Continuum Mechanics and Atomistic Modeling of Graphene

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Graphene is a one-atom-thick planar sheet of sp²-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. The term *Graphene* was coined as a combination of graphite and the suffix -ene by Hanns-Peter Boehm, who described single-layer carbon foils in 1962. Graphene is most easily visualized as an atomic-scale chicken wire made of carbon atoms and their bonds.
Graphene Based Devices

Patterned graphene on oxide for bipolar p-n-p junctions

Suspension nanoribbons for NEMS devices

Ozyilmaz et al., 2007.

Garcia-Sanchez, et al., 2008.
Mechanical properties of monolayer graphene

- High in-plane stiffness (Young’s modulus)
- High tensile strength
- High bending stiffness (relative to its own weight)

- Isotropic, linearly elastic under infinitesimal deformation
- Anisotropic, nonlinear under finite deformation

- Graphene nanoribbons: edge effects?
- Substrate-supported graphene: adhesive interactions?
Nonlinear Continuum Mechanics of 2D Sheets

2D-to-3D deformation gradient:

\[ F_{ij} = \frac{\partial x_i}{\partial X_j} \]

In-plane deformation: 2D Green-Lagrange strain tensor

\[ E_{JK} = \frac{1}{2} (F_{ij} F_{iK} - \delta_{JK}) \]

Bending: 2D curvature tensor (strain gradient)

\[ K_{IJ} = n_i \frac{\partial F_{il}}{\partial X_j} = n_i \frac{\partial^2 x_i}{\partial X_l \partial X_j} \]

Strain energy (hyperelasticity):

\[ U = \int_A \Phi(E, K) dA \]

Lu and Huang, Int. J. Applied Mechanics 1, 443-467 (2009).
2D Stresses and Moments

2\textsuperscript{nd} Piola-Kirchoff stress and moment (work conjugates)

\[ S_{IJ} = \frac{\partial \Phi}{\partial E_{IJ}} \quad M_{IJ} = \frac{\partial \Phi}{\partial K_{IJ}} \]

**Tangent moduli:**

\[ C_{IJKL} = \frac{\partial S_{IJ}}{\partial E_{KL}} = \frac{\partial^2 \Phi}{\partial E_{IJ} \partial E_{KL}} \]

\[ D_{IJKL} = \frac{\partial M_{IJ}}{\partial K_{KL}} = \frac{\partial^2 \Phi}{\partial K_{IJ} \partial K_{KL}} \]

\[ \Lambda_{IJKL} = \frac{\partial S_{IJ}}{\partial K_{KL}} = \frac{\partial M_{KL}}{\partial E_{IJ}} = \frac{\partial^2 \Phi}{\partial E_{IJ} \partial K_{KL}} \]

Intrinsic coupling between tension and bending

**An incremental form of the generally nonlinear and anisotropic behavior:**

\[
\begin{align*}
(dS_{11}) &= \begin{bmatrix} C_{11} & C_{12} & C_{13} \end{bmatrix} (dE_{11}) + \begin{bmatrix} \Lambda_{11} & \Lambda_{12} & \Lambda_{13} \end{bmatrix} (dK_{11}) \\
(dS_{22}) &= \begin{bmatrix} C_{21} & C_{22} & C_{23} \end{bmatrix} (dE_{22}) + \begin{bmatrix} \Lambda_{21} & \Lambda_{22} & \Lambda_{23} \end{bmatrix} (dK_{22}) \\
(dS_{12}) &= \begin{bmatrix} C_{31} & C_{32} & C_{33} \end{bmatrix} (2dE_{12}) \end{align*}
\]

\[
\begin{align*}
(dM_{11}) &= \begin{bmatrix} D_{11} & D_{12} & D_{13} \end{bmatrix} (dK_{11}) + \begin{bmatrix} \Lambda_{11} & \Lambda_{12} & \Lambda_{13} \end{bmatrix} (dE_{11}) \\
(dM_{22}) &= \begin{bmatrix} D_{21} & D_{22} & D_{23} \end{bmatrix} (dK_{22}) + \begin{bmatrix} \Lambda_{21} & \Lambda_{22} & \Lambda_{23} \end{bmatrix} (dE_{22}) \\
(dM_{12}) &= \begin{bmatrix} D_{31} & D_{32} & D_{33} \end{bmatrix} (2dK_{12}) + \begin{bmatrix} \Lambda_{31} & \Lambda_{32} & \Lambda_{33} \end{bmatrix} (2dE_{12}) \end{align*}
\]

