Discrete breathers in graphene and related 2-D materials

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1. INTRODUCTION

Discrete breathers or intrinsic localized modes have been theoretically predicted in many different materials. This is also the case for graphene [1, 2], hydrogenated graphene [3] etc. However, the results presented in [1] and [2] are not completely compatible and clearly further research is necessary. More importantly, experimental evidence is still lacking. In this work we present our current research using classical molecular dynamics (MD) and selected interatomic potentials (Tersoff, AIREBO, LCBOP and reaxFF). Our MD simulations show the existence of breathers but, for example, the lifetime can change one order of magnitude or more depending on the force field used to describe the carbon–carbon interaction (in fact this can be also observed comparing the lifetimes and frequencies presented in [1] and [2]). Hence, the properties of the breathers clearly depend on the interatomic potential and the differences between the potentials has to be considered.

2. MOLECULAR DYNAMICS (MD)

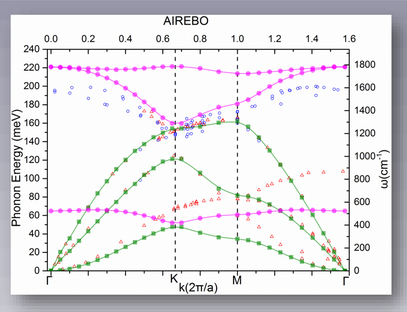
- To clarify the properties of discrete breathers (DB) molecular dynamics (MD) simulations are a very suitable tool.
- The main goal of these MD calculations is to understand the dependence of the DB properties on the interatomic potential used to describe the carbon–carbon interaction and to identify what properties are universal, i.e, independent on the simulation details.

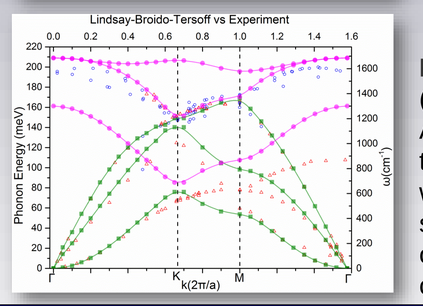
$$V_{ij} = f_C(r_{ij})[f_R(r_{ij}) + b_{ij} f_A(r_{ij})], \quad (1)$$

$$E = \frac{1}{2}\sum_i \sum_{i \neq j} \left[E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k \neq i,j} \sum_{l \neq i,j,k} E_{kijl}^{Torsion} \right] \quad (2)$$

$$E_b = \frac{1}{2}\sum_{i,j}^{N} \left(f_{c,ij} V_{ij}^{SR} + S_{ij} V_{ij}^{LR} \right) \quad (3)$$

General description of the potentials used here to simulate the CC interaction (1) Tersoff (2) AIREBO and (3) LCBOP. Red lines stress the long range part of the of the different potentials.





What potential should be more accurate to describe the properties of breathers?
Here we compare the different phonon calculations using the AIREBO and Tersoff potentials.

The revised Tersoff (2010) predicts worst TA and ZO, and better ZA, LO and TO branches, than AIREBO.

What impact does the quality of the calculated phonon dispersion curves have on the proper description of the behavior of DB in graphene?

Fig. 2. Dispersion curves of graphene (GE) calculated using the (top) AIREBO and (bottom) Lindsay-Broido-Tersoff(2010) potentials. Acoustic modes *LA* and *TA* correspond to the longitudinal and transverse oscillations in the GE plane, respectively. The acoustic wave *ZA* describes the transverse oscillations normal to the GE sheet. Solid symbols correspond to theoretical calculations using our in-house developed computer code. Hollow symbols correspond to experimental measurements [5,6].

