Molecular simulations of carbon allotropes in processes with creation and destruction of chemical bonds

Rafael I. González

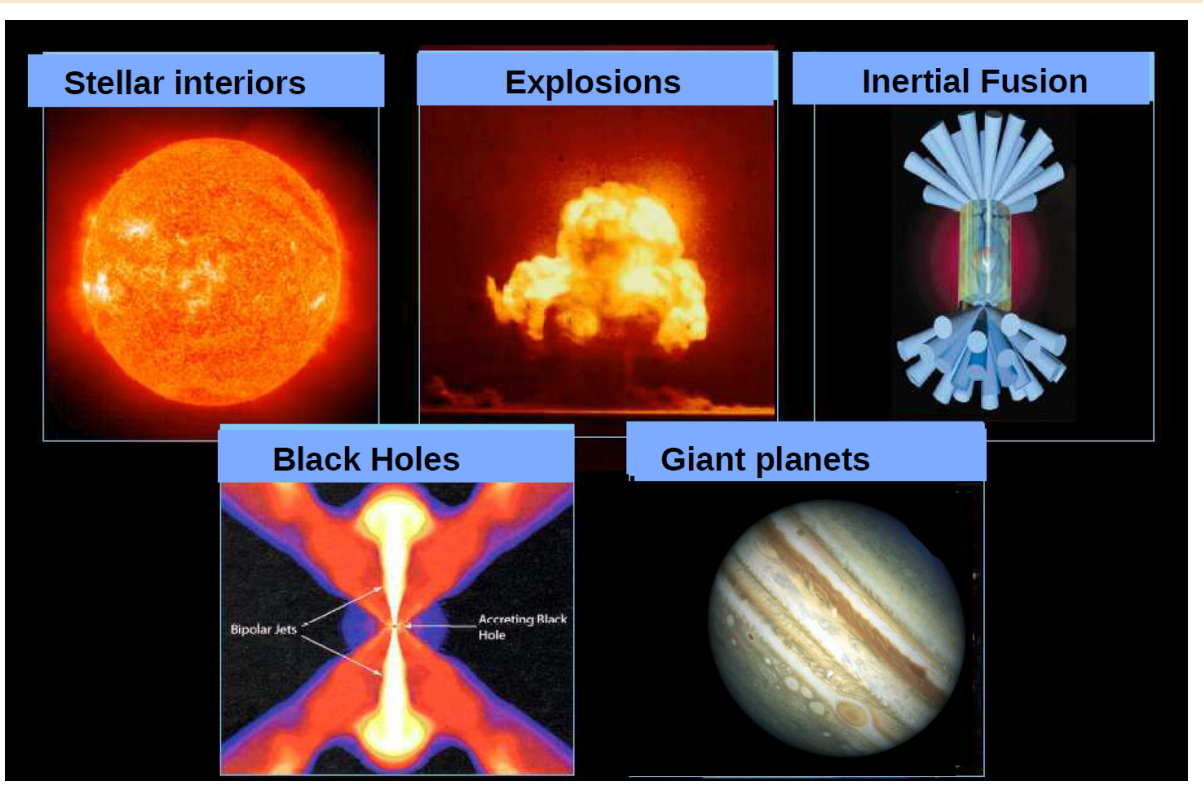
August 15, 2019

Center for Applied Nanotechnology - CNAP, Universidad Mayor, Chile

And

Centro para el Desarrollo de la Nanociencia y la Nanotecnología - CEDENNA, Chile

Materials under extreme conditions of temperature, pressure, radiation, etc.
Experiments difficult or impossible to carry out: need models and simulations



In this presentation

- We are going to consider carbon materials under extreme conditions.
- In particular, we study carbon materials in conditions of bond destruction (creation).
- We are going to discuss about the problems that arise when interatomic potentials are used beyond their initial purpose (REBO and AIREBO).

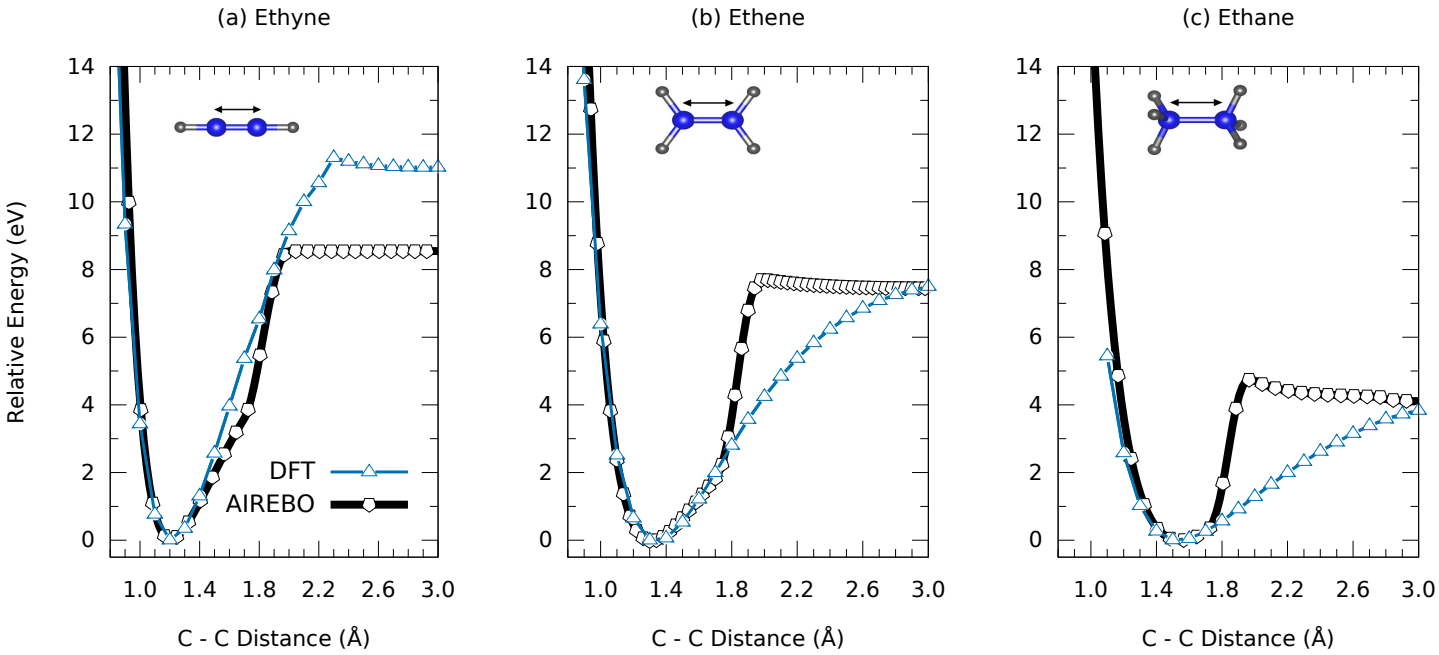
Methods

- MD simulations with **LAMMPS**.
- Post-processing with **OVITO**.
- NVT/NPT with Nosé-Hoover like thermostat/barostat
- Typical time-step Δt between $0.1 - 1$ fs
- Force fields . . .

