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Long-lived discrete breathers in free-standing graphene

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ABSTRACT

Intrinsic localized modes or discrete breathers (DBs) are investigated by molecular dynamics simulations in free-standing graphene. DBs are generated either through thermal quenching of the graphene lattice or by proper initialization, with frequencies and lifetimes sensitively depending on the interatomic potential describing the carbon-carbon interaction. In the most realistic scenario, for which temperature-dependent molecular dynamics simulations in three dimensions using a graphene-specific interatomic potential are performed, the DBs lifetimes increase to hundreds of picoseconds even at relatively high temperatures. These lifetimes are much higher than those anticipated from earlier calculations, and may enable direct breather observation in Raman spectroscopy experiments. Our simulations provide clear estimation for the temperatures in which DBs are expected to be thermally excited (1500–2000 K) representing a step forward for understanding the nonlinear physics of graphene and designing experiments in order to detect DBs, with possible impact in graphene-based future technological applications.

1. Introduction

Recent technological achievements have allowed for the isolation of single graphene sheets either by chemical exfoliation of bulk graphite [1,2] or by epitaxial growth on metal substrates through thermal decomposition of SiC [3]. As a truly two-dimensional (2D) system, it provides a framework for new type of electronic and magnetic devices [4]. While the electronic properties of graphene have been exhaustively investigated [5], its mechanical and thermal properties are not quite thoroughly analyzed. In particular, while a reliable linear phonon spectrum can be obtained numerically and compared with the experimental one, much less is known about the nonlinear vibrational modes in graphene. Since all potentials used for modelling the vibrational properties of graphene are nonlinear, it is natural to expect that intrinsic localized modes, i.e. discrete breathers (DBs), may be formed. DBs are spatially localized and time-periodic vibrational modes that form spontaneously in nonlinear lattices [6–8]; they have been assessed experimentally in several systems, including solid state mixed-valence transition metal complexes [9], quasi-one dimensional antiferromagnetic chains [10], micromechanical oscillators [11], optical waveguide systems [12], Josephson-junction arrays [13,14], proteins [15], and NaI crystals [16].

DBs have been studied in graphene using MD in graphene [17,18], strained graphene [19–21], graphane [22] and in carbon nanotubes [23,24]. Recently they have been studied as well using *ab intio* MD techniques in graphene [25] and graphane [26].

A reliable computational prediction of possible DB excitations in graphene, their lifetime and spectral features, will enable their direct experimental observation and facilitate the design of efficient future devices at relatively high temperatures. In the present work we perform extensive molecular dynamics (MD) simulations that reveal the existence of DBs in free-standing graphene both at zero temperature in 2D as well as at finite-temperatures in three dimensions (3D). To this end, we resort to Sandia National Laboratories Large-Scale Atomistic/Molecular Massively Parallel Simulator (LAMMPS) [27]. In order to demonstrate the DB onset and stability range we have tested several interatomic potentials (IPs) that have been utilized in the past to model carbon systems (Tersoff [28], AIREBO [29], LCBOP [30], CBOP [31], among others). However, we eventually focus on a graphene-specific Tersoff potential [28], hereafter referred to as Tersoff'10, which is of the form

$$E_{ij} = V_{ij}^R + b_{ij} V_{ij}^A \tag{1}$$

The functions $V_R(r)$ and $V_A(r)$ are pair-additive interactions that represent all interatomic repulsions (core–core, etc.) and attraction

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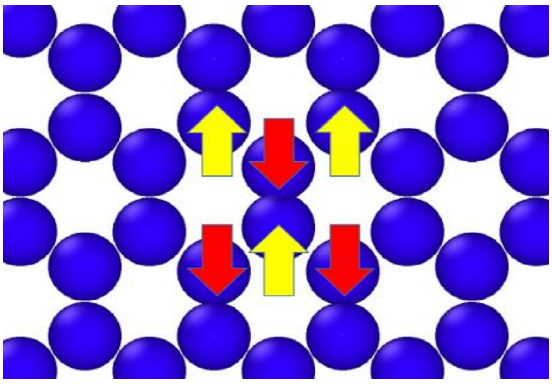

Fig. 1. Schematic illustration of the initial condition to generate discrete breathers (arrows are not at scale).

from valence electrons, respectively. The quantity r_{ij} is the distance between pairs of nearest-neighboring atoms i and j and b_{ij} is a bond order between atoms i and j. As it would be expected, the stability and lifetimes of DBs in graphene is strongly potential-dependent [17–21]. AIREBO and LCBOP potentials include angular, dihedral (out of plane distortions), as well as long-range terms. The comparison of the results obtained using AIREBO and LCBOP points to a destructive effect of the long-range part of the potentials on the stability of the DBs. This is more evident when LCBOP is compared with the CBOP. The Tersoff'10 potential is a reparametrized version of the original Tersoff'89 IP that provides much better agreement with the experimental phonon velocities and frequencies, without significantly altering the agreement to other structural data. The choice of that potential is based on its performance on particular features regarding the vibrational properties of graphene. Along with LCBOP, the Tersoff'10 IP provides the most accurate overall description for its phonon dispersion curves. In particular, the Tersoff'10 IP produces more accurate LA and ZA branches but less accurate ZO and TA branches than LCBOP at temperature T = 300 K. Moreover, it is the only one to produce a linear temperature-dependence of the doubly degenerate Raman active E_{2g} mode of the Γ point [32]. We consider these two features important for the correct simulation of DBs in free-standing graphene.

