Elastic Properties of Hydrogenated Graphene

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in collaboration with

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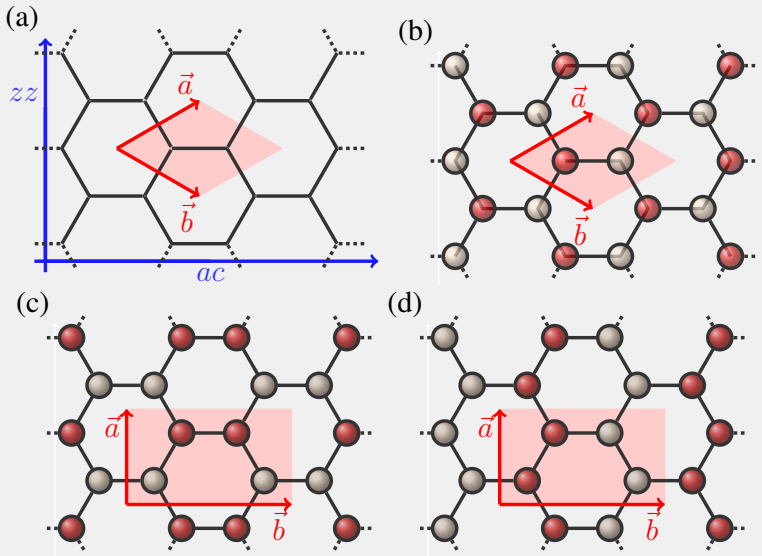
1. Introduction
   - Basic definitions
   - Hybridization vs. properties
   - This work
2. Theoretical set-up
3. Structure and stability
   - Structure
   - Stability
4. Calculation of elastic constants
   - Method
   - Validation
   - Second-order stiffness constants (linear elasticity)
5. Mechanical behavior under loading
   - Linear regime
   - Nonlinear elasticity
6. 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 orthorombic)

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

  Phys. Rev. B **75**, *153401 (2007) - Phys. Rev. B* **77**, *035427 (2008)*

  eventually grown

  Science **323**, *610 (2009)*

  since then, many more papers...

- **Attractive feature**

  hydrogenation: $sp^2 \rightarrow sp^3$ change in orbital hydridization $\rightarrow$ **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
     Phys. Rev. B **75**, *153401 (2007) - Phys. Rev. B* **77**, *035427 (2008)*
  2. partially H-covered and disordered samples show unlike electronic and phonon properties than graphene
     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
     Topsakal et al., Appl. Phys. Lett. 96, 091912 (2010)

Our perspective: sp^2-to-sp^3 change in orbital hybridization is expected to cause

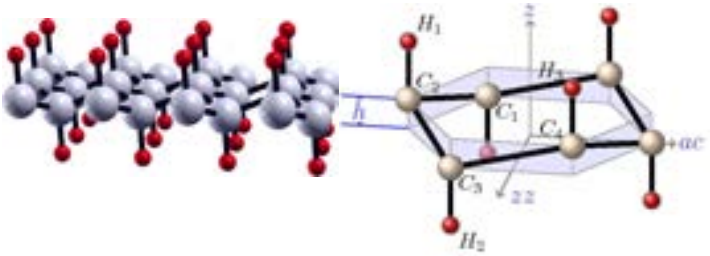
major variations in the mechanical properties of hydrogenated graphene

Highlights

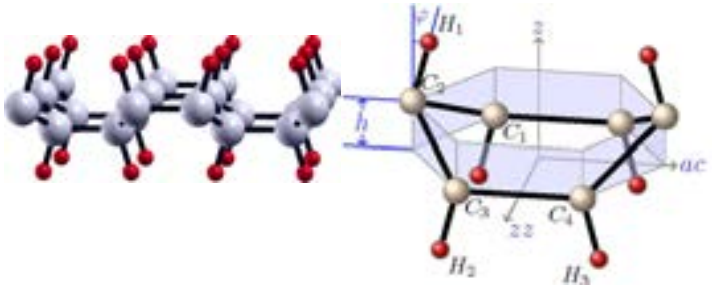
1. characterize non-isotropic linear elastic features
   *contrary to graphene: Science **321**, 385 (2008) - Phys. Rev. Lett. **102**, 235502 (2009)*
2. increased or reduced "rigidity" ?
   linear elastic moduli most likely affected
3. investigate overall mechanical behavior of the systems
   anisotropic dependence of its respose to external loads