REBOII[1] - AIREBO[2]: Comparison with DFT.

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

$$E_{ij}^{REBO} = [V^R(r_{ij}) - b_{ij}V^A(r_{ij})]$$



[1] Brenner *et al.* J. Phys. Condens. Matter **14** (2002) 783. (3317 cites - Google Scholar 08/13/19)

[2] Stuart *et al.* J. Chem. Phys **112** (2000) 6472. (2855 cites - Google Scholar 08/13/19)

REBOII: Cutoff scheme based on a switching function

$$f(r) = \begin{cases} 1 & r < R_{min} \\ \frac{1}{2}\left[1 + \cos\left(\pi \frac{r - R_{min}}{R_{max} - R_{min}}\right)\right] & R_{min} < r < R_{max} \\ 0 & r > R_{max} \end{cases}$$

$$R_{min} = 1.7 \text{ Å}$$
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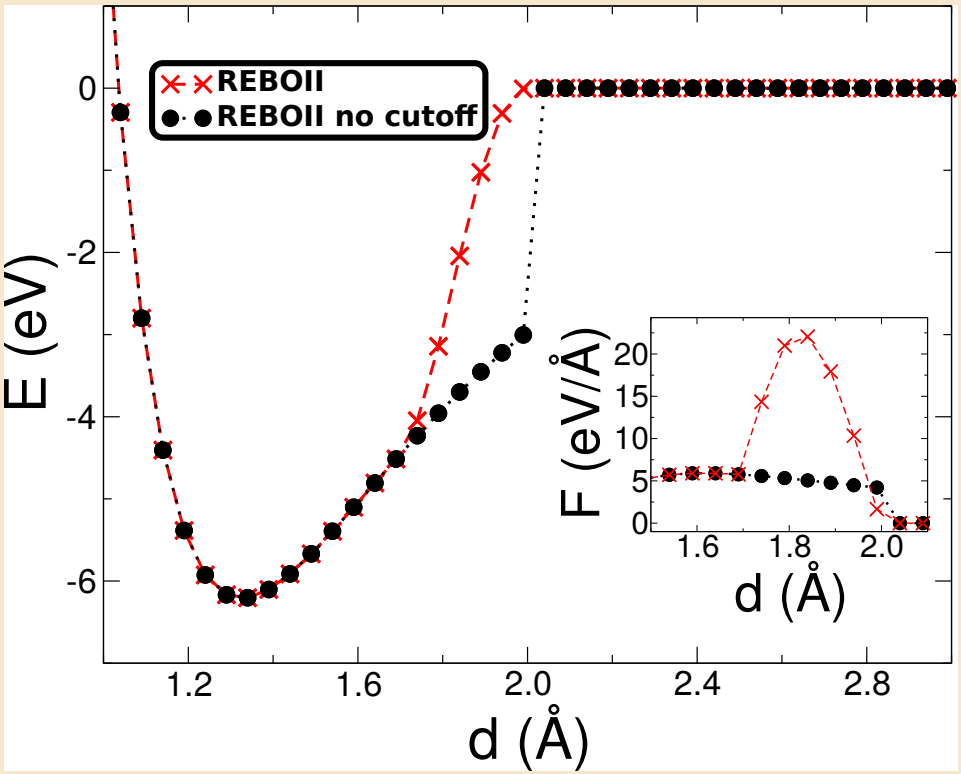
This function develops unrealistic large forces in situations involving bond breaking, but it exists for a good reason: **Energy conservation.**

The problem: many people is playing with R_{min} and R_{max} as **free parameters.**

Cutoff scheme for C-C dimer: with and without SF

$$\frac{\partial f(r)}{\partial r} \propto \sin\left(\pi \frac{r - R_{min}}{R_{max} - R_{min}}\right)$$



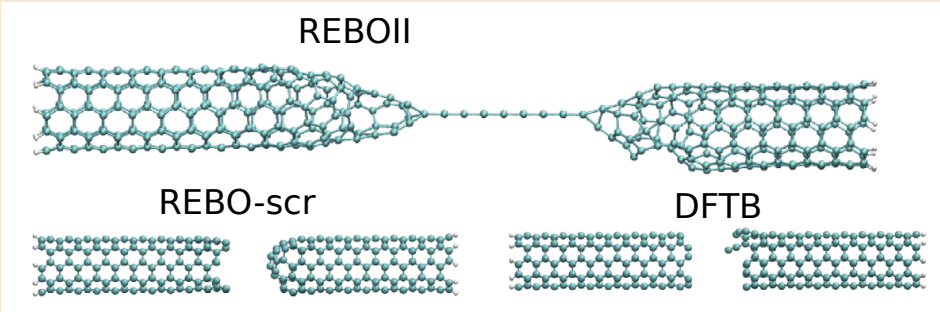
For a deeper discussion about C bond breaking and the switching function, please read: Pastewka *et al.* MRS Bull. **37** (2012) 493.

Previous works: REBO-scr and SED-REBO

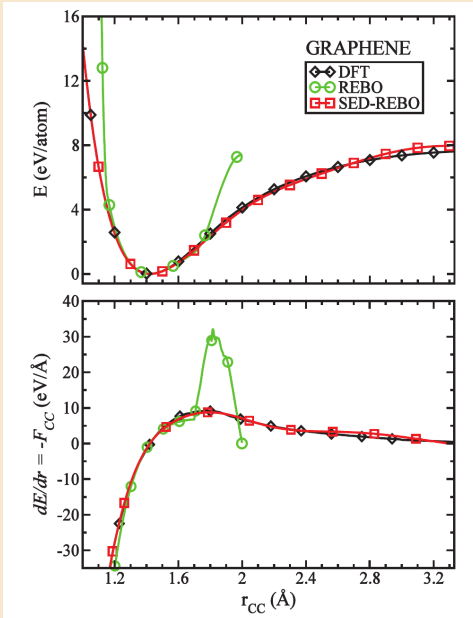
Alternative switching schemes based on screening concepts

REBOII predicts ductile necking under tensile stress for CNT.

Experimentally, the CNT have a fragile behavior under tension..[1]



SED-REBO: Graphene binding energy and its derivative for isotropic expansion and compression.[2]



[1] Pastewka *et al.* Phys. Rev. B **78** (2008) 161402(R). Use with LAMMPS: https://github.com/Atomistica/atomistica

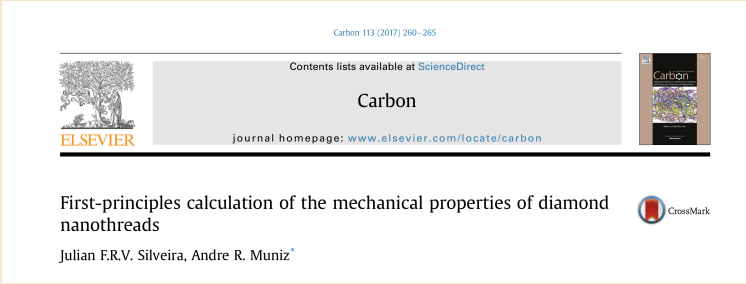
[2] Perriot *et al.* Phys. Rev. B **88** (2013) 64101.