Lu and Huang, Int. J. Applied Mechanics 1, 443-467 (2009).
Units for 2D quantities

\[ \Phi(E, K) \] strain energy density function: \( \text{J/m}^2 \)

\[ S_{ij} = \frac{\partial \Phi}{\partial E_{ij}} \] 2D stress: \( \text{N/m} \)

\[ C_{ijkl} = \frac{\partial S_{ij}}{\partial E_{kl}} = \frac{\partial^2 \Phi}{\partial E_{ij} \partial E_{kl}} \] 2D in-plane modulus: \( \text{N/m} \)

\[ M_{ij} = \frac{\partial \Phi}{\partial K_{ij}} \] moment intensity: \( \text{(N-m)/m} \)

\[ D_{ijkl} = \frac{\partial M_{ij}}{\partial K_{kl}} = \frac{\partial^2 \Phi}{\partial K_{ij} \partial K_{kl}} \] bending modulus: \( \text{N-m} \)

\[ \Lambda_{ijkl} = \frac{\partial S_{ij}}{\partial K_{kl}} = \frac{\partial M_{kl}}{\partial E_{ij}} = \frac{\partial^2 \Phi}{\partial E_{ij} \partial K_{kl}} \] coupling modulus: \( \text{N} \)

> Analogous to the 2D plate/shell theories (but no thickness).
Atomistic Modeling of Graphene

- 2\textsuperscript{nd}-generation REBO potential (Brenner et al., 2002)
  - Bond angle effect (second-nearest neighbors)
  - Dihedral angle effect (third-nearest neighbors)
  - Radical energetics (defects and edges)

- Molecular Mechanics: energy minimization for static equilibrium states.

- Stress and moment calculations
  - Energy derivation
  - Virial stress calculations
  - Direct force evaluation
Nominal stress-strain relation:

\[ P_{11}(\varepsilon) = \frac{d\Phi}{d\varepsilon} \]
Graphene is linear and isotropic under infinitesimal deformation, but becomes nonlinear and anisotropic under finite deformation.

Lu and Huang, Int. J. Applied Mechanics 1, 443-467 (2009).
Fracture occurs as a result of intrinsic instability of the homogeneous deformation:

- The nominal stress and strain to fracture depend on the direction of uniaxial stretch.

\[
\frac{\partial P}{\partial \varepsilon} = \frac{\partial^2 \Phi}{\partial \varepsilon^2} = 0
\]

Lu and Huang, Int. J. Applied Mechanics 1, 443-467 (2009).
Monolayer graphene under uniaxial tension

- **Disagreement:** the REBO potential underestimates the initial Young’s modulus.
- **Agreement:** the fracture stress/strain is higher in the zigzag direction than in the armchair direction.
Bending Modulus of Monolayer Graphene

- Bending moment-curvature is nearly linear, with slight anisotropy.
- Including the dihedral angle effect leads to higher bending energy and bending modulus.

\begin{equation}
V_{ij} = V_R(r_{ij}) - \bar{b}_{ij}V_A(r_{ij})
\end{equation}

\begin{equation}
\bar{b}_{ij} = \frac{1}{2} (b^{\sigma-\pi}_{ij} + b^{\sigma-\pi}_{ji}) + b^{DH}_{ij} + \Pi^R_{ij}
\end{equation}

\begin{equation}
b^{DH}_{ij} = \frac{T_0}{2} \sum_{k,l(\neq i,j)} \left[ (1 - \cos^2 \Theta_{ijkl}) f_c(r_{ik}) f_c(r_{jl}) \right]
\end{equation}

\begin{equation}
\cos \Theta_{ijkl} = \mathbf{n}_{jik} \cdot \mathbf{n}_{ijl}
\end{equation}

Physical Origin of Bending Modulus

Bending modulus of a thin elastic plate:

\[ D = \frac{dM}{d\kappa} \sim Eh^3 \]

For monolayer graphene, bending moment and bending stiffness result from multibody interatomic interactions (second and third nearest neighbors).

\[ D = \frac{V_A(r_0)}{2} \left( \frac{\partial b^\sigma_{ij}}{\partial \theta_{ijk}} - \frac{14T_0}{\sqrt{3}} \right) \]

- \( D = 0.83 \text{ eV} \) (0.133 nN-nm) by REBO-1
- \( D = 1.4 \text{ eV} \) (0.225 nN-nm) by REBO-2
- \( D = 1.5 \text{ eV} \) (0.238 nN-nm) by first principle

Coupling between bending and stretching

The tube radius increases upon relaxation, leading to simultaneous bending and stretching.

\[ W(\kappa, \epsilon) \approx \frac{1}{2} D\kappa^2 + M(\kappa - \kappa_0) + \sigma \epsilon + \frac{1}{2} D(\kappa - \kappa_0)^2 + \frac{1}{2} C\epsilon^2 \]

\[ R_0 = 0.397 \text{ nm} \]

