Elastic Properties of Hydrogenated Graphene

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in collaboration with

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Gran Sasso Natl. Lab. (l’Aquila) - May 15-18, 2011
Introduction
- Basic definitions
- Hybridization vs. properties
- This work

Theoretical set-up

Structure and stability
- Structure
- Stability

Calculation of elastic constants
- Method
- Validation
- Second-order stiffness constants (linear elasticity)

Mechanical behavior under loading
- Linear regime
- Nonlinear elasticity

Conclusions
Graphane is the hydrogenated form of graphene

- a two-dimensional, periodic, and covalently bonded hydrocarbon with a C:H ratio of 1
- hydrogen atoms decorate the carbon honeycomb lattice on both the top and bottom side
- any graphane conformer retains high crystallographic symmetry (either trigonal or orthorhombic)

Possible hydrogen decorations

Red: top hydrogen atoms
Gray: bottom hydrogen atoms

Shaded areas: unit cell with lattice vectors

(a): graphene scaffold (full lines) with zigzag (zz) and armchair (ac) directions
(b, c, d): chair-, boat-, and washboard-graphane
Graphane

at first theoretically predicted


eventually grown

\textit{Science 323, 610 (2009)}

since then, many more papers...

Attractive feature

\textbf{hydrogenation: }sp^2 \rightarrow sp^3 \text{ change in orbital hybridization }\rightarrow \text{ new properties}

Change in the orbital hybridization

1. it has been calculated that graphane is an insulator, with an energy gap as large as $\sim 3$ eV


2. partially H-covered and disordered samples show unlike electronic and phonon properties than graphene

\textit{Science 323, 610 (2009)}

3. calculated in-plane stiffness and Poisson ratio of graphane are smaller than those of graphene

4. yield strain is predicted to vary upon temperature and stoichiometry

\textit{Topsakal et al., Appl. Phys. Lett. 96, 091912 (2010)}
Our perspective: $sp^2$-to-$sp^3$ change in orbital hybridization is expected to cause major variations in the mechanical properties of hydrogenated graphene.
Approach: blending together atomistic and continuum modeling

- **Step 0** - Search for equilibrium structures of graphane conformers and establish their stability
- **Step 1** - Calculate 2nd-order $C_{ij}$ and 3rd-order $C_{ijk}$ elastic constants
- **Step 2** - Elaborate a continuum description for (anisotropic) elastic moduli
- **Step 3** - Investigate mechanical behavior upon loading
Graphane conformes have very different structures

1. **specific H sublattice** and **different buckling**
   - C-graphane: H alternate on both sides
   - B-graphane: H alternate along ac
   - W-graphane: H along zz double rows on both sides

2. **C-C bond length**
   - C-graphane and W-graphane: similar to $sp^3$ systems and much larger than in graphene
     \[ \rightarrow \text{bond length } 1.54\text{{\AA}} \]
   - B-graphane: two types of C-C bonds
     - connecting two C atoms lying on opposite sides
       \[ \rightarrow \text{bond length } 1.57\text{{\AA}} \]
     - connecting two C atoms lying on same sides
       \[ \rightarrow \text{bond length } 1.54\text{{\AA}} \]

3. **C-H bond length**
   - typical of any hydrocarbon: 1.1Å
**Phonons** and energetics

1. **Phonon branches**
   - No soft modes (i.e. no instabilities)
   - Linear $k$-dependence for LA and TA modes
   - $k^2$-dependence for flexural (ZA) mode

2. **Anisotropic elastic behavior**
   - C-graphane: isotropic speed of sound
   - B- and W-graphane: different sound velocities

3. **Energetics**
   - C-graphane: energetically favored conformer
   - W- and B-graphane: higher GS energy
     - 0.05 and 0.10 eV per C-H unit
   - All conformers thermodynamically accessible, as indeed experimentally guessed

* Compare well with
  ◇ arXiv:1011.0018v1 [cond-mat.mtrl-sci]
**Total-energy calculations** performed by Density Functional Theory (DFT)

- GGA-like XC functional - Vanderbilt ultrasoft pseudopotential
- 50Ry energy cutoff - (18x18x3) Monkhorst-Pack grid for BZ sampling