In spite of all these warnings, many papers are constantly published modifying the cutoff scheme of REBOII (or AIREBO) under extreme conditions:

In spite of all these warnings, many papers are constantly published modifying the cutoff scheme of REBOII (or AIREBO) under extreme conditions:

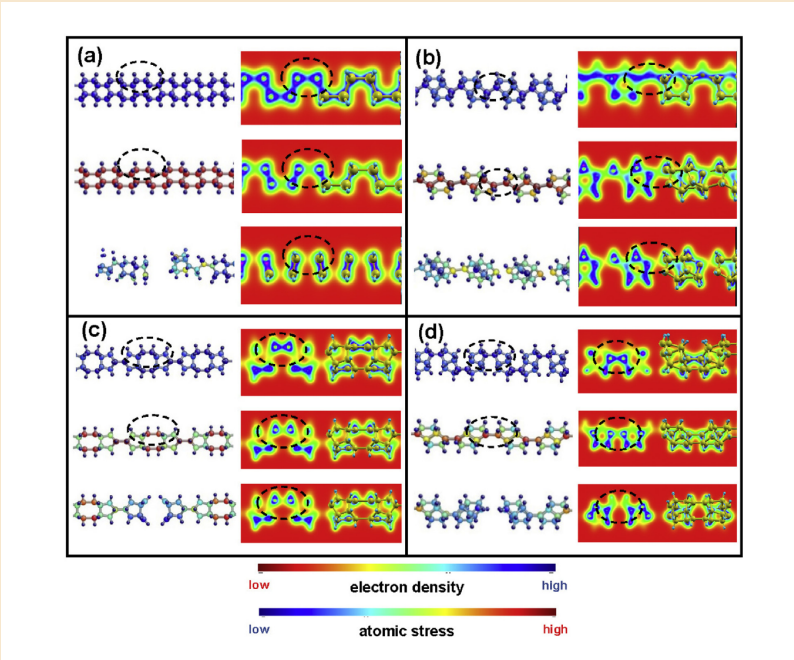
- Eliminating the S.F., *i.e.*, $R_{min} = R_{max} = 2.0$ Å. Or using other values like $1.9 - 2.1$ Å and beyond.
- Varying the values of R_{min} and R_{max} as free parameters. We will discuss the case $R_{min} = 1.92$ Å and $R_{max} = 2.0$ Å

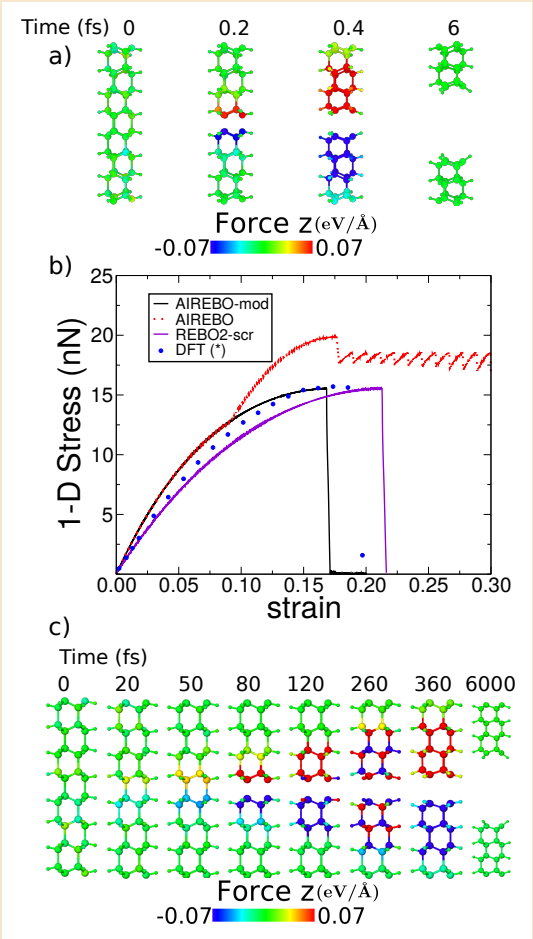
Eliminating the switching function. DNT SS curves


Carbon 113 (2017) 260–265
Contents lists available at ScienceDirect
Carbon
journal homepage: www.elsevier.com/locate/carbon