Approach: blending togheter atomistic and continuum modeling

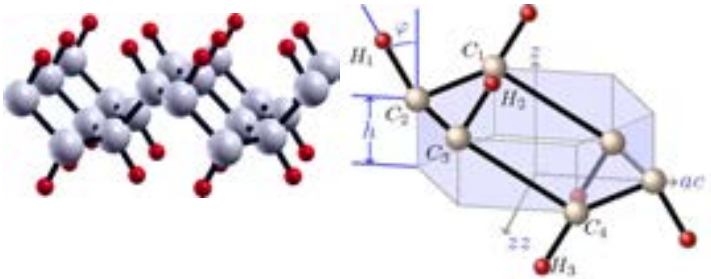
- **Step 0 -** Search for equilibrium structures of graphane conformers and establish their stability
- **Step 1 -** Calculate 2nd-order C_{ij} and 3rd-order C_{ijk} elastic constants
- **Step 2 -** Elaborate a continuum description for (anisotropic) elastic moduli
- **Step 3 -** Investigate mechanical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



(a) C-graphane



(b) B-graphane



(c) W-graphane

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*
     $\longrightarrow$ *bond length 1.54Å*
   - *B-graphane: two types of C-C bonds*
     - ◇ *connecting two C atoms lying on opposite sides*
       $\longrightarrow$ *bond length 1.57Å*
     - ◇ *connecting two C atoms lying on same sides*
       $\longrightarrow$ *bond length 1.54Å*

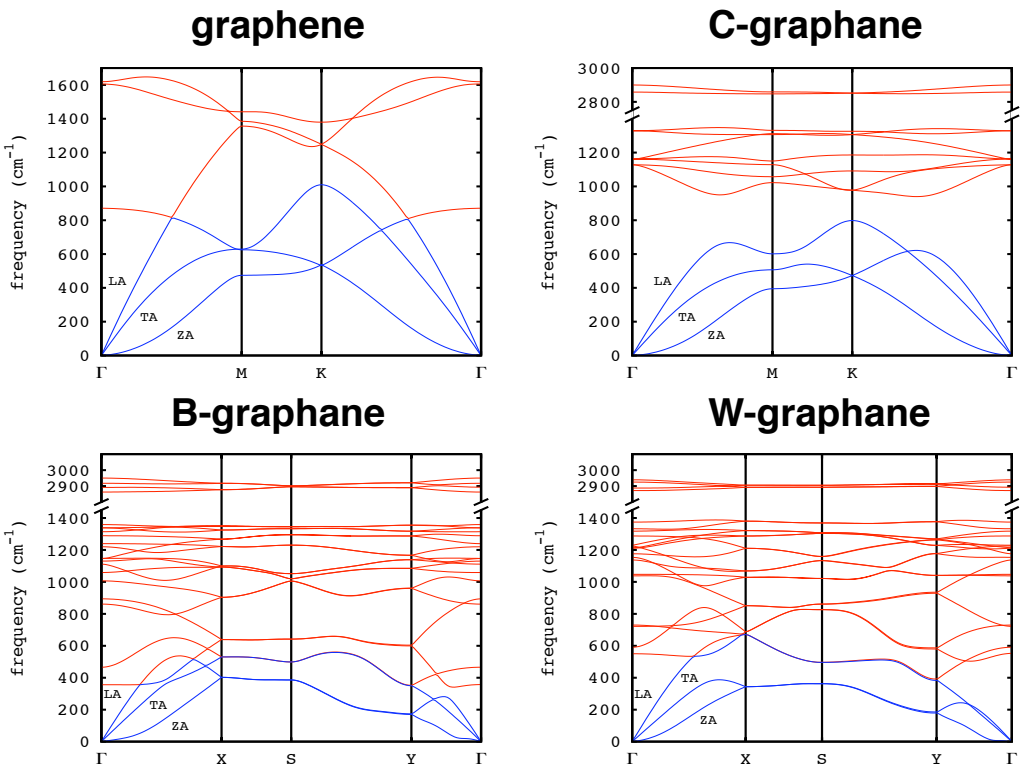
3. **C-H bond length**
   typical of any hydrocarbon: 1.1Å

