Theoretical and experimental studies of the properties of nanostructured graphene

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• Graphene Nano Flakes (GFN’s) – magnetic properties (theory – WW, OY)
• Ripples in graphene (exp.+th. – WW)
• Functionalized graphene: mechanical, optical, magnetic, dielectric properties (theory – WW, ES)
• Single-atom chisel to sculpt graphene (exp.+th. – WW, ES)
• Graphene as substrate: organic PV’s (exp.+th. – WW, ES)
• Graphene in 2D layered devices (BN, MoS$_2$, ...) (theory – ES)
Real-space imaging of graphene (Wei Li Wang)

Libra MC 200-80
- Monochromated
- Aberration Corrected
- Operated at 80 kV
Intrinsic ripples in graphene

Experiment:

Theory:
Graphene Structures at an Extreme Degree of Buckling
Youdong Mao, Wei L. Wang, Dongguang Wei, Efthimios Kaxiras, and Joseph G. Sodroski
ACS NANO, 5, 1395–1400 (2011)
Imaging ripples in real space of CVD suspended graphene

Simulate scattering of incident electron beam by total electrostatic potential
Calculate total potential with a transferable core correction

DFT:
• Pseudopotential: wrong core
• All electron: too expensive
• Pseudopotential + core correction
Image matching
Ambiguity: inversion symmetry

Matching based on a normalized cross-correlation functional:

\[
C(f_{exp}, f_{sim}) = \frac{\sum_{xy} (f_{exp}(x, y) - \overline{f}_{exp})(f_{sim}(x, y) - \overline{f}_{sim})}{\sqrt{\sum_{xy} (f_{exp}(x, y) - \overline{f}_{exp})^2 \sum_{xy} (f_{sim}(x, y) - \overline{f}_{sim})^2}}
\]

Kirkland, E. J. *Advanced computing in electron microscopy* (Springer, 2010).
Topography Reconstruction

Amplitude: 0.5 nm
Std. dev.: 0.13 nm
Typical width: 45 nm

NanoLetters (2012)

Experiment:
- Wei Li Wang, D. Bell, Wei Yi, S. Bhandari, R. Westervelt

Theory:
- Wei Li Wang, E. G.J. Santos, E.Kaxiras
Origin of magnetism in graphene

- Defects

Chemisorptions of H π orbitals

Vacancy both π and sp² orbitals (reactive)

- Edge states – graphene nanoribbon

Flat band at the Fermi level

Antiferromagnetic coupling at zigzag edges

Magneto-electric effect in covalently functionalized few-layer graphene

concentration: ~3%
Impurity concentration plays a significant role

Magnetoelectric coefficient: \[ \alpha = \mu_0 \frac{\Delta S}{\Delta E} \]

Same order of magnitude as in ferromagnetic films: Fe (001), Ni(001) and Co(001)
Interplay of defect-level and electric field on the electronic structure

(a) 

(b) 

(c) 

Wavefunction [ blue: +, red: - ]

(d) 

(e) 

(f)
Spin-polarized states in functionalized graphene bilayer

Selection of the spin-channel with an electric bias

\[ P = \frac{N_{\uparrow} - N_{\downarrow}}{N_{\uparrow} + N_{\downarrow}} \]
Magnetic behavior from topological frustration

- Frustration: prevents simultaneous minimization of the interaction energies acting at a given site.
- Generalization of a simple counting rule.

Generalization in arbitrary 2-D network
Graphene Nano Flakes (GNFs) of high symmetry
Hexagonal graph theory

Tight binding Hamiltonian:

\[ \mathcal{H} = -t \sum_{\langle ij \rangle, \sigma} c^\dagger_{i\sigma} c_{j\sigma} \]

\( \alpha = \) pairwise non-adjacent vertices
\( \beta = \) non-adjacent edges
\( \eta = \) number of zero eigenvalues
\( \theta = \) number of positive eigenvalues
\( \nu = \) number of negative eigenvalues


Graph theory

\[ \theta, \nu, \eta \]

\[ \alpha = \beta + \eta \]
\[ \beta = \theta = \nu \]
\[ N = \theta + \nu + \eta \]