First-principles calculation of the mechanical properties of diamond nanothreads

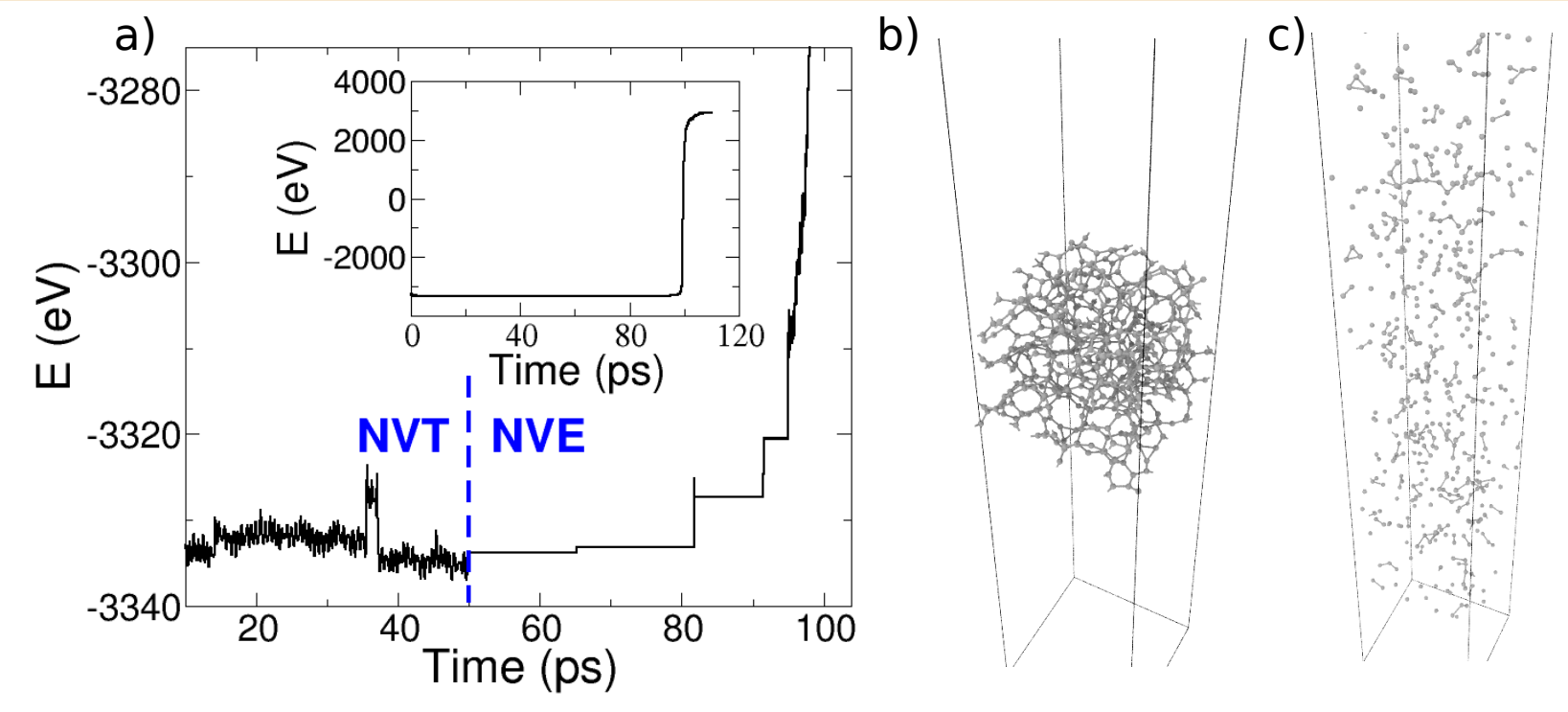
Julian F.R.V. Silveira, Andre R. Muniz*





* DFT calculations from Silveira and Muniz Carbon **113** (2017) 260.

Eliminating the switching function. Amorphous carbon vaporization at room temperature?



Many people is using
$R_{min} = 1.92$ and $R_{max} = 2.0$
for carbon simulations.

But: Is there something special with these cutoff values?

Defining cutoff scheme: $R_{min} = R_{max} = 1.92$Å

nature materials
LETTERS
PUBLISHED ONLINE: 1 JULY 2012 | DOI: 10.1038/NMAT3370

The nature of strength enhancement and weakening by pentagon–heptagon defects in graphene

Yujie Wei[1]*, Jiangtao Wu[1], Hanqing Yin[1], Xinghua Shi[1], Ronggui Yang[2]* and Mildred Dresselhaus[3]

Methods

The Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) Potential[29] for Carbon is used for MD simulations. Following ref. 10, we have also used a switch function parameter $r_{CC} = 1.92$ Å (Table 1 in ref. 29), beyond which a C–C bond breaks. The choice of $r_{CC} = 1.92$ Å in the AIREBO potential[29] is further validated by comparing the density functional theory calculations and MD simulations for the stress–strain curves in pristine graphene in either the armchair or zigzag direction (see Supplementary Information S2 for details).

10. Grantab, R., Shenoy, V. B. & Ruoff, R. S. Anomalous strength characteristics of tilt grain boundaries in graphene. *Science* **330,** 946–948 (2010).

REPORT

Anomalous Strength Characteristics of Tilt Grain Boundaries in Graphene

Rassin Grantab[1], Vivek B. Shenoy[1,*], Rodney S. Ruoff[2,*]
+ See all authors and affiliations

Science 12 Nov 2010:
Vol. 330, Issue 6006, pp. 946-948
DOI: 10.1126/science.1196893

An adaptive intermolecular reactive bond order (AIREBO) potential (*2*) as implemented in LAMMPS, was used to model the atomic interactions in graphene. Following the work of Pei *et al.* (*3*), we have used an interaction cut-off parameter of 1.92Å. In order to calculate the stress-

Graphene under SS simulations behaves brittle!

Using $R_{min} = 1.92$ Å

. . . maybe it's a good idea.

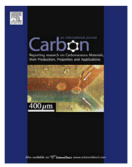
CARBON 48 (2010) 898–904

available at www.sciencedirect.com

ScienceDirect

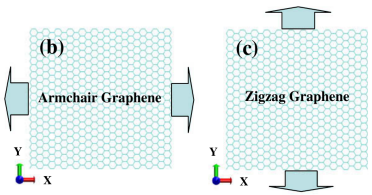
journal homepage: www.elsevier.com/locate/carbon

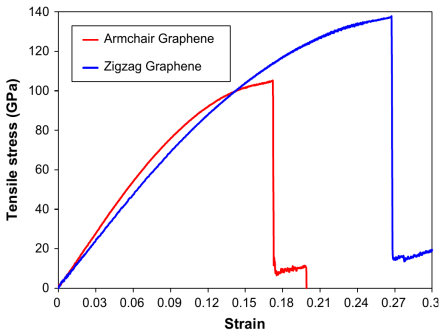
ELSEVIER



A molecular dynamics study of the mechanical properties of hydrogen functionalized graphene

Q.X. Pei [a], Y.W. Zhang [a,b], V.B. Shenoy [c,*]





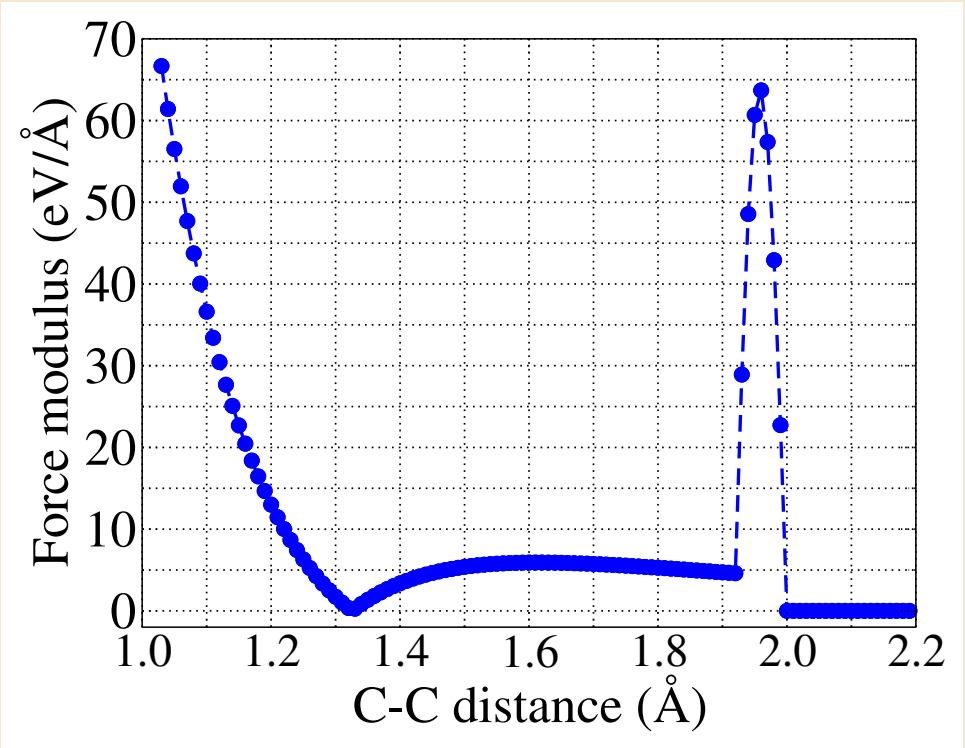
which is realized by using a Berendsen thermostat [26]. The simulation time step is 0.001 ps. The adaptive intermolecular reactive bond order (AIREBO) potential [27] as implemented in the software package LAMMPS [28] is used in our simulations.

* They do not mention anything about any cutoff modification.