**Atomic positions optimized** by using the quasi-Newton algorithm and PBCs

*interactions between adjacent atomic sheets hindered by a large spacing > 10 Å*

**Elastic moduli obtained from the (energy) vs. (in-plain strain) curves** \( U = U(\zeta) \)

\[
U(\zeta) = U_0 + \frac{1}{2} U^{(2)} \zeta^2 + \frac{1}{6} U^{(3)} \zeta^3 + O(\zeta^4)
\]
Benchmark calculations

- energy-vs-strain obtained by in-plane deformations through very many data-points
  *a technically important issue!*
- in-plane deformations defined by a single parameter $\zeta$
- deformations applied up to 5%

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### Qualitative trends

1. $C_{11} - C_{12}$ difference
   - $\rightarrow$ W-graphane the most elastically anisotropic conformer

2. $C_{44}$ modulus
   - $\rightarrow$ resistance to a shear deformation decreases monotonically

3. $C_{12}$ modulus (or, similarly, the Poisson ratio)
   - $\rightarrow$ much smaller than in pristine graphene
   - $\rightarrow$ lateral contraction upon extension affected by the new hybridization

4. B-conformer characterized by a negative $C_{12}$ value

### Table: Elastic Properties of Hydrogenated Graphene

<table>
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units of Nm$^{-1}$

$(*): 2C_{44} = C_{11} - C_{12}$
C-graphane: trigonal symmetry (i.e. elastically isotropic as hexagonal graphene)

\[
U_{\text{trigo}} = \frac{1}{2} C_{11} \left( \epsilon_{xx}^2 + \epsilon_{yy}^2 + 2 \epsilon_{xy}^2 \right) + C_{12} \left( \epsilon_{xx} \epsilon_{yy} - \epsilon_{xy}^2 \right)
\]

B- and W-conformers: orthorhombic symmetry (i.e. anisotropic linear elastic)

\[
U_{\text{ortho}} = \frac{1}{2} C_{11} \epsilon_{xx}^2 + \frac{1}{2} C_{22} \epsilon_{yy}^2 + C_{12} \epsilon_{xx} \epsilon_{yy} + 2 C_{44} \epsilon_{xy}^2
\]

Constitutive in-plane stress-strain equation are straightforwardly

\[
\hat{T} = \frac{\partial U}{\partial \epsilon} \rightarrow \begin{cases} T_{xx} = C_{11} \epsilon_{xx} + C_{12} \epsilon_{yy} \\ T_{yy} = C_{22} \epsilon_{yy} + C_{12} \epsilon_{xx} \\ T_{xy} = 2 C_{44} \epsilon_{xy} \end{cases}
\]

Procedure to get elastic moduli

- apply an axial tension \( \sigma \) along the arbitrary direction \( \vec{n} = \cos \theta \hat{e}_x + \sin \theta \hat{e}_y \)
  \( \rightarrow \theta \) is the angle between applied tension and zigzag direction
- get stress components: \( T_{xx} = \sigma \cos^2 \theta \quad T_{xy} = \sigma \cos \theta \sin \theta \quad T_{yy} = \sigma \sin^2 \theta \)
- invert the constitutive equation \( \rightarrow \) get longitudinal strain \( \epsilon_l \) transverse strain \( \epsilon_t \)
- elastic moduli:

\[
E_{\vec{n}} = \frac{\sigma}{\epsilon_l} \quad \nu_{\vec{n}} = -\frac{\epsilon_t}{\epsilon_l}
\]
Orthogonal symmetry

- Young modulus

\[
E_{\vec{n}} = \frac{\Delta}{c_{11}s^4 + c_{22}c^4 + \left(\frac{\Delta}{c_{44}} - 2c_{12}\right)c^2s^2}
\]

- Poisson ratio

\[
\nu_{\vec{n}} = -\frac{\left(c_{11} + c_{22} - \frac{\Delta}{c_{44}}\right)c^2s^2 - c_{12}\left(c^4 + s^4\right)}{c_{11}s^4 + c_{22}c^4 + \left(\frac{\Delta}{c_{44}} - 2c_{12}\right)c^2s^2}
\]

where: \(\Delta = C_{11}C_{22} - C_{12}^2\)

\[c = \cos \theta \quad s = \sin \theta\]

Trigonal symmetry

- obtained by imposing the symmetry condition \(C_{11} = C_{22}\) and the Cauchy relation \(2C_{44} = C_{11} - C_{12}\)

