Strains and pseudo-magnetic fields in Graphene nano-structures

Reza Asgari

In collaboration with:
N. Abedpour
F. Giunea
Congratulations

Premio Nacional de Investigación
2011
Francisco José Guinea López
Instituto de Ciencia de Materiales de Madrid
1. Introduction
   Short overview (Experiments & Theories)

2. Theory and simulations
   • Analytical results for strains in graphene ring
   • Molecular dynamics simulations: Wrinkles
   • Circular graphene and its pseudo-magnetic filed

3. Conclusion !!!
   Heavy pseudo-magnetic fields, effect of wrinkles
Why do we need study strains in graphene?

- Corrugation, wrinkles/ripples
- What is the morphology of the surface?
- Existence of tensions
- Impact of the corrugations on electronic properties?
- .......
Gaussian Distribution

\[ H = \frac{1}{2} \int d\vec{r} d\vec{r}' h(\vec{r}) G(\vec{r} - \vec{r}') h(\vec{r}') \equiv \frac{1}{2} \sum_q h(\vec{q}) G(\vec{q}) h(-\vec{q}) \]

- In thermal equilibrium, the surface even solids are not perfectly flat.
- Thermal fluctuations roughen the interface.

\[ 2D: \quad \langle |h(\vec{q})|^2 \rangle \approx \begin{cases} \log(L/\Lambda) & \text{Low T} \\ \frac{L^2}{L^2} & \text{High T} \end{cases} \]

where \( \Lambda \) is the ultraviolet momentum cutoff.

- For solids, the periodic potential tends to decrease the roughness of the interface.

\[ \langle |h(\vec{r})|^2 \rangle = \frac{T}{2\pi\gamma} \log(L/a) \]
How flat graphene is?

Free boundaries, $T=300\text{ K}$.

Role of thermal fluctuations in the behavior of membranes

- How do fluctuations modify the elastic bending constants?

- On a classical level, the rigidity coefficient does not depend on the linear size.

- \( \kappa \) is decreasing with increasing \( L \) due to thermal excitations (Soft membranes).

\[
\lambda \approx L^{-1}
\]

- \( T < T_c \) the rigidity \( \kappa \) increases with \( L \)
and the membrane behaves as a flat. Only for \( T > T_c \) that the membrane is crumpled.

- 2D membranes are always in the crumpled phase like polymers. However, the long-range forces can lower the critical dimension \( D = 2 \). 2D solids would have \( T_c > 0 \)

Static ripples on graphene

200 X 400 atoms at 50 K

Thermal fluctuations can be suppressed by anharmonic coupling between bending and stretching modes.

Strain Engineering

Elasticity Theory  ➔  Quantum electrodynamics
Deformed graphene lattice

\[ H = \sum_{<ij>} t_{ij} a_i \perp b_j \]

\[ t_{ij} = t + \frac{\beta t}{\alpha^2} \tilde{\rho}_{ij} \cdot (\tilde{u}_{ij} - \tilde{u}_0) \]

\[ \tilde{u}_{ij} - \tilde{u}_0 \propto (\tilde{\rho}_{ij} \nabla) \tilde{u}(\tilde{r}) \]
Graphene is distorted, the effective Hamiltonian will be changed into

$$ H = v_F \left( P - eA \right) \cdot \sigma + V I $$

$$ H(P) = v_F \begin{pmatrix} \nu_F^{-1} V & P^* - eA^* \\ P - eA & \nu_F^{-1} V \end{pmatrix} $$

$$ H_-(p) = v_F \begin{pmatrix} \nu_F^{-1} V & -p + eA \\ -P^* + eA^* & \nu_F^{-1} V \end{pmatrix} $$

$$ A = A_x + iA_y $$

Induced vector potential field is defined through the deformations of sample

\[ v_F e A_x = \frac{3\kappa \beta}{4} \hbar t (u_{xx} - u_{yy}) \]
\[ v_F e A_y = -\frac{3\kappa \beta}{2} \hbar t u_{xy} \]

\[ \beta = \frac{\partial \ln(t)}{\partial \ln(a)} \approx 2 \quad \kappa \approx 0.56 \]

Strains:

\[ 2u_{\alpha\beta} = \partial_\alpha u_\beta + \partial_\beta u_\alpha + \partial_\alpha h \partial_\beta h \]