We suppose they used $R_{min} = R_{max} = 1.92$ Å

However, some authors are using $R_{min} = 1.92$ and $R_{max} = 2.0$ Å citing Pei *et al.* work.

Force magnitude during C-C dimer dissociation.

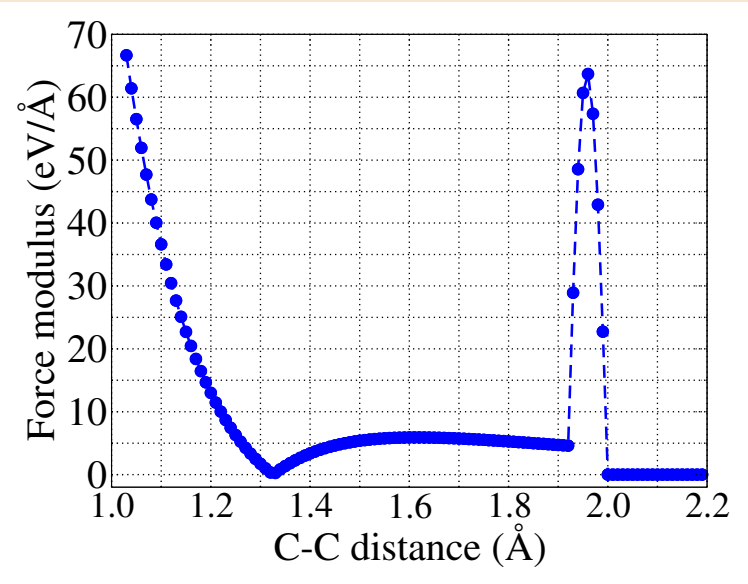


Deng *et al.* 2D Mater. **4** (2017) 021020
Yang *et al.* Physica E **96** (2018) 46
Jian *et al.* Carbon **132** (2018) 520

Is it possible to break C-C bonds with this modification?

Estimation of the displacement of 1 C atom in 1 time-step around the cutoff zone

Considering displacement: $\Delta x \approx \frac{1}{1} a \cdot \Delta t^2$



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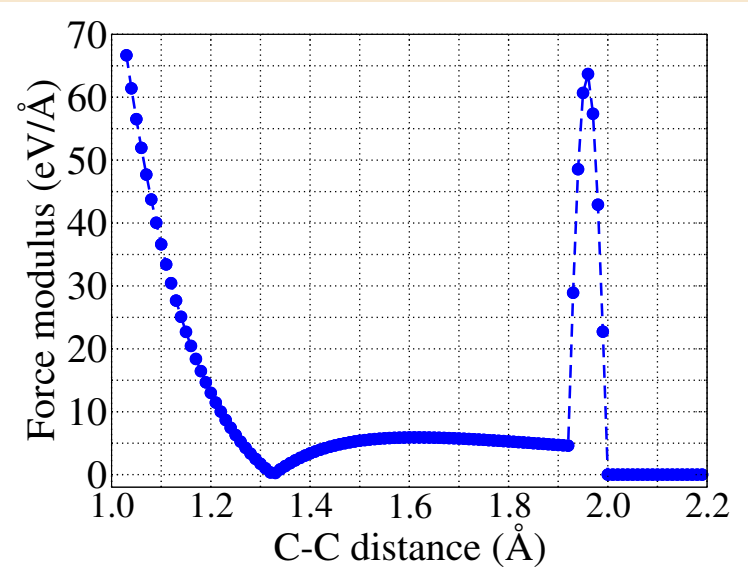
$F_{max} \approx 65$ eV/Å



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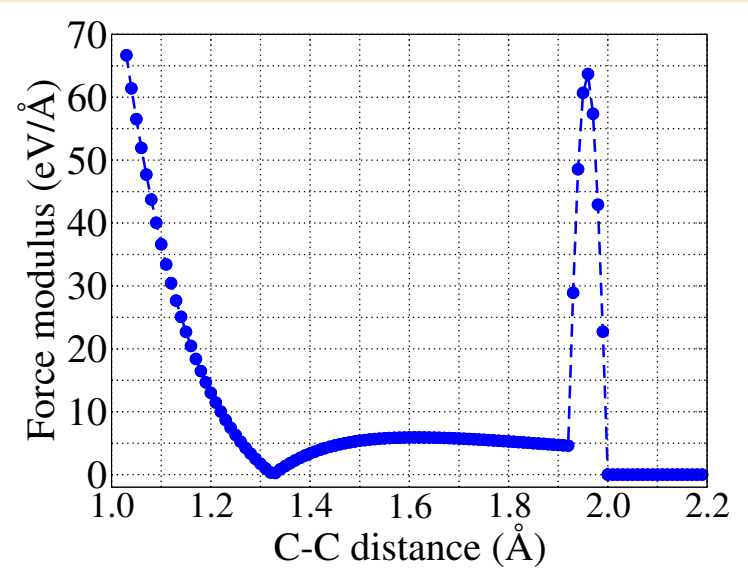

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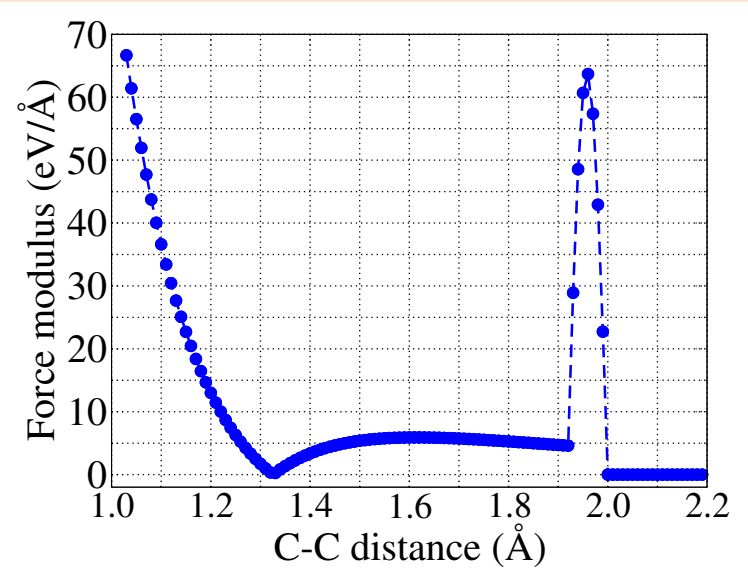

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The displacement in 1 time-step is
$\Delta x = 2.5 \times 10^{-2}$ Å

