2$ are the lattice vectors of graphene, $\vec{b}_1$ and $\vec{b}_2$ are the reciprocal lattice vectors.
Note that the Brillouin zone of ZGNRs ist idealized; in actual nanoribbons it reaches the K-M-K' line only in the limit of large nanoribbons.

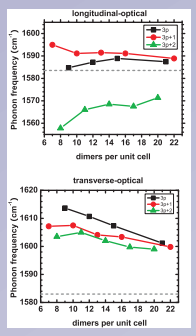
All calculations were performed with the SIESTA code in the local density approximation (LDA). Force constants were obtained by finite differences.

Armchair nanoribbons

Family behaviour

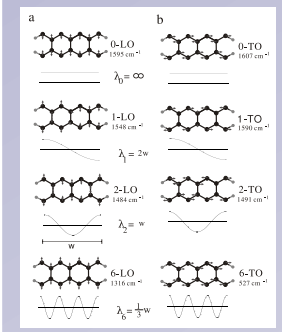


The band gap of AGNRs shows a family dependence and can be classified into 3p, 3p+1 and 3p+2. (see Son *et al.*)



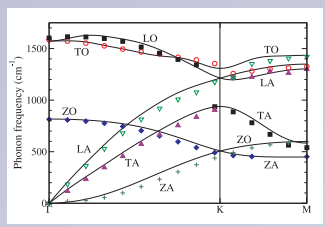
LO and TO mode frequencies of armchair nanoribbons over their width. The dashed line indicates the E_{2g}-frequency of graphene.
The LO-modes of the 3p+2 ribbons are strongly softened due to strong e-ph coupling (similar to metallic carbon nanotubes).

Overtones

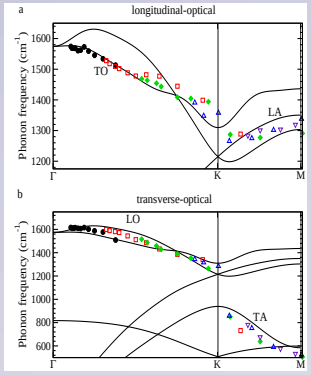


Displacement patterns of (a) longitudinal-optical (LO) and (b) transverse-optical (TO) fundamental and overtone modes at the Γ point of a 7-AGNR. For the n-LO(n-TO), the eigenvectors of the atoms reverse n-times compared to 0-LO(n-TO)(indicated by the envelope curves). The wavelength of the standing waves perpendicular to the ribbon axis is $\lambda = \frac{2}{n}w_{AGNR}$.

Mapping on graphene dispersion

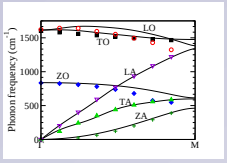


Mapping of fundamental and overtone frequencies of an 15-AGNR onto phonon dispersion of graphene (solid lines).



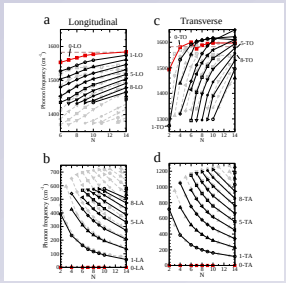
(a) n-LO and (b) n-TO overtones of N-AGNRs with $N = 5-15$ and $n = 1$ (filled circles), $n = 3$ (empty squares), $n = 5$ (filled diamonds), $n = 8$ (empty triangles) and $n = 11$ (crosses).

Zigzag nanoribbons

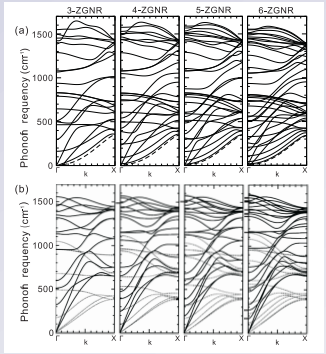


Mapping of ribbon LO (filled squares), TO (circles), ZO (filled diamonds), TA (down triangles), LA (filled up triangles), ZA (crosses) fundamental and overtone frequencies of an 8-ZGNR onto the calculated phonon dispersion of graphene (solid lines).

$k_{\perp,N-1}$ does not reach the graphene M-point. For ZGNRs of small width, the wavelengths obtained by fitting the displacement pattern of the calculated phonons are larger than the theoretically predicted ideal values.



Calculated longitudinal (a,b) and transverse (c,d) Γ-point frequencies of the ZGNR in dependence of nanoribbon width. Filled (red) squares are fundamental oscillations, empty symbols are overtones. Solid black lines connect overtones of equal order n for different ribbons. Filled grey symbols connected with dashed lines show the results of calculations (force field model) of Yamada *et al.* for comparison.



Phonon dispersions of hydrogenated N-ZGNRs with N=2-6: (a) this work (DFT) and (b) MO/8 calculations done by Yamada *et al.* The dashed lines in (a) indicate the fourth acoustic mode, typical for 1D-crystals. Dashed lines in (b) are out-of-plane vibrations.

Conclusion

- LO-modes in 3p+2 AGNRs are strongly softened
- Γ-point phonons of graphene nanoribbons can be interpreted as six fundamental oscillations and their overtones
- Γ-point phonons of nanoribbons can be mapped onto the phonon dispersion of graphene (unfolding).

References

S. Reich, C. Thomsen, and J. Maultzsch, Carbon Nanotubes: Basic Concepts and Physical Properties (Wiley-VCH, Berlin, 2004)

R. Gillen, M. Mohr, J. Maultzsch and C. Thomsen, subm. to Phys. Rev. B

M. Yamada *et al.*, Phys. Rev. B **77**, 054302 (2008)

Y.-W. Son *et al.*, Phys. Rev. Lett. **97**, 216803 (2006)

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

roland.gillen@freenet.de

Kirchberg, March 2009