3. POTENTIAL DEPENDENCE

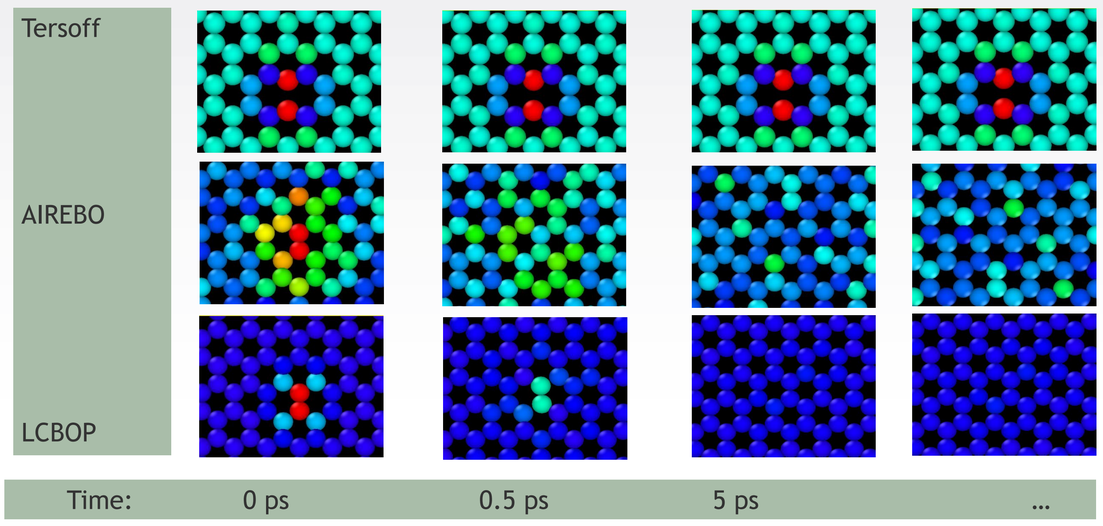


Figure 3.1: Single breather in a MD simulation using 3 different potentials (NPT, 10 K). Top, Tersoff, center AIREBO and bottom LCBOP. Color scale corresponds to the energy of the different atoms.

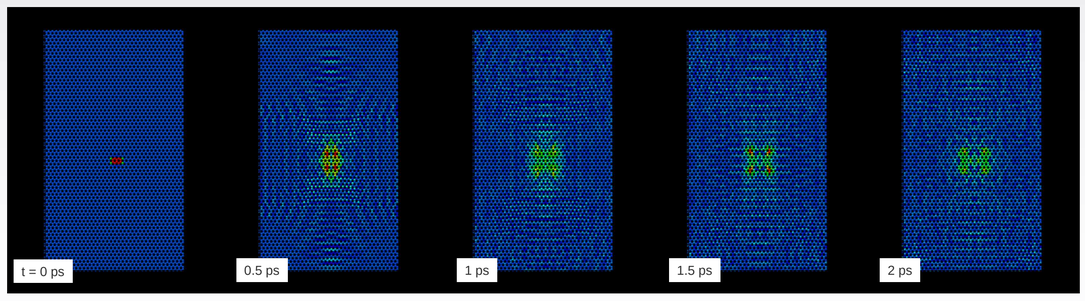
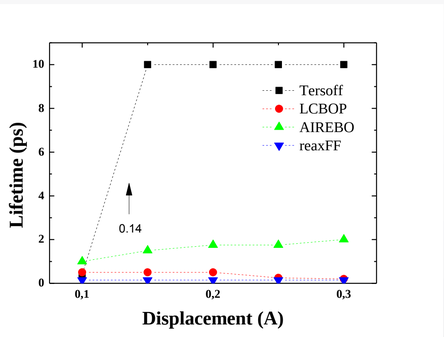


Fig. 3.2. Sequence of a breather simulation with AIREBO potential (NVE, 0 K). Initial displacement 0.2 A, Number of atoms 5000.

3.1 Size effects

- **Size effects are clearly important. In the above figure we show how the "energy wave" created by the initial displacement interacts with the DB after reflecting on the boundaries of the sample, even for large samples (N=5000 atoms). This interference leads to a significant dependence of the results on the sample size.**

4. RESULTS & EXPERIMENTAL IDEAS



- The Tersoff potential is the only one that produces robust and stable breathers (lifetime > 20 ps).
- For small displacements (< 0.14 A) the lifetime is small (0.5 ps)
- For all the other potentials that we have examined the lifetimes have a weak dependence on the initial displacement and are the same order of magnitude.

