Interactions of charged particles with graphene

Zoran Miskovic

Department of Applied Mathematics
University of Waterloo, Ontario, Canada

Collaborators:

University of Waterloo:
F. Goodman
D. Mowbray
J. Zuloaga
M. Ghaznavi
K. Allison

Vinca Institute, Belgrade, Serbia:
Lj. Hadzievski
N. Bibic
I. Radovic
D. Borka
V. Borka Jovanovic

Dalian University of Technology, China:
Y.-N. Wang
Y.-H. Song
D.-P. Zhou

Centro Atomico Bariloche, Argentina:
N. Arista
J. Gervasoni
S. Segui

Support:
Outline

- Introduction
- Ion interactions with graphene
  - Nonlinear screening
  - Image potential
  - Stopping force
  - Wake effect
- Plasmon excitations by electron beams
  - HREELS, energy $E \sim 20$ eV, substrate phonons
  - EELS, energy $E \sim 100$ keV, layered electron gas
- Outlook
Graphene as building block of carbon nanostructures

- Fullerene, $C_{60}$
- Nanotube, CNT
- Graphite, HOPG
Why study carbon nanostructures?

- **Physical properties:**
  - Electrical, mechanical, thermal
  - Dependent on: molecular structure, dielectric environment, local modification

- **Applications:**
  - Nanoelectronic devices
  - Biochemical sensors
  - New composite materials
  - Ion storage (H, Li)
  - Nanoelectromechanical systems (NEMS)
Electronic response to external charged particles (regime of electronic stopping for moving charges)

- **Electrons**
  - EELS in STEM: plasmon excitations of $\sigma$ and $\pi$ electrons in CNTs & graphene
  - HREELS: plasmon excitations of $\pi$ electrons in graphene
  - image potential states: CNTs & graphene

- **Ions**
  - ion channeling in CNTs
  - grazing scattering of ions on graphene
  - friction forces on slowly moving ions
  - static screening of charged impurities
Electronic structure of graphene

Band structure

low-energy excitations involve $\pi$ bands only

$\varepsilon_k = \hbar v_F |k|$
Ambipolar electric field effect in single-layer graphene on top of an oxidized Si wafer

Applying gate potential $V_g$ shifts Fermi energy $E_F$ above/below Dirac point (electron or hole doping)

Equilibrium charge carrier density vs chemical potential $\mu$ may be $>0$ and $<0$

$$n(\mu) = \int_0^\infty d\varepsilon \rho(\varepsilon) \left[ \frac{1}{1 + e^{\beta(\varepsilon - \mu)}} - \frac{1}{1 + e^{\beta(\varepsilon + \mu)}} \right]$$

Linear DOS: $\rho(\varepsilon) \approx \frac{g_sg_v}{2\pi} \frac{|\varepsilon|}{(\hbar v_F)^2}$, Fermi speed: $v_F \approx \frac{c}{300}$
Ion bombardment vs ion adsorption on graphene


**Ne⁺ irradiation** (lattice defects)

**K doping** (charged impurities)

Conductivity [e²/h]

-50 -25 0 25 50

Gate Voltage [V]

500 eV Ne⁺
Nonlinear screening of external charge by graphene


Study several effects:
• doping via gate potential
• finite temperature
• exchange interaction effects
• distance $z_0$ from graphene
• size of gap $h$ to the substrate

Thomas-Fermi model at finite $T$

$$U(r) = U_{\text{ext}}(r) - e^2 \int d^2 r' \left[ n(\mu + U(r')) - n(\mu) \right] \left[ \frac{1}{||r - r'||} - \frac{\epsilon_s - 1}{\epsilon_s + 1} \frac{1}{\sqrt{(r - r')^2 + 4h^2}} \right]$$

Self-consistent solution for screened potential $U_{\pm}(r)$ in graphene when $\mu \geq 0$
Screened potential in graphene due to external charge

\[ U(r) \]

graphene on SiO\(_2\) (nonlinear results)

graphene on SiO\(_2\) (linear TF and RPA)

free graphene (nonlinear results)

free graphene (linear TF and RPA)

- solid lines: \( n > 0 \)
- dashed lines: \( n < 0 \)
- dotted lines: RPA
- dash–dotted lines: linear T–F

Friedel oscillations
Ratio $U_-(r)/U_+(r)$ of screened potentials for $n \leq 0$
Nonlinear image interaction for external charge

Observation of image potential states on epitaxial graphene:

Nonlinear image potential

![Graph showing nonlinear image potential](image)

- Free graphene
- SiO₂

- $E_{m1} = 3.95 \text{ eV}$
- $E_{m1} = 3.3 \text{ eV}$

- Density (arb. units)
- Bias voltage (V)

- $V_{im} (\text{eV})$
- $z_0 (\text{Å})$

- $n = 0$
- $n = +10^{13} \text{ cm}^{-2}$
- $n = -10^{13} \text{ cm}^{-2}$
- $n = 0; \text{RPA}$
- $|n| = 10^{13} \text{ cm}^{-2}; \text{RPA}$
- $|n| = 10^{13} \text{ cm}^{-2}; \text{linear T–F}$
Interaction of moving external charge with graphene

Study several effects:
- doping via gate potential
- damping via Mermin approach
- local field effects
- phonons in polar substrate
- size of gap to the substrate

Dielectric function of graphene + substrate: Random Phase Approximation

\[ \epsilon(q, \omega) = \left[ 1 - \frac{\epsilon_{\text{sub}}(\omega) - 1}{\epsilon_{\text{sub}}(\omega) + 1} e^{-2qh} \right]^{-1} + \frac{2\pi e^2}{q} \Pi_{\text{gra}}(q, \omega; \gamma) \]

Stopping force