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
◇ *Phys. Rev. Lett.* **105**, *037002 (2010) for C-graphane*
◇ *arXiv:1011.0018v1 [cond-mat.mtrl-sci]*

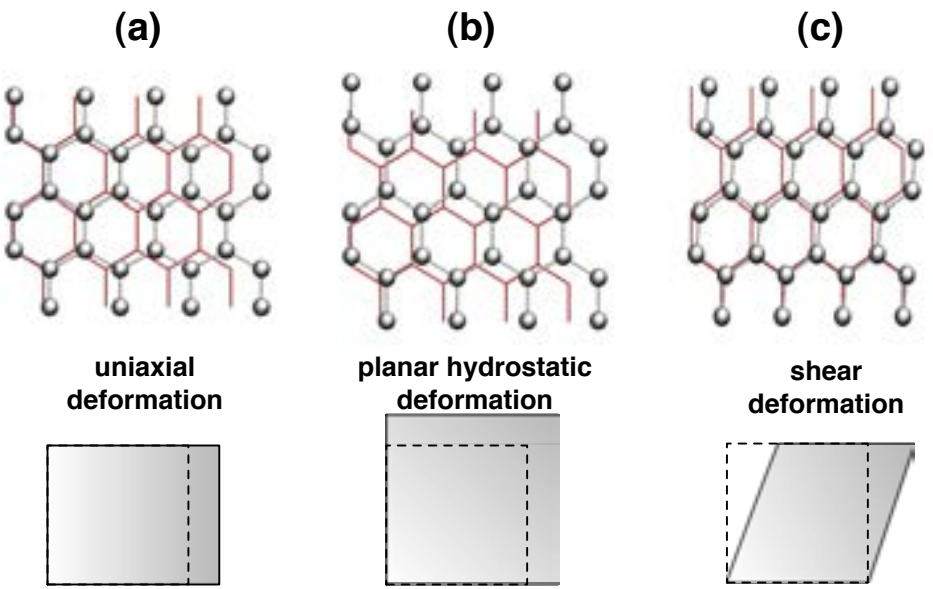
1. **Total-energy calculations** performed by Density Functional Theory (DFT)

   QUANTUM ESPRESSO *package - J. Phys.: Condens. Matter* ***21*** *395502 (2009)*
   - GGA-like XC functional - Vanderbilt ultrasoft pseudopotential
   - 50Ry energy cutoff - (18x18x3) Monkhorst-Pack grid for BZ sampling

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

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

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



$$U(\zeta) = U_0 + \tfrac{1}{2}U^{(2)}\zeta^2 + \tfrac{1}{6}U^{(3)}\zeta^3 + O(\zeta^4)$$

Becnhmark 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 ζ
- deformations applied up to 5%

		Young [Nm^{-1}]	Poisson
graphene			
	this work	344	0.169
	PRB **64**, 235406 (2001)	345	0.149
	PRB **76**, 064120 (2007)	350	0.186
C-graphane			
	this work	246	0.080
	APL, **96**, 091912 (2010)	243	0.070

	graphene	**graphane**		
		C-	B-	W-
C_{11}	354	248	258	280
C_{22}			225	121
C_{12}	60	20	-1.7	14
C_{44}	$147^{(*)}$	$114^{(*)}$	93	81

units of Nm^{-1} $^{(*)} 2C_{44} = C_{11} - C_{12}$

Qualitative trends

1. $C_{11} - C_{12}$ difference
   → **W-graphane the most elastically anisotropic conformer**
2. C_{44} modulus
   → **resistance to a shear deformation decreases monotonically**
3. C_{12} modulus (or, similarly, the Poisson ratio)
   → much smaller than in pristine graphene
   → **lateral contraction upon extension affected by the new hybridization**
4. **B-conformer characterized by a negative C_{12} value**