Number of Nonbonding States:

\[ \eta = \alpha - \beta = N - 2\beta \]
Lieb theorem

Hubbard model $(\pi$ band$)\)

$$\mathcal{H} = -t \sum_{\langle ij \rangle, \sigma} c_i^{\dagger} c_j \sigma + U \sum_i n_i^{\uparrow} n_i^{\downarrow}$$

$$S = |N_A - N_B|/2$$

for $U>0$ in bipartite lattices

$N_A=6, \ N_B=5$

$N_A=3, \ N_B=3$

$S = |N_A-N_B|/2 = 1/2$

$S = |N_A-N_B|/2 = 0$

Two classes of GNFs

Class I. \( \beta = \min\{N_A, N_B\} \)  
Frustration on one or no sublattice

therefore, \( \eta = |N_A - N_B| \)  and \( S = \eta/2 \)  FM order

Class II. \( \beta < \min\{N_A, N_B\} \)  
Frustration on both sublattices

therefore, \( \eta > |N_A - N_B| \)  and \( S < \eta/2 \)  AFM order

\( \eta \)-2S pairs of spin orbitals are AFM coupled

\( N_A - N_B = 2 \)  \( \eta = 2 \)  
\( N_A - N_B = 0 \)  \( \eta = 0 \)  
\( N_A - N_B = 0 \)  \( \eta = 2 \)
GNFs vs. Graphene Nano Ribbons

- No frustration in GNRs
- No strict zero energy eigenstates in GNRs
- No net spin in GNRs
- Different spin-size/U dependent
Ferrimagnetic order in triangular zigzag-edged GNF

Spin orbitals in bowtie GNFs

Symmetry broken: spin orbitals degenerate but spatially separated.

Frustration on both sub-lattices
Magnetic couplings in bowtie GNFs

Coupling strength:
\[ 2J = E_{FM} - E_{AF} \]

Minimum 2J for RT switching.
Logic device

Set $\uparrow = 1$, $\downarrow = 0$

$$C = (A \cap B) \cup (B \cap D) \cup (A \cap D)$$

$$C = (A \cap B) \cup ((A \cup B) \cap D)$$

$$C = \begin{cases} (A \cup B) & D = 1 \text{ NOR gate} \\ (A \cap B) & D = 0 \text{ NAND gate} \end{cases}$$
Advantages of GNF spintronics

• Customizable magnetic coupling mediated by $\pi$ bond: 20 – 180 meV.
• Ultra fast switching: subpicosecond spin flipping
  $$J = \frac{\pi \hbar}{10^{-12}} \text{ sec} \simeq 2 \text{ meV}$$
• Manageable error rate at room temperature,
  $$p = e^{-2J/kT_B} = 0.001$$

Compare to GNR:
• More “nano” – do not rely on long range correlation
• More natural – for some formation processes, such as TEM
• Easy to create spin polarization – no need for strong external field
Spin transport

(Wimmer 09, PRL 100, 177207)

\[
\eta = |N_A - N_B| = 8
\]

\[
\eta = |N_A - N_B| = 15
\]
Sculpting suspended graphene
Punching nanopore with STEM

ADF Cs STEM Image at 200 KV

Imaging at 80 KV
Cs TEM Image
Magnetic coupling in GNFs

Graphene edge shows distinct restructure and reformation under the 80KV electron beam.

“Upper layer” carbon atoms relocate on the bottom layer under excitation, and fill defects to reduce the total energy.
Cutting graphene edges
An atomic-scale chisel for sculpting graphene

By Wei Li Wang

Expts. carried out at LBNL’s NCEM
\[ \mathbf{a} = \mathbf{r}_p - \mathbf{r}_{Si} \]

\[ \mathbf{b} = \mathbf{r}_m - \mathbf{r}_{Si} \]
Simulation of C atom removal from G with and without Si impurities
Sculpting of graphene with atomic scale precision clearly feasible!

Many possibilities for new physics and devices

Theory:
• Dr. Wei Li Wang (Harvard)
• Prof. Oleg Yazyev (EPFL)
• Dr. Elton Gomes Santos (Harvard)

Experiment:
• Dr. Wei Li Wang (Harvard-UCB)
• Prof. Robert Westervelt (Harvard)
• Dr. David Bell (Harvard, CNS)

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