Ideas

Elasticity theory

Deformed lattice

Pseudo-magnetic field
Effective Hamiltonian

\[ H = H_{\text{subs}} + H_{\text{elastic}} + H_{\text{elec}}, \]

\[ H_{\text{subs}} = \frac{g}{2} \int d^2 \vec{r} [h(\vec{r}) - h_0(\vec{r})]^2, \]

\[ H_{\text{elastic}} = \frac{\kappa}{2} \int d^2 \vec{r} [\nabla^2 h(\vec{r})]^2 \]
\[ + \int d^2 \vec{r} \left\{ \frac{\lambda}{2} \left[ \sum_i u_{ii}(\vec{r}) \right]^2 + \mu \sum_{ij} \left[ u_{ij}(\vec{r}) \right]^2 \right\}, \]

\[ H_{\text{elec}} = v_F \int d^2 \vec{r} \overline{\Psi}_1(\vec{r}) \{ \sigma_x [-i \partial_x - A_x(\vec{r})] + \sigma_y [-i \partial_y - A_y(\vec{r})] \}
\[ - A_y(\vec{r}) \} \Psi_1(\vec{r}) - v_F \int d^2 \vec{r} \overline{\Psi}_2(\vec{r}) \{ \sigma_x [-i \partial_x + A_x(\vec{r})] + \sigma_y [-i \partial_y + A_y(\vec{r})] \}
\]

References:
Motivations

Strain can be used to engineer graphene electronic states through the creation of a pseudo–magnetic field. This effect is *UNIQUE* to graphene because of its massless Dirac fermion-like band structure and particular lattice symmetry. Strains change the bonds length between atoms and affects the way electrons move among them.
First example: Triangular Nanobubbles

**Experiment**

**Fig. 2.** (A) Sequence of eight $dl/dV$ spectra ($T \sim 7.5$ K, $V_{\text{mod}} = 20$ mV) taken in a line across a graphene nanobubble shown in the image in (B). Red lines are data with quartic background subtracted; black dotted lines are Lorentzian peak fits (center of peaks indicated by dots, with blue dots indicating $n = 0$). Vertical dash-dot lines follow the energy progression of each peak order. (C) Normalized peak energy versus $\text{sgn}(n) \sqrt{|n|}$ for peaks observed on five different nanobubbles follow expected scaling behavior from Eq. 1 (dashed line).

$$E_n = \text{sgn}(n) \hbar \omega_c \sqrt{|n|} + E_{\text{Dirac}},$$

$$\omega_c = \sqrt{\frac{2e\hbar^2}{m_F B_s}}$$

Exp vs Theory

**MD Simulations**

Same conditions as experiment.
Uniform strain value about %10 is acted on all lines segment

Fixed boundaries, $T=10$ K, $l=3.4$ nm.
Triangular Nanobubbles

$A_\alpha (x, y)$
Numerical Results vs Experiment data
Numerical Results: Larger line segments

\[ B_{\text{eff}}(T) \propto L^\alpha \]

\[ \alpha \approx -2.8 \]
Graphene Ring

N. Abedpour, R. A., F. Guinea, PRB 84, 115437 (2011)
Graphene ring: analytical solutions

\[ h(r, \vartheta) = 0 \]

\[
\begin{cases}
  u_\vartheta(R_1, \vartheta) = u_r(R_1, \vartheta) = 0 \\
  u_\vartheta(R, \vartheta) = U_\vartheta \\
  u_r(R, \vartheta) = 0
\end{cases}
\]

\[
\begin{cases}
  u_r(r, \vartheta) = 0 \\
  u_\vartheta(r, \vartheta) = U_\vartheta \left[ -\frac{R R_1^2}{r(R^2 - R_1^2)} + \frac{R r}{R^2 - R_1^2} \right]
\end{cases}
\]

Graphene ring: analytical solutions

Strains:

\[ 2 u_{r,\theta}(r, \theta) = \left( \frac{\partial u_\theta}{\partial r} + \frac{1}{r} \frac{\partial u_r}{\partial \theta} - \frac{u_\theta}{r} \right) = \frac{2U_\theta R R_1^2}{r^2 (R^2 - R_1^2)} \]

Induced gauge field:

\[
A_r = \Phi_0 \frac{c \beta U_\theta}{a} \frac{2R_1^2 R}{r^2 (R^2 - R_1^2)} \sin(3\theta) \\
A_\theta = \Phi_0 \frac{c \beta U_\theta}{a} \frac{2R_1^2 R}{r^2 (R^2 - R_1^2)} \cos(3\theta)
\]

where

\[ c = \sqrt{3} \kappa / (2\pi) \]
Analytical solutions: Pseudo-magnetic field

\[ B(r, \vartheta) = \Phi_0 \frac{4\sqrt{3} \kappa \beta}{\pi a} \frac{U_{\vartheta} R R_1^2}{r^3 (R^2 - R_1^2)} \cos(3 \vartheta) \]

\[ \Phi_0 = \frac{h}{2e} \]

example:

\[ B(r, R_1, \vartheta) \approx 0.56 \times 10^4 \vartheta \frac{R_1^2}{r^3} \]

\[ B(R_1 \approx 10 \, nm, \vartheta = 19^0) \approx 10 \, T \]
**MD simulations**

A representative atomic configuration in MD simulations for circular graphene ring at T=50 K. The outer boundary is rotated about $12^\circ$ in x-y plane.

WRINKLES!! noticeable and might be considered

\[
R = 7 \text{ nm} \\
R_1 = 3 \text{ nm} \\
\vartheta = 12^\circ
\]
**Numerical results**

Distribution of the pseudo-magnetic field on graphene ring. Green, red and black colors correspond to positive, negative and zero values of the pseudo-magnetic field, respectively. The dark-green (or dark-red) correspond to the strongest pseudo-magnetic filed larger than 1000 T.

\[ B(x, y) \quad \text{and} \quad A_\alpha(x, y) \]
Numerical results

\[ B(r, \vartheta) \propto \cos(3\vartheta) \]
**MD simulations**

The outer boundary is rotated about 6° in x-y plane and the central part is pulled down

\[
B(r, \vartheta) \propto \cos(3\vartheta)
\]
Graphene circular
Circular graphene, $R=10$ nm, at $T=50$ K.
Uniform strain value about %10 is acted on clamped boundary.

most wrinkle structures appear near to the boundary. Then this morphology of flake helps the system to have less stress in the middle part.

N. Abedpour, R. A., F. Guinea, To be submitted
The averaged pseudo-magnetic field value is larger than 800 T and it decreases by increasing the radius. This reduction can be fitted very well by $R^{-\frac{1}{2}}$. 
Conclusion

• In graphene ring the field diverges near the inner clamped as $r^{-3}$ however the strains diverge as $r^{-2}$
• Our numerical simulation results are in good agreement with those measured in experiment for triangular graphene shape nano- bubbles. We show that the domain which the pseudo-magnetic field remains constant, increases with increasing the line segments of triangular.
• Wrinkles structures on graphene flakes make significant enhancement of the pseudo-magnetic field.
• Averaged pseudo-magnetic field value decreases by increasing the radius in circular graphene and behaves like $R^{-0.5}$. 
Thanks for your attention
\begin{align*}
V_{ij} &= V_R(r_{ij}) - \bar{b}_{ij}V_A(r_{ij}), \\
\bar{b}_{ij} &= (b_{ij} + b_{ji}) / 2,
\end{align*}

\begin{align*}
V^R(r) &= f^C(r)(1 + Q/r)Ae^{-ar}, \\
V^A(r) &= f^C(r) \sum_{n=1,3} B_ne^{-\beta_nr},
\end{align*}

\begin{align*}
 f^C_{ij}(r) &= \begin{cases}
 1 & r < D^\text{min}_{ij} \\
 1 + \cos \left[ \frac{(r - D^\text{min}_{ij})}{(D^\text{max}_{ij} - D^\text{min}_{ij})} \right] / 2 & D^\text{min}_{ij} < r < D^\text{max}_{ij} \\
 0 & r > D^\text{max}_{ij}
\end{cases},
\end{align*}

\begin{align*}
 b_{ij} &= \frac{1}{2}b^\sigma_{ij} + b^\alpha_{ij}, \\
b^\alpha_{ij} &= \{1 + \sum_{k(\neq i,j)} f^C_{ik}(r_{ik})G[\cos(\theta_{ijk})]\}^{-1/2}.
\end{align*}

\(A\ Q\ \alpha\ \beta\_n\ B\_n\) are parameters for the carbon-carbon pair terms.

Molecular Dynamics

• Follows the time evolution of a system
• Solve Newton’s equations of motion:

\[
\vec{F}(t) = -\frac{d\vec{E}}{d\vec{x}} = m\vec{a}(t) = m\frac{d^2\vec{x}(t)}{dt^2} \Rightarrow
\]

\[
\vec{x}(t) = \vec{x}(t_0) + \vec{v}(t_0) \cdot (t - t_0) + \int_{t_0}^{t} dt' \int_{t_0}^{t'} \frac{1}{m} \vec{F}(t'') dt''
\]

• Treats electrons quantum mechanically
• Treats nuclei \textit{classically}
• Allows study of dynamic processes
• Annealing of complex materials
• Examines the influence of temperature
• Time averages Vs Statistical averages
Different ensembles, different Lagrangians, different Conserved magnitudes

- NVE (Verlet): Microcanonical.
- Integrates Newton’s equations of motion, for N particles, in a fixed volume V.
- Natural time evolution of the system: E is a constant of motion

- NVT (Nose): Canonical
- System in thermal contact with a heat bath.
- Extended Lagrangian:
  - N particles + Thermostat, mass Q.

- NPE (Parrinello-Rahman) (isobaric)
- Extended Lagrangian
- Cell vectors are dynamical variables with an associated mass.

- NPT (Nose-Parrinello-Rahman)
- 2 Extended Lagrangians
- NVT+NPE.
Verlet algorithm

The most commonly used algorithm:

\[
\begin{align*}
\mathbf{r}(t+h) &= \mathbf{r}(t) + \mathbf{v}(t) \, h + \frac{1}{2} \mathbf{a}(t) \, h^2 + \mathbf{b}(t) \, h^3 + O(h^4) \quad \text{(Taylor series expansion)} \\
\mathbf{r}(t-h) &= \mathbf{r}(t) - \mathbf{v}(t) \, h + \frac{1}{2} \mathbf{a}(t) \, h^2 - \mathbf{b}(t) \, h^3 + O(h^4) \\
\mathbf{r}(t+h) &= 2 \, \mathbf{r}(t) - \mathbf{r}(t-h) + \mathbf{a}(t) \, h^2 + O(h^4) \quad \text{Sum} \\
\mathbf{v}(t) &= \frac{\mathbf{r}(t+h) - \mathbf{r}(t-h)}{2h} + O(h^2) \quad \text{Difference (estimated velocity)}
\end{align*}
\]

- Trajectories are obtained from the first equation. Velocities are not necessary.
- Errors in trajectory: \( O(h^4) \)
- Preserves time reversal symmetry.
- Excellent energy conservation.
- Modifications and alternative schemes exist (leapfrog, velocity Verlet), always within the second order approximation.
- Higher order algorithms: Gear
Nose-Hoover thermostat

- MD in canonical distribution (TVN)
- Introduce a friction force $\zeta(t)$

$$\frac{dp}{dt} = F(q, t) - \zeta(t)p(t)$$

Dynamics of friction coefficient to get canonical ensemble.

$$Q \frac{d\zeta}{dt} = \sum \frac{1}{2} m_i v_i^2 - \frac{3N}{2} k_BT$$

Feedback makes K.E.=$3/2kT$

$Q =$ fictitious “heat bath mass”. Large $Q$ is weak coupling
Which Ensemble should we use?

- **NVE (Verlet): Microcanonical**
  - Good trajectories.
  - Time reversible (up to numerical error)
  - Dynamical variables are well defined.
  - Initial X and V are relevant: necessity of equilibration.

- **NVT (Nose): Canonical**
  - Good T control
  - Equilibrates the system.
  - Choice for Structural sampling.
  - Sensitive to Nose mass.

- **NPE (Parrinello-Rahman)**
  - Phase transitions systems under pressure.
  - 1 mass parameter (barostat)

- **NPT (Nose-Parrinello-Rahman)**
  - Phase transitions under P and T
  - 2 mass parameters, barostat and thermostat. (Fluctuations!!)

Same sampling in the thermodynamic limit
Ripples structures