Excess Edge Energy and Edge Force

Zigzag edge:

Armchair edge:

\[ U(W) = U_0 + \frac{2\gamma}{N} = U_0 + \frac{S_0}{W} \gamma \]

<table>
<thead>
<tr>
<th></th>
<th>Edge energy (eV/nm)</th>
<th>Edge force (eV/nm)</th>
<th>( r_0 ) (nm)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Armchair</td>
<td>Zigzag</td>
<td>Armchair</td>
</tr>
<tr>
<td>DFT [17] (GPAW)</td>
<td>9.8</td>
<td>13.2</td>
<td>-</td>
</tr>
<tr>
<td>DFT [18] (VASP)</td>
<td>10</td>
<td>12</td>
<td>-14.5</td>
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<tr>
<td>DFT [22] (SIESTA)</td>
<td>12.43</td>
<td>15.33</td>
<td>-26.40</td>
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<tr>
<td>MM [20] (AIREBO)</td>
<td>-</td>
<td></td>
<td>-10.5</td>
</tr>
<tr>
<td>MD [21]</td>
<td>-</td>
<td></td>
<td>-20.4</td>
</tr>
<tr>
<td>MM (REBO)</td>
<td>10.91</td>
<td>10.41</td>
<td>-8.53</td>
</tr>
</tbody>
</table>

Lu and Huang, Phys. Rev. B 81, 155410 (2010).
Edge buckling of GNRs

Zigzag GNR

Intrinsic wavelength \(\sim 6.2\) nm

Armchair GNR

Intrinsic wavelength \(\sim 8.0\) nm

The wavelengths for edge buckling do not scale with \(D/f\).

Lu and Huang, Phys. Rev. B 81, 155410 (2010).
GNRs under Uniaxial Tension

\[ U(\varepsilon) = \Phi(\varepsilon)WL + 2\gamma(\varepsilon)L \]

\[ \delta U = FL\delta\varepsilon \]

\[ \sigma = \frac{F}{W} = \frac{1}{WL} \frac{dU}{d\varepsilon} = \frac{d\Phi}{d\varepsilon} + \frac{2}{W} \frac{d\gamma}{d\varepsilon} \]

Zigzag GNRs

Armchair GNRs
GNRs under Uniaxial Tension

\[ \sigma(\varepsilon) = \frac{F}{W} = \frac{d\Phi}{d\varepsilon} + \frac{2}{W} \frac{d\gamma}{d\varepsilon} \]

2D Young’s Moduli of GNRs

\[ \sigma(\varepsilon) = \frac{d\Phi}{d\varepsilon} + \frac{2}{W} \frac{d\gamma}{d\varepsilon} \]

\[ E(\varepsilon) = \frac{d^2\Phi}{d\varepsilon^2} + \frac{2}{W} \frac{d^2\gamma}{d\varepsilon^2} \]

Young’s modulus under infinitesimal strain:

\[ E_0 = E_0^{bulk} + \frac{2}{W} E_0^{edge} \]

The nonlinear dependence of the excess edge energy on strain leads to anisotropic, width-dependent Young’s modulus for GNRs.

Fracture of graphene nanoribbons

Graphene on Oxide Substrates

Ozyilmaz et al., 2007.

The 3D morphology is important for the transport properties of graphene-based devices.

Ishigami et al., 2007.
Van der Waals Interaction

Lennard-Jones potential for particle-particle interactions:

\[ W_{LJ}(r) = -\frac{C_1}{r^6} + \frac{C_2}{r^{12}} \]

Monolayer-substrate interaction (energy per unit area):

\[ U(h) = -\Gamma_0 \left[ \frac{3}{2} \left( \frac{h_0}{h} \right)^3 - \frac{1}{2} \left( \frac{h_0}{h} \right)^9 \right] \]

Van der Waals Thickness and Energy

- Interlayer spacing in graphite \( \sim 0.34 \text{ nm} \);
- AFM measurements of \( h_0 \) for graphene on oxide range from 0.4 to 0.9 nm;
- The adhesion energy (\( \Gamma_0 \)) has not been measured directly;
- Theoretically estimated values for \( \Gamma_0 \) range from 0.6 to 0.8 eV/nm\(^2\).
Flat Graphene on Flat Surface

Interfacial strength:
\[ \sigma_{\text{max}} = 1.466 \frac{\Gamma_0}{h_0} \]

Initial stiffness:
\[ k_0 = \frac{27\Gamma_0}{h_0^2} \]

Representative values:
- \( h_0 = 0.6 \text{ nm} \)
- \( \Gamma_0 = 0.6 \text{ eV/nm}^2 \)
- \( \sigma_{\text{max}} = 230 \text{ MPa} \)
- \( k_0 = 7200 \text{ MPa/nm} \)

The competition between the elastic strain energy of graphene and the van der Waals interaction energy sets a critical strain for instability as well as the equilibrium corrugation wavelength beyond the critical strain.