1. **C-graphane**: trigonal symmetry (i.e. elastically isotropic as hexagonal graphene)

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

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

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

3. **constitutive in-plane stress-strain equation** are straightforwardly

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

Procedure to get elastic moduli

- **apply an axial tension** σ along the arbitrary direction $\vec{n} = \cos\theta\vec{e}_x + \sin\theta\vec{e}_y$
  $\rightarrow$ *θ is the angle between applied tension and zigzag direction*
- **get stress components**: $T_{xx} = \sigma\cos^2\theta \qquad T_{xy} = \sigma\cos\theta\sin\theta \qquad T_{yy} = \sigma\sin^2\theta$
- invert the constitutive equation $\rightarrow$ get **longitudinal strain** ϵ_l **transverse strain** ϵ_t
- **elastic moduli**:

$$E_{\vec{n}} = \frac{\sigma}{\epsilon_l} \qquad \nu_{\vec{n}} = -\frac{\epsilon_t}{\epsilon_l}$$

1. **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

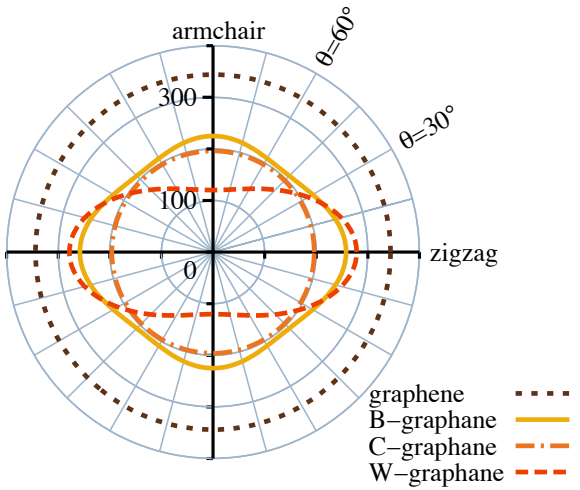
$$\nu_{\vec{n}} = -\frac{\left(C_{11} + C_{22} - \frac{\Delta}{C_{44}}\right)c^2s^2 - C_{12}\left(c^4 + s^4\right)}{C_{11}s^4 + C_{22}c^4 + \left(\frac{\Delta}{C_{44}} - 2C_{12}\right)c^2s^2}$$

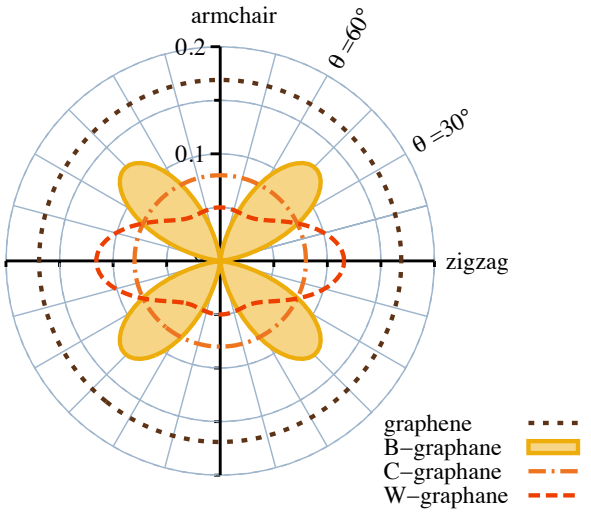
   where: $\Delta = C_{11}C_{22} - C_{12}^2$ $\quad c = \cos\theta$ $\quad s = \sin\theta$

2. **Trigonal symmetry**
   - obtained by imposing the symmetry condition $C_{11} = C_{22}$ and the Cauchy relation $2C_{44} = C_{11} - C_{12}$

