Dislocation accommodation mechanisms in monolayer and bilayer graphene

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In collaboration with: M. Ortiz, J.P. Méndez, F. Arca, J. Ramos
Motivation

Graphene

- Graphene is a truly 2D material
- Fabricated by:
  - Mechanical/chemical exfoliation
  - Epitaxial growth
  - Chemical vapor deposition
- Electronic, thermal, chemical and mechanical properties sensitive to lattice imperfections

Key material: Next generation electronic devices

- Changes in electronic properties due to:
  - Presence of point defects: dislocation arrangements, vacancies, etc.
  - Geometry or linear defects: grain boundary structures, armchair or zig-zag nanoribbons, etc.
  - Doping elements.


Graphene-based flexible electronic devices.

TIGHT BINDING POTENTIALS

- Stability of defects due to thermal loading
Graphene: electronic properties

Graphene lacks energy band gaps

Band Structures & Density of State (unit cell)

Nanoribbons

(armchair conf.)

Band gap: 0 eV

Grain boundaries

Band gap: ~ 1 eV

DFT studies


Defects in graphene – Our Approach

Main issues of interest:

• Properties of individual defects: Core structure, core energies, limiting behaviors (dilute, continuum...)

**Our harmonic approach:**

✓ Discrete lattice elasticity, discrete defects
✓ Discrete dislocations as eigendeformations
✓ Discrete Fourier transform, closed-form solutions ($u$ and $E$)

• Stability of defects: Relaxed core structures, thermal stability,...

1. **Anharmonic approach:**

✓ Extension of the Discrete Dislocation theory

2. **Molecular dynamics:** LAMMPS code

thermal effects
Discrete Dislocation Theory

- Harmonic energy of defective graphene:
  \[ E_H(u, \beta) = \frac{1}{2} \langle B(du - \beta), (du - \beta) \rangle - \langle f, u \rangle \]

  \( u \equiv \text{displacement field} \quad du \equiv \text{bond deformation} \quad \beta \equiv \text{eigendeformations} \quad f \equiv \text{applied forces} \)

- Displacement equilibrium problem:
  \[ E_H(\beta) = \min_u E_H(u, \beta) \rightarrow u^*_H = A^{-1}(f^E + f) \]

  \[ DE(u^*_H) \neq 0 \]


- Non-equilibrium anharmonic energy function \( E(u^*_H) \):
  \[ f^{(k+1)} = f^{(k)} - \alpha_k \cdot \delta DE(A^{-1}(f^E + f^{(k)})) \]

  Fixed point iteration method

  \[ DE(A^{-1}(f^E + f^{(k)}) - \alpha_k \delta DE(A^{-1}(f^E + f^{(k)}))) = 0 \]

  \[ u^* = A^{-1}(f^E + f^*) \]
Energy minimization

Harmonic deformed lattice $E_H, u_H$ → NVT MD relaxation

$E_i = E_H, u_i = u_H$ → $u_i = u_H + u'$ → CG energy minimization

$\Delta E < \Delta E_{\text{min}}$ → Yes → Relaxed deformed lattice $E_{Nh}, u_{Nh}$

$\Delta E = |E_i - E_{i-1}|$ → No

Periodic Boundary Conditions

NVT relaxation $T = 1K$

Non-rigid PBC

$\sigma_y = 0$

$\sigma_x = 0$

CG minimization
Graphene: interatomic potentials

### Harmonic potentials

\[
E(u) = V_1 + V_2 + V_3 + V_4 + V_5 + V_6
\]

### Bond order potentials

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

#### AIREBO potential

\[
E_b = \frac{1}{2} \sum_{i,j}^{N_{at}} \left( S_{sr,ij}^{\text{down}} V_{ij}^{sr} + S_{sr,ij}^{\text{up}} V_{ij}^{lr} + \frac{1}{Z_i} S_{mr,ij}^{\text{up}} V_{ij}^{mr} \right)
\]

### Interaction with substrate

\[
\alpha_1, \alpha_2, \gamma_1, \gamma_2, \delta, \alpha_5
\]

\[
\psi \left( \frac{l}{\alpha, \beta} \right)
\]


Stuart SJ, Tutein AB, Harrison JA

Jan H. Los et al.
Phys. Rev. B, 2005
## Graphene: interatomic potentials

### Tight-binding potentials

Xu, C. H. et al.,  

<table>
<thead>
<tr>
<th></th>
<th>Wirtz <em>et al.</em></th>
<th>Tewary <em>et al.</em></th>
<th>Ariza <em>et al.</em></th>
<th>Ariza <em>et al.</em></th>
<th>Mendez <em>et al.</em></th>
<th>Arca <em>et al.</em></th>
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*Wirtz et al.*  
*Solid State Comm.*  
*2004*  

*Tewary et al.*  
*Phys. Rev. B,* *2009*  

*Ariza et al.*  
*JPMS,* *2010*  

*Mendez et al.*  
*JPMS,* *2016*  

*Arca et al.*  
*Acta Materialia,* *2019*
Graphene: interatomic potentials

\[ \psi \left( l_{\alpha, \beta} \right) \]

\[ \Phi \left( l_{\alpha, \beta} \right) \]
Our approach – Stability of core structures

- Dislocation cores predicted by the discrete-dislocation are stable with respect to fully non-linear potentials and in agreement with observation and first-principles calculations.
- Dislocation cores appear stable up to high temperatures (2500 K).
Linear defects: grain boundaries in graphene

O. V. Yazyev et al.  
Nature Materials, 2010

J. Zhang et al.  
Carbon, 2013

<table>
<thead>
<tr>
<th>Angle θ (°)</th>
<th>θ_a (°)</th>
<th>θ_b (°)</th>
<th>GB configuration</th>
<th>H (Å)</th>
<th>Energy (eV/Å)</th>
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Stable ASYMMETRIC grain boundaries

Cell sizes: 380 – 9772 atoms

Local wrinkle structures
Stable ASYMMETRIC grain boundaries

Together with secondary wrinkle structure.