**Elastic strain energy of graphene:**

\[
\tilde{U}_g \approx \left[ \frac{C \varepsilon}{4} \left( \frac{2\pi}{\lambda} \right)^2 + \frac{D}{4} \left( \frac{2\pi}{\lambda} \right)^4 \right] \delta_g^2 + \frac{3C}{64} \left( \frac{2\pi}{\lambda} \right)^4 \delta_g^4
\]

**Van der Waals Interaction Energy:**

\[
\tilde{U}_{vdW} \approx \Gamma_0 \left( -1 + \frac{27}{4} \left( \frac{\delta_g}{h_0} \right)^2 + \frac{675}{8} \left( \frac{\delta_g}{h_0} \right)^4 \right)
\]

**Total free energy:**

\[
\tilde{U} = \tilde{U}_g + \tilde{U}_{vdW}
\]

Strain-Induced Corrugation of Graphene

On a flat surface, a graphene monolayer is flat and stable below a critical compressive strain;
Beyond the critical strain, the monolayer corrugates with increasing amplitude and decreasing wavelength.

Representative values:

\[ \varepsilon_c = -\frac{6\sqrt{3\Gamma_0 D}}{Ch_0} \]

\[ \lambda_c = 2\pi \left( \frac{Dh_0^2}{27\Gamma_0} \right)^{\frac{1}{4}} \]

\[ h_0 = 0.6\text{nm} \quad \Gamma_0 = 0.6\text{eV/nm}^2 \]
\[ C = 353\text{N/m} \quad D = 1.5\text{eV} \]

Graphene on a Corrugated Surface

van der Waals interaction energy:

\[
\tilde{U}_{vdW}(h, \delta_g) \approx U_{vdW}(h) + U_1(h) \left[ \left( \frac{\delta_g}{h_0} \right)^2 + \left( \frac{\delta_s}{h_0} \right)^2 \right] + U_2(h) \frac{\delta_g \delta_s}{h_0^2}
\]

\[
U_1(h) = \frac{9\Gamma_0}{2} \left[ -\left( \frac{h_0}{h} \right)^5 + 5 \left( \frac{h_0}{h} \right)^{11} \right] = \frac{h_0^2}{4} k_{vdW}(h)
\]

\[
U_2(h) = 9\pi^3 \Gamma_0 \left[ \frac{h_0^5}{\lambda^3 h^2} K_3 \left( \frac{2\pi h}{\lambda} \right) - \frac{\pi^3 h_0^{11}}{24 \lambda^6 h^5} K_6 \left( \frac{2\pi h}{\lambda} \right) \right]
\]

Total free energy:

\[
\tilde{U} = \tilde{U}_g + \tilde{U}_{vdW}
\]

Given \(\delta_s\) and \(\lambda\), minimize the total energy to find \(\delta_g\) and \(h\)

Substrate Induced Corrugation of Graphene

\[
\frac{\delta_g}{\delta_s} = f\left(\lambda, \frac{\delta_s}{h_0}, D, \frac{C\epsilon}{\Gamma_0} h_0^2, \Gamma_0\right)
\]

\[
h \frac{h_0}{h_0} = g\left(\lambda, \frac{\delta_s}{h_0}, D, \frac{C\epsilon}{\Gamma_0} h_0^2, \Gamma_0\right)
\]

- **Conformal** at long wavelengths.
- **Non-conformal** at short wavelengths.
- Transition between the two states depends on the amplitude of substrate surface corrugation, becoming more abrupt with increasing amplitude.

The adhesion energy decreases as the corrugation wavelength decreases, approaching a plateau at the short-wavelength limit.

The adhesion energy decreases with increasing amplitude of the substrate surface corrugation.

Better adhesion at the conformal state than the non-conformal state.

Effects of Mismatch Strain

A tensile strain tends to flatten the supported graphene, while a compressive strain tends to increase the corrugation amplitude.

A “snap-through” instability occurs at a critical tensile strain.

A “buckling” instability occurs at a critical compressive strain.

Critical Strain for Buckling Instability

- With increasing amplitude of the substrate surface corrugation:
  - The critical compressive strain for buckling decreases.
  - The corresponding buckling wavelength increases.

Summary

- Nonlinear continuum mechanics for 2D graphene monolayer
- Atomistic modeling of graphene under bending and stretching
- Excess edge energy, edge forces, and induced edge buckling
- Graphene nanoribbons under uniaxial tension: edge effects on elastic modulus and fracture
- Graphene on oxide: van der Waals interaction and corrugation; strain-induced corrugation