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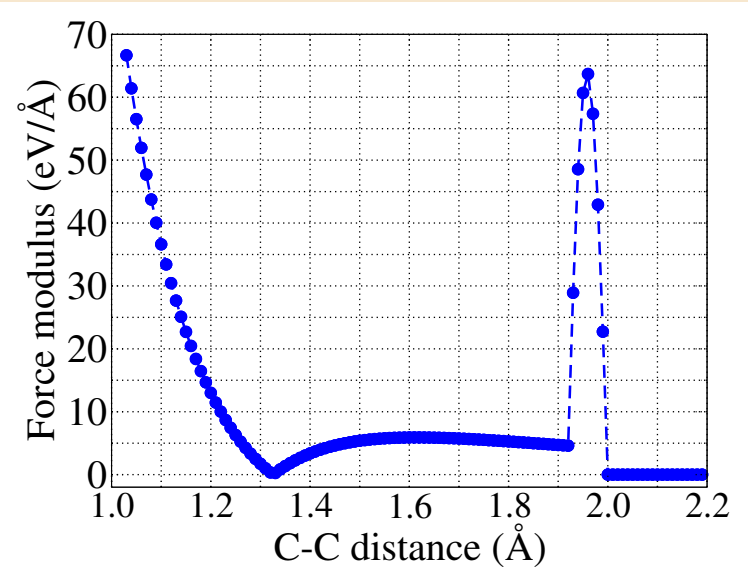

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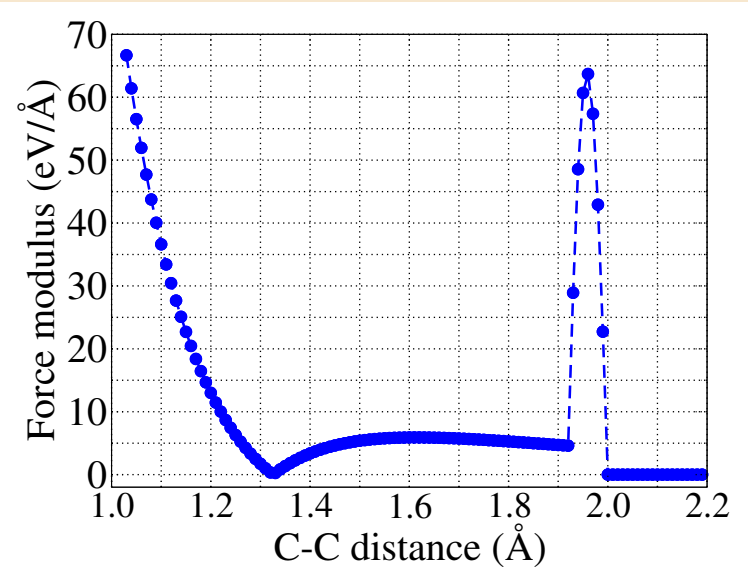
The force Barrier length is:
$R_{max} - R_{min} = 8 \times 10^{-2}$ Å

Is it possible to break C-C bonds with this modification?

Estimation of the displacement of 1 C atom in 1 time-step around the cutoff zone



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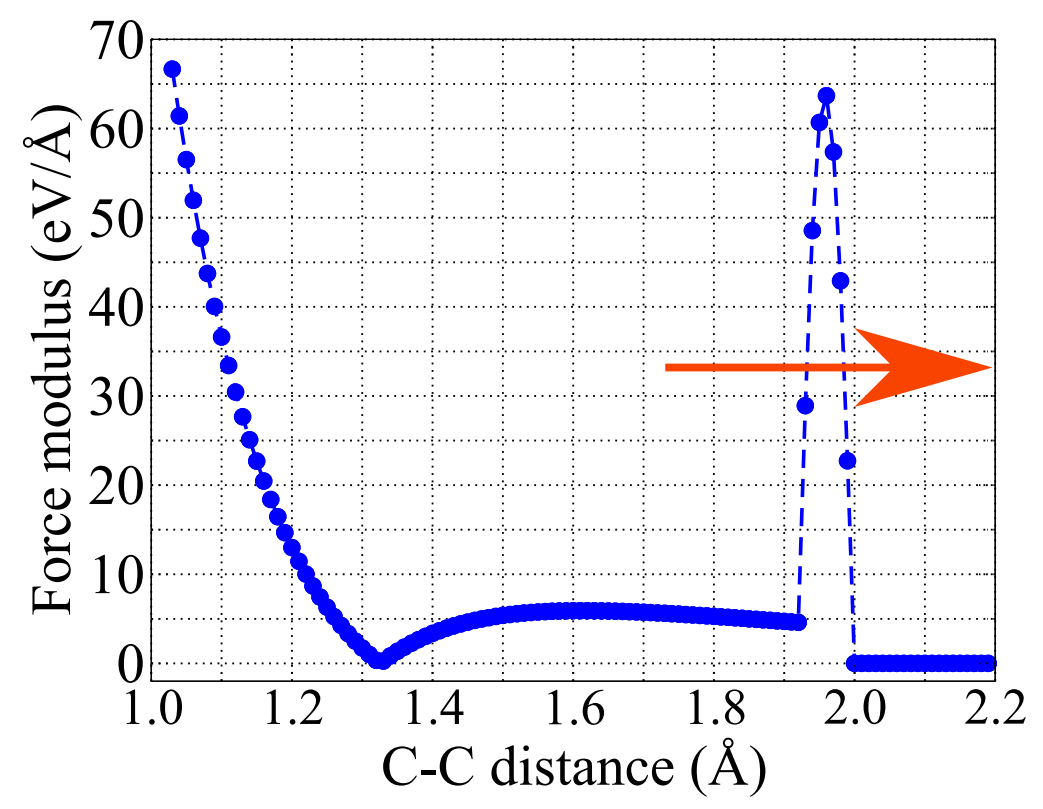
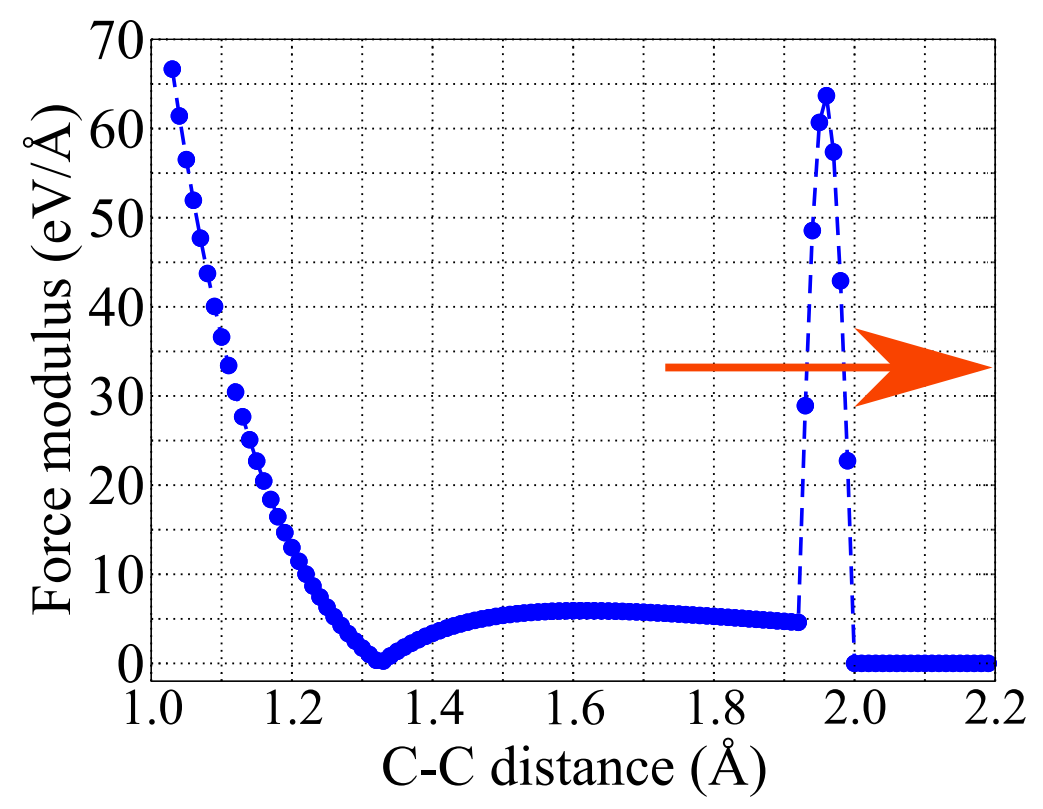
Roughly, in 4 time-step is possible to cross the force barrier

How is this possible?