Key features

1. \(E_{\vec{n}}\) and \(\nu_{\vec{n}}\) directly obtained by the linear elastic constants \(C_{ij}\)
   - no need to mimic a traction experiment along the arbitrary direction identified by \(\vec{n}\) or \(\theta\)

2. In-plane homogeneous deformations
   - **Isotropic case**: (i) an axial deformation along the zigzag direction; and (ii) an hydrostatic planar deformation
   - **Anisotropic case**: (iii) an axial deformation along the armchair direction; and (iv) a shear deformation
MEMO

circular shape:
fully isotropic behavior

Unconventional behavior of B-graphane

- Poisson ratio vanishingly small along zz and ac
- actually, Poisson is negative!
1 **Trigonal symmetry**

\[ U_{\text{trigo}} = \frac{1}{2} C_{11} (\epsilon_{xx}^2 + \epsilon_{yy}^2 + 2\epsilon_{xy}^2) + C_{12} (\epsilon_{xx} \epsilon_{yy} - \epsilon_{xy}^2) + \frac{1}{6} C_{111} (\epsilon_{xx}^3 + \epsilon_{yy}^3) + \frac{1}{2} C_{112} (\epsilon_{xx}^2 \epsilon_{yy} + \epsilon_{xx} \epsilon_{yy}^2) + 2C_{144} (\epsilon_{xx} \epsilon_{xy}^2 + \epsilon_{yy} \epsilon_{xy}^2) + C_{114} (\epsilon_{xx}^2 \epsilon_{xy} + \epsilon_{yy}^2 \epsilon_{xy}) + 2C_{124} \epsilon_{xx} \epsilon_{xy} \epsilon_{yy} + \frac{4}{3} C_{444} \epsilon_{xy}^3 \]

2 **Orthogonal symmetry**

\[ U_{\text{ortho}} = \frac{1}{2} C_{11} \epsilon_{xx}^2 + \frac{1}{2} C_{22} \epsilon_{yy}^2 + 2C_{44} \epsilon_{xy}^2 + C_{12} \epsilon_{xx} \epsilon_{yy} + \frac{1}{6} C_{111} \epsilon_{xx}^3 + \frac{1}{6} C_{222} \epsilon_{yy}^3 + \frac{1}{2} C_{112} \epsilon_{xx} \epsilon_{yy} + \frac{1}{2} C_{122} \epsilon_{xx}^2 \epsilon_{yy} + 2C_{144} \epsilon_{xx} \epsilon_{xy}^2 + 2C_{244} \epsilon_{yy} \epsilon_{xy}^2 \]

<table>
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<td>$C_{444}$</td>
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**Qualitative trends**

1 **H-distribution largely affects nonlinear features**
   - graphene & B-graphane $\rightarrow$ inverted anisotropy
   - graphene & W-graphane $\rightarrow$ same anisotropy

2 **$C_{444} \neq 0$ for trigonal symmetry (C-graphane)**
   - additional mirror symmetry $\rightarrow C_{444} = 0$
Nonlinear constitutive equation

\[ \sigma_{\vec{n}} = E_{\vec{n}} \epsilon_{\vec{n}} + D_{\vec{n}} \epsilon_{\vec{n}}^2 \]

1. \(D_{\vec{n}}\) is a complicated expression of \(C_{ijk}\)

2. **orthogonal symmetry:**
   
   all \(C_{ijk} < 0 \rightarrow D_{\vec{n}}^{(orth)} < 0\)

   *both B- and W-graphane show an hyperelastic softening behavior*

3. **trigonal symmetry:**
   
   \(C_{114}, C_{144} > 0\)

   *C-graphane shows both hyperelastic hardening or hyperelastic softening behavior*
Conclusions - Cadelano, Palla, Giordano, Colombo, PRB 82, 235414 (2010)

1. **All graphane conformers** respond to any arbitrarily-oriented extension with a much smaller lateral contraction than graphene.

2. **B-graphane** has a small and negative Poisson ratio along zz and ac directions → axially auxetic elastic behavior.

3. **C-graphane** admits both softening and hardening hyperelasticity.

Next steps

- disordered systems & H-motifs: tailoring elastic moduli through H-decorantion (?)
- thermo-elasticity

Acknowledgements

**Financial support under project M4C**

*Multiscale Modeling of Complex Materials*

**Computational support**

*UniCa - A sud di nessun nord*