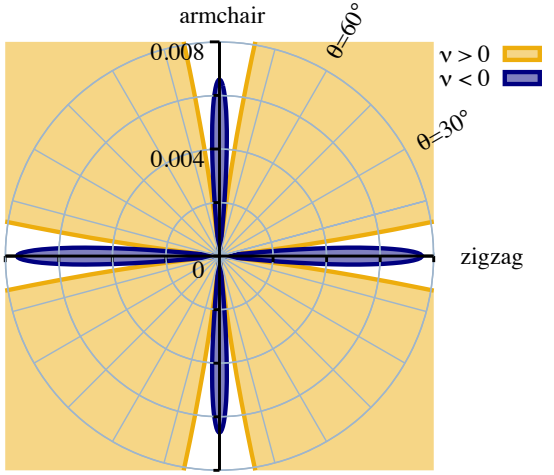
Key features

1. $E_{\vec{n}}$ and $\nu_{\vec{n}}$ directly obtained by the linear elastic constants C_{ij}
   $\longrightarrow$ *no need to mimic a traction experiment along the arbitrary direction identified by* $\vec{n}$ *or* θ
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**

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

2. **Orthogonal symmetry**

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

	graphene	graphane		
		C-	B-	W-
C_{111}	-1910	-1385	-1609	-1756
C_{222}	-1764		-1827	-487
C_{112}	-341	-195	-20	-75
C_{122}			-55	-296
C_{124}		-411		
C_{114}		530		
C_{144}		568	-161	-143
C_{244}			-159	-287
C_{444}		$\sim 10^{-5}$		

units of Nm^{-1}

Qualitative trends

1. **H-distribution largely affects nonlinear features**
   - graphene & B-graphane $\longrightarrow$ inverted anisotropy
   - graphene & W-graphane $\longrightarrow$ same anisotropy
2. $C_{444} \neq 0$ for trigonal symmetry (C-graphane)
   - **additional mirror symmetry** $\longrightarrow C_{444} = 0$

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**:

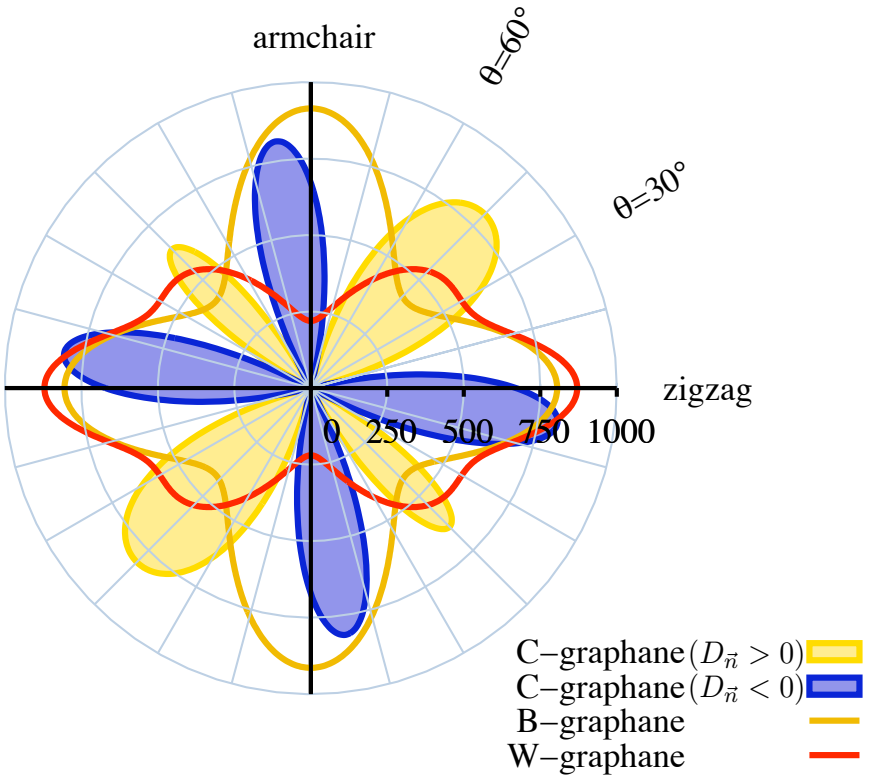
$$\text{all } C_{ijk} < 0 \rightarrow D_{\vec{n}}^{(ortho)} < 0$$

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 extention with **a much smaller lateral contraction** than graphene
2. **B-graphane** has a **small and negative Poisson ratio** along zz and ac directions $\rightarrow$ **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

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CASPUR
PON
CYBERSAR