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**

Armchair | Zigzag
---|---

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

**Reciprocal space**

Brillouin zones of graphene, armchair (10-AGNR) and zigzag (10-ZGNR) nanoribbons. \( a_1 \) and \( a_2 \) are the reciprocal lattice vectors. Nota that the Brillouin zone of ZGNRs is idealized, in actual nanoribbons it reaches the K-\( \Gamma \)-L 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.

**Zigzag 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.)

**Overtones**

Displacement patterns of (a) longitudinal-optical (LO) and (b) transverse-optical (TO) fundamental and overtone modes at the Γ point of a 15-AGNR. For the n-LO(n-TO), the eigenvectors of the atoms reverse n times compared to 0-LO(0-TO) (indicated by the envelope curves). The wavelength of the standing waves perpendicular to the ribbon axis is \( \lambda = \frac{2\pi}{K_n} \).

**Armchair nanoribbons**

LO and TO mode frequencies of armchair nanoribbons over their width. The dashed line indicates the \( E_2 \) frequency of graphene.

The LO-modes of the 3p+2 nanoribbons are strongly softened due to strong e-p coupling (similar to metallic carbon nanotubes).

**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**

- All calculations were performed with the Vienna code.

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