The temperature-dependence of the vibrational graphene spectra was investigated using the original Tersoff'89, Tersoff'10, LCBOP, and AIREBO potentials. The MD simulations were performed using a periodic triclinic computational cell of 20×20 unit cells (overall 800 carbon atoms). The computational cell was relaxed for each potential and the corresponding lattice parameter was calculated and used in defining the BZ edges in each case. A very fine time-step of 0.05 fs was used and the trajectory and velocities were saved every 10 time-steps. These simulations typically run for about 32.8 ps each (655,360 time-steps). For the Tersoff'10 potential, the graphene vibrational response was analyzed by producing the dispersion curves at temperatures T = 60 K, 500 K, and 1500 K [30]. For that IP, the strongest temperature-dependence is observed on the optical branches. Upon increasing of temperature, the frequencies lower by as much as 64 cm–1 (~2 THz).

2. Results

2.1. NVE simulations

Discrete breathers in graphene may be generated by either local initial displacements (and subsequent MD evolution), or by thermal quenching of the graphene lattice. The former method consists of displacing a few atoms deeply in the graphene lattice according to an approximate solution obtained by the rotating wave approximation of the equations of motion (Fig. 1) [33]. The simulations were carried out in the microcanonical ensemble (NVE) in 2D using the Tersoff'10 potential with a time-step $\Delta t = 10^{-5}$ ps and periodic boundary conditions. The graphene samples typically contain 15,000 atoms, so that edge effects do not affect DB stability.

Finite size effects have been investigated by performing repeated simulations using computational cells of different sizes. The initial displacement, d, ranges from 0.1 to 0.3 Å (We limited ourselves to displacements just up to 0.3 Å since larger displacements can create defects, even trigger melting, instead of generating stable DBs). Depending on the value of d, two different DB configurations, say Type-1 and Type-2, have been observed. Type-1 breathers are observed for d in the range 0.15–0.19 Å (Fig. 2a), while type-2 DBs are observed for d in the range 0.27–0.3 Å (Fig. 2b). Both Type-1 and Type-2 DBs exhibit almost steady evolution for relatively long times. The *central* atoms of Type-1 DBs (red atoms in Fig. 2a) execute large amplitude periodic oscillations while the outer ones (blue atoms in Fig. 2a) small amplitude oscillations. Typical oscillation patterns of the inner (central) and outer atoms of a Type-1 DB are shown in Fig. 3 (supporting information video 1). The phases of large and small amplitude oscillations differ by π in that DB configuration. The frequency of the oscillations of the inner atoms here is not constant with time but increases up to twice its value at the same time that the amplitude of the oscillations clearly decreases (after 20 ps). The periodicity is not exact so these DBs could be seen as well as quasi-breathers, as in the work of Chechin et al. [34].

The configuration of Type-2 DBs is much more complex and only some of the atoms exhibit regular oscillations (supporting information video 2). In both types of DBs however the energy remains almost constant for long times, during which their fre-

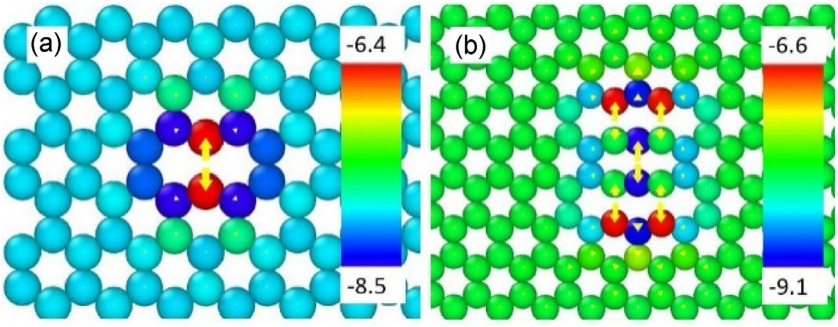

Fig. 2. Type-1 (a) and Type-2 (b) breathers in a single graphene sheet at T = 10 K. Color scale correspond to the total energy in eV/atom. The yellow arrows show the displacements with respect to the equilibrium position after stabilization. The length of the arrows is 3 times the real value for the shake of clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)