Fig 4.1. Lifetimes (in ps) of discrete breathers in our MD simulations with four different potentials as labeled. Dashed lines are a guide to the eye.

The simulations presented in [1] showed DBs of frequency 47 THz and lifetimes around 1 ps while those in [2] gave frequencies around 27-32 THz and lifetimes about 30 ps.

Potential	Cutoff (A)	Lifetime (ps)	Frequency (THz)	Period (fs)
Tersoff	2	0.5 to 10 and more	44	18
AIREBO	6	1.75	10	90-100
LCBOP	10	0.5	50	20
reaxFF	10	0.15	50	20

4.1 QUENCHING

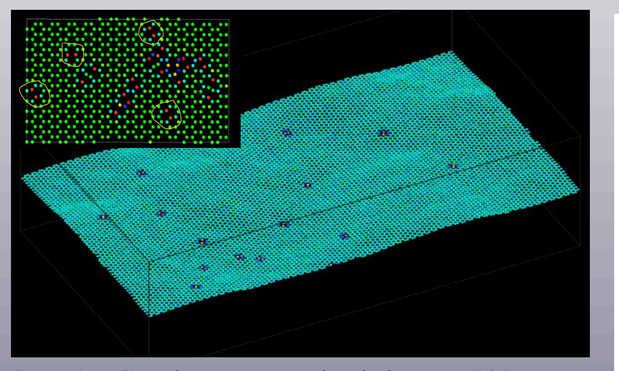


Fig 4.2. GE sheet quenched from 4500 K to 500 K. DBs like the artificially created (See Fig 3.1) are clearly seen. Color scale correspond to the total energy.

- **High temperature creates defects that survive as breathers in Tersoff MD simulations.**
- **However using AIREBO or LCBOP high Temperatures does not create the same kind of structures at least up to very high Ts very close to melting point.**
- **Can we heat up the sample and quench it fast enough to observe DBs using Raman spectroscopy?**

4.2 RAMAN SPECTROSCOPY (RS)

RS is a sensitive method to study phonons in graphene. The G and 2D modes are well resolved and they evolution with temperature can be easily followed. The D band at 1350 cm^{-1} is a disorder activated band which is can be used to estimate the amount of structural disorder in a given sample.

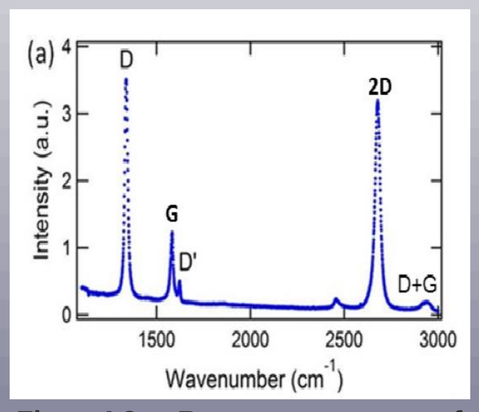


Fig. 4.3. Raman spectra of disordered graphene.

We intent to use **time-resolved RS** to examine the hot phonon decay of the G mode by tuning the temporal decay between pump and probe pulses The ultrafast pump pulse generates a population of electron-hole pairs that is cooled by emission of phonons.
The dynamics of the phonons which follows the relaxation dynamics of the e-h pairs will be monitored by the intensity of the **anti-stokes Raman signal**. Since the intensity of the anti-Stokes signal is proportional to the population of optical phonons involved, one can directly monitor the phonon decay by varying the delay between the ultrafast pump and probe pulses.

5. CONCLUSIONS

- **The behaviour of DBs in graphene is still far from being well understood. MD simulations can be useful to understand and analyze current experiments.**
- **We have determined some elementary properties of DBs in graphene. Our MD calculations show that the properties strongly depend on the interatomic potential as well as the sample size and technique employed to create the breather.**
- **In general we can not conclude that breathers exist and survive for a long in graphene except if we trust the results using the Tersoff potential.**
- **The period (and hence, the frequency) of the DB oscillations depends on the initial displacement and also on the thermodynamical ensemble.**
- **More extensive MD simulations along with experiments are still necessary.**

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