(2,2) | (1,3), \( \theta = 16.1^\circ \)

(6,0) | (4,3)-1, \( \theta = 34.7^\circ \)

Wu and Wei, JMPS 511, 61 (2013) 1421–1432

Zhang and Zhao, Carbon 55 (2013) 151–159

Transport properties across grain boundaries

A tight binding model (C.H. Xu et al., 1992) and the Landauer-Büttiker formalism


| GB configuration | Transport gap (eV) | H (Å)  | $|\Delta d|/d_{min}$ (%) |
|------------------|--------------------|--------|--------------------------|
| (2,2)(1,3)       | 1.15               | 8.5    | 4.08                     |
| (13,4)(9,9)      | 0.29               | 37.6   | 1.26                     |
| (4,0)(3,2)       | 0.24               | 9.9    | 8.96                     |
| (3,5)(0,7)       | 0.0                | 16.9   | 0.0                      |
| (0,5)(3,3)-1     | 0.88               | 12.2   | 3.92                     |
| (0,5)(3,3)-2     | 0.59               | 62.8   | 0.07                     |
| (6,0)(4,3)-1     | 0.72               | 14.6   | 1.40                     |
| (6,0)(4,3)-2     | 0.77               | 14.6   | 1.40                     |
| (6,0)(4,3)-3     | 0.68               | 14.6   | 1.40                     |

Correlation between transport gap and lattice mismatch $|\Delta d|/d_{min}$
Transport properties across grain boundaries

Model I: flat cell
Model II: fully relaxed
Transport properties across grain boundaries

Energy (eV)

$E = -0.01\text{eV} \approx \text{Fermi level}$

$E = 0.24\text{eV}$

$E = 1.74\text{eV}$

$(6,0)\parallel(4,3)-1$
Point defects: dislocations in graphene

Slip systems

Periodic Boundary Conditions

NVT relaxation $T = 1\, \text{K}$

Non-rigid PBC

CG minimization

Periodic arrangement of dislocations

dipoles

quadrupoles
Dislocation dipoles

Arca et al. Nanomaterials 9 (2019) 1012

Symmetric (metaestable)

\[ E = 9.46\text{eV} \]

Asymmetric

\[ E = 7.94\text{eV} \]
Dislocation quadrupoles

After relaxation

Arca et al. Nanomaterials 9 (2019) 1012
Arrays of dislocation dipoles

Spontaneous twinning as an accommodation and relaxation mechanism

significant reduction in energy

After relaxation
Arrays of dislocation dipoles

Dipolar arrays – Accommodation mechanism

\[ F = \begin{pmatrix} 1 & b/h \\ 0 & 1 \end{pmatrix} \]

Twinning: kinematical mode of deformation

red – AIREBO potential
blue – LCBOP potential

angle: 11.1  
energies: 0.717 vs 0.548
Arrays of dislocation dipoles

$T = 3500 K$

$T = 4000 K$

$T = 4500 K$
Transport properties across twin boundaries

Dislocation structures (11,8)
Stone-Wales array (3,8)
Pristine graphene

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<td>$\theta$ (°)</td>
<td>$gap$ (eV)</td>
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<td>16.1</td>
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<tr>
<td>$n = 31$</td>
<td>0.95</td>
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Transport properties across twin boundaries

Dislocation structures (19,8)
Dislocation structures (19,16)
Dislocation structures (19,24)

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<td>0.1 9.4</td>
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<td>$n=19$</td>
<td>1.1 16.1</td>
<td>0.95 11.1</td>
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<td>0.95 16.1</td>
<td>0.75 11.1</td>
<td>0.6 8.2</td>
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Charge carrier transmission coefficient per period across twin boundaries $n=19$
Transport properties across twin boundaries

- Tight-binding model
- Pristine graphene
- First principles

Model I
Model II
First principles

Energy (eV)
T(E)

Transport properties across twin boundaries
Transport properties across twin boundaries

- Dislocation structures (11,8)
- Stone-Wales array (3,8)
- Pristine graphene

E=0 eV ≈ Fermi level
E=0.25 eV
E=1.55 eV
Transport properties across twin boundaries

E=0 eV ≈ Fermi level
E=0.25 eV
E=0.55 eV
E=0.60 eV
E=2.64 eV
Isolated dislocation cores - Bilayers

Out-of-plane displacements → Steric interactions between layers

Two dipoles $n = 9$ in registry

Energy per layer: $E = 7.96 \text{ eV}$

Bilayer energy: $E = 15.70 \text{ eV}$

modest attractive interaction between the layers
Isolated dislocation cores - Bilayers

Two dipoles $n = 9$
separated 15Å

Energy per layer: $E = 7.96\,\text{eV}$
Bilayer energy: $E = 23.0\,\text{eV}$

Strong steric interference between the layers
The steric interference between the monolayers:

1. Strong attractive interaction between the dipoles, which relaxed to a zero-distance configuration of energy 15.7 eV.
2. The attractive interaction between dipoles is not strong enough and the dipoles remain offset to each other, resulting in comparatively larger energies.
Isolated dislocation cores - Bilayers

Relaxation of a bilayer containing two unmatched dislocation dipoles

Initial condition (stacking sequence AA)

Upon relaxation (stacking sequence AB)
Dislocation accommodation mechanisms in monolayer and bilayer graphene

Thank you for your attention !!!