Coherency and anharmonicity in flexural phonons of graphene: a simulation study

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Due to the combination of large resistance to strain with extreme flexibility graphene sustains low frequency transverse out of plane acoustic phonons (the ZA branch), also called “flexural”. These are characterized by a quadratic dispersion near the Brillouin zone center for symmetry reasons, with coefficient proportional to the out-of-plane bending rigidity. The corresponding transverse out-of-plane mechanical vibrations appear as traveling ripples or cavities, if excited coherently, with high amplitude and in counter-phase in alternate multilayers. It was demonstrated in simulations[1] that this system allows to move actively and pump gases (e. g. hydrogen), provided coherent ZA phonons of given wavelength and amplitude can be generated and maintained in the multilayer.

Here we analyze how thermal effects and anharmonicity affect the behavior of ZA phonons, by means of classical molecular dynamics simulations. While the general issue of anharmonicity on thermally excited phonons was recently addressed, in this work we have the specific aim to study how intrinsic anharmonicity and thermal coupling act on the coherency of singly excited phonons.

We performed two series of molecular dynamics simulations: the first with singly excited coherent ZA phonons of different amplitude, different wavelength, the second with increasing amount of thermally excited phonons. This strategy is motivated by the fact that for a practical device based on this effect to work, the ZA component must be prevalent on all the others, which implies that a mechanism to excite and maintain a coherent ZA phonons must be included. Therefore, the interplay with the thermal effects has been evaluated, since the latter degrade the coherency and must be considered in the design of a practical device.

To describe the interaction among C atoms in large-scale simulations, we use the Tersoff empirical force field [2] with the parameters optimized by Broido et al. [3] known to accurately reproduce the ZA branch of phonons. Frequencies and modes eigenvectors are obtained from dynamical trajectories both by spectral analysis (SA) of the velocity and displacement autocorrelation functions and principal component analysis (PCA). It is shown that normal modes and principal modes coincide in the harmonic case, but give different information on anhamonicity.

For sinusoidally excited coherent ZA phonons, SA displays a very clear and sharp main peak, and in most cases also a secondary or tertiary one. For small amplitudes, the main peaks frequencies quantitatively follow the harmonic dispersion curves of ZA phonons, as expected. The analysis of the secondary and tertiary ones reveals a coupling of the latter with Longitudinal Acoustic (LA) and Longitudinal Optical (LO), originated by intrinsic anharmonicity; moreover, while the LA(O) branch displays a softening of the frequencies, in agreement with what previously reported as an effect of anharmonicity, the ZA branch shows an appreciable k-dependent increase of frequencies as a function of the excitation amplitude, which, we show to be specifically due to the ZA/LA coupling. In fact, the very good fitting of the whole series of analytic functions with a single parameter confirms that the stress due to the elongation is the main cause of this frequency increase and the main effect of anharmonicity for ZA phonon in these conditions. Moreover, we identify the aspect ratio (i.e. ratio between amplitude and wavelength) region of the waves for which these excitation becomes mechanically unstable. These findings give indications on how to design a device for gas transport through multilayers.
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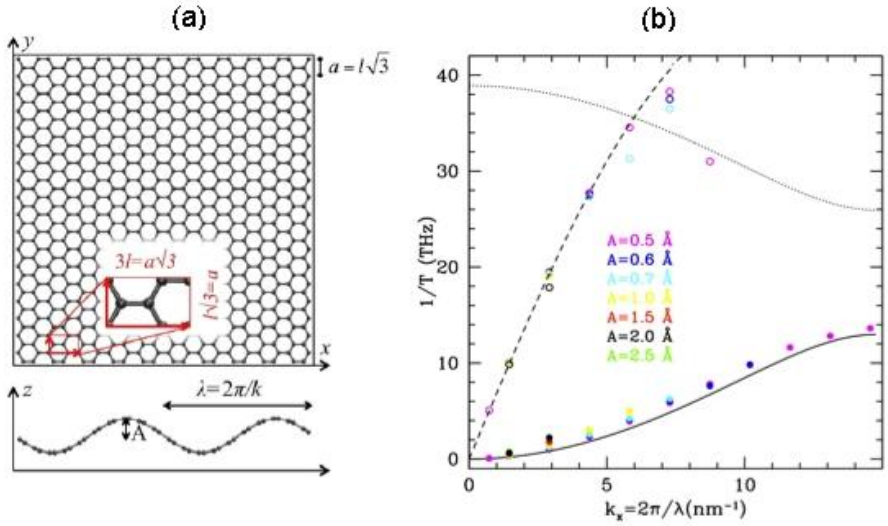

Fig. 1 (a) Schematic representation in the real space of the model system, with top and side views of the calculations super-cell. In the side view the displacement profile corresponding to a ZA phonon is represented. (b) Dispersion relations along the Γ-M line, at different phonons amplitude A (color coding reported in the plot). The filled (empty) dots correspond to the primary (secondary) peaks; the solid (dotted) line represents the harmonic dispersion of ZA (LO) branch; the dashed line represents the harmonic dispersion relation of $LA_{1/2}$ at half the wavelength (double wavevector).