First Principles Investigation of Graphene-Metal Interfaces

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Background and Motivation

- Graphene has exceptional properties making it suitable for potential use in nanoelectronics applications
  - High electron mobility
  - Can be grown epitaxially on metal substrates (i.e. nickel)
- Discovery of an extended defect with metallic properties
  - 1-D chain of pentagonal and octagonal carbon rings
- Here we investigate the interaction at graphene-metal interfaces
  - Nickel is an attractive substrate due to small lattice mismatch
Techniques and Methods

- Density functional theory (DFT)
  - Solve Schrödinger equation using electron density instead of explicitly treating each individual electron
- Local density approximation (LDA)
  - Solutions based only on electron density at a single point
  - LDA interface distance agrees better with experiment than GGA for graphene-on-metal systems
- DMol$^3$ DFT code package used
Structural Optimization

- Nickel: LDA: 3.45 Å (Experimental: 3.52 Å)
- Magnetic moment: 0.56 \( \mu_B \) (Experimental 0.6 \( \mu_B \))
- Graphene: nearest neighbor distance 1.415 Å (exp. 1.42)
- Graphene was matched to nickel (mismatch 0.6%)
Nickel-Graphene Models

- Investigated interfacial properties:
  - Work of adhesion
    - Fcc favored
  - Magnetic effects of Ni-graphene interaction
Nickel-Graphene-Metal Models

- All structures based on fcc configuration
- Investigate effects of metal adlayers:
  - Work of adhesion
- Place metal atoms below graphene to model intercalation
- Top configuration is favored
Interface Interactions

\[ W = \frac{(E_a + E_b - E_{ab})}{\text{unit cell area}} \]

<table>
<thead>
<tr>
<th>Interface</th>
<th>( W ), J/m²</th>
<th>( d ), Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>fcc</td>
<td>0.81</td>
<td>2.16</td>
</tr>
<tr>
<td>hcp</td>
<td>0.77</td>
<td>2.17</td>
</tr>
<tr>
<td>hollow</td>
<td>0.31</td>
<td>3.26</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Interface</th>
<th>( W_1 ), J/m²</th>
<th>( d_1 ), Å</th>
<th>( W_2 ), J/m²</th>
<th>( d_2 ), Å</th>
<th>( \Delta d_c ), Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(s)/gr/Ni</td>
<td>3.47</td>
<td>2.15</td>
<td>3.65</td>
<td>2.16</td>
<td>0.30</td>
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<tr>
<td>Ni(s)/gr/Cu</td>
<td>0.51</td>
<td>2.91</td>
<td>1.40</td>
<td>2.13</td>
<td>0.05</td>
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<tr>
<td>Ni(s)/Ni/gr</td>
<td>0.81</td>
<td>2.16</td>
<td>5.36</td>
<td>2.01</td>
<td>0.03</td>
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<tr>
<td>Ni(s)/Cu/gr</td>
<td>0.34</td>
<td>3.12</td>
<td>3.77</td>
<td>2.04</td>
<td>0.002</td>
</tr>
</tbody>
</table>

• Fcc and top structures favored
• Metal adlayer on top of graphene increases work of adhesion \( W_2 \)
  • for nickel adlayer: 3.65 J/m² (4.0 times)
  • for copper adlayer: 1.40 J/m² (1.7 times)
• Nickel adlayer causes significant graphene corrugation \( \Delta d = 0.30 \) Å.
• Interaction between graphene and intercalated copper is much weaker.
Top interfacial layer (5) has reduced magnetic moment
- $\mu = 0.33 \mu B$ at equilibrium $d = 2.16 \text{ Å}$
- Increases towards value for clean nickel surface, $\mu = 0.64 \mu B$.

Reduced magnetic moment of subsurface layers (2-4)
- value increases for deeper layers, approaching $\mu = 0.56 \mu B$

Carbon atoms have induced magnetic moment:
- $\mu_1 = -0.02 \mu B$ at equilibrium $d = 2.16 \text{ Å}$
- $\mu_2 = 0.04 \mu B$ at equilibrium $d = 2.16 \text{ Å}$
- Consistent with experiment*
- Not monotonic

Conclusions

- Understanding the graphene-metal interface is important for the realization of graphene-based nanoelectronics and other applications

- Identified stable configurations of graphene on nickel substrates

- Observed increase in graphene-substrate binding when additional metal layers are deposited

- Observed reduced magnetic moment of nickel substrate, and induced magnetic moment in carbon atoms