. . . Classical tunneling effect!!

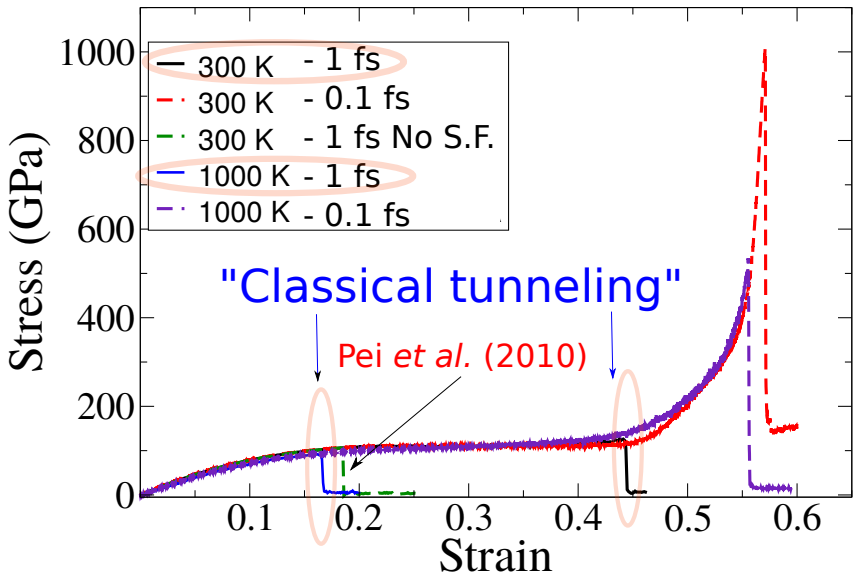
How is this possible?

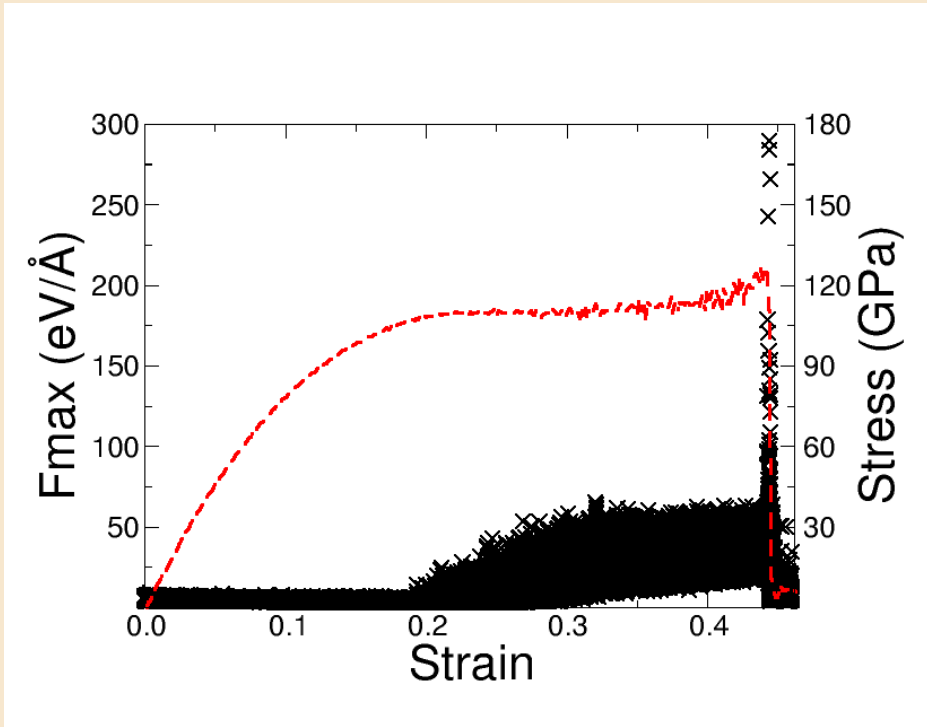


Not really . . .

Numerical errors due choosing the incorrect potential parameters and a large time-step.

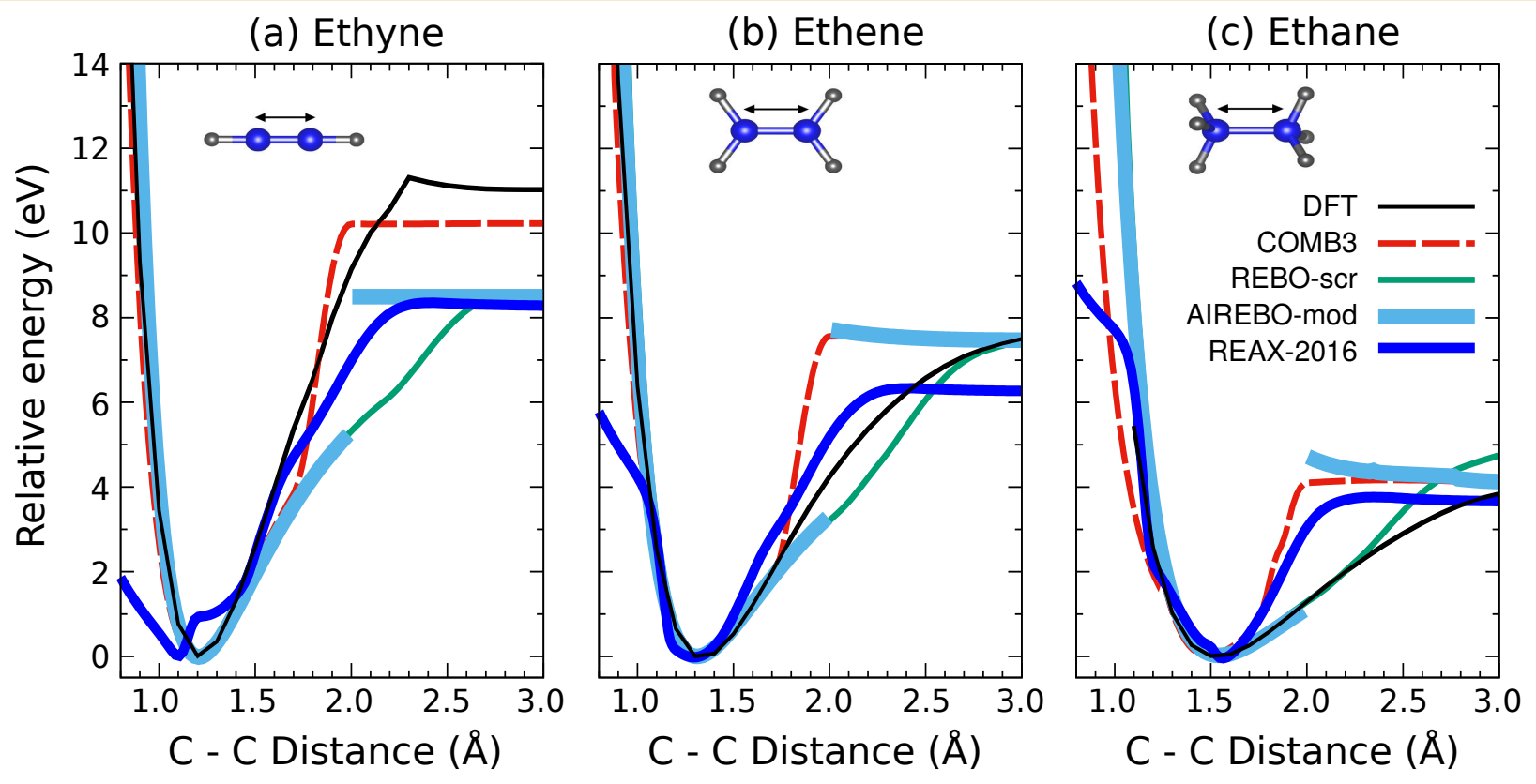
Graphene Sress-Strain simulations varying time-step and temperature





F_{max} computed using *thermo style* **fmax**

Finally, a comparison of some carbon potentials against DFT calculations



Conclusions and General Remarks

- Our work seeks to put some critical points that **have not been mentioned (clearly) in the literature** on modifying the cutoff radius for REBO - AIREBO potentials.
- Many authors are still using REBO and AIREBO for carbon under extreme conditions without any modification to the S.F. where the results could be even worse.
- Reproducing DFT or experimental results is a good test for any potential. But also, **you must configure your MD simulation properly:** time-step, integrator, etc

Work recently published:
Tangarife *et al.* Carbon **119** (2019) 177-184

Acknowledgments

Funding:

- Center for the Development of Nanoscience and Nanotechnology - CEDENNA
- FONDECYT #11180557
- Universidad Mayor

Co-authors:

- Edwin Tangarife (U. Mayor)
- Francisco Munoz (U. de Chile)
- Carlos Cardenas (U. de Chile)
- Eduardo M. Bringa (U. de Mendoza)

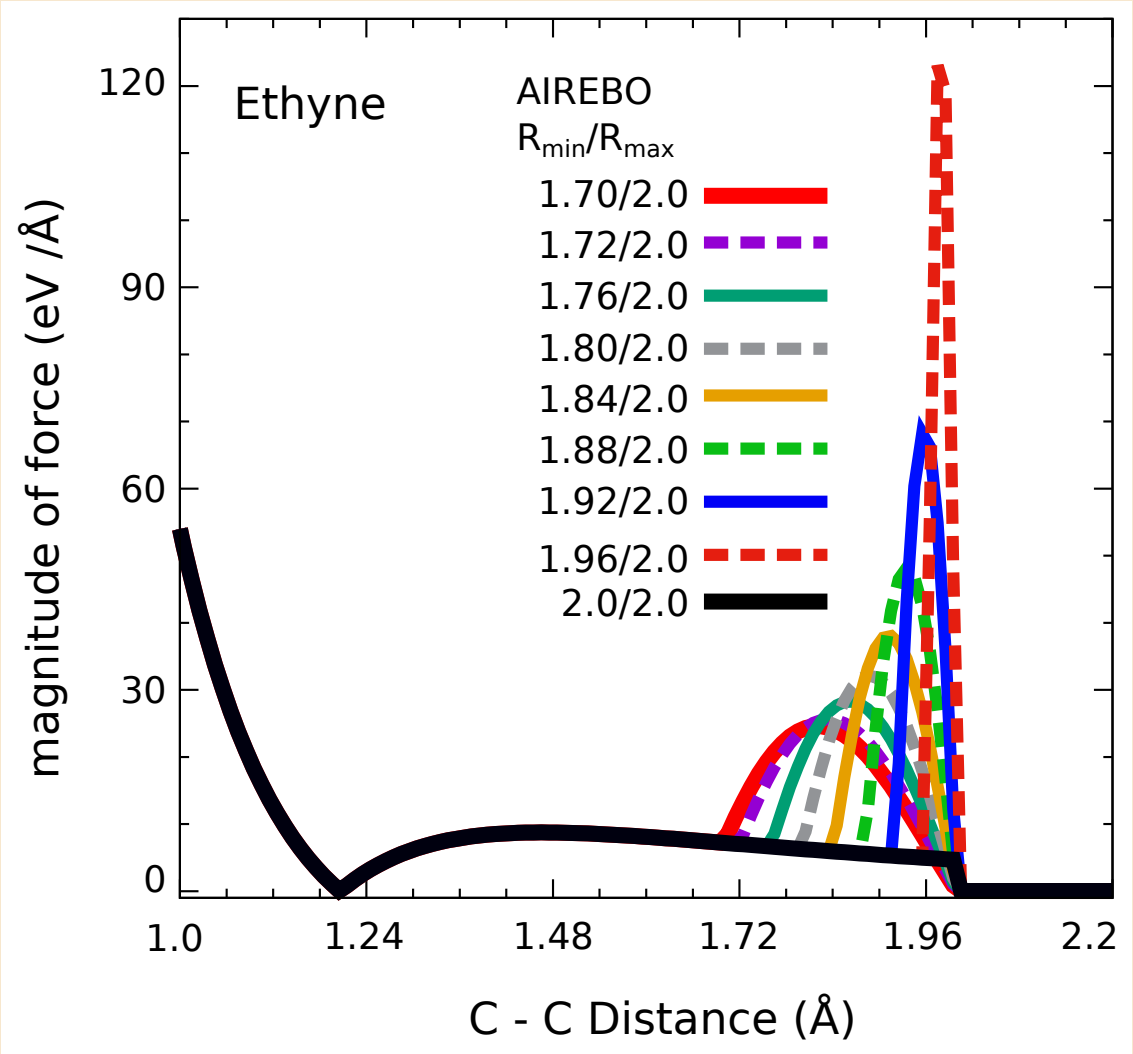
Events coming soon in Chile

International Conference on Materials Science
October 14-17, 2019. Valdivia, Chile
More info visit:
https://www.icmschile.com/

Second Symposium in Nanotechnology
(Free registration)
October 29-31, 2019. Santiago, Chile
For more info: rafael.gonzalez@umayor.cl

Work recently published:
Tangarife *et al.* Carbon **119** (2019) 177-184

Playing with R_{min} and R_{max} values



Comparison of some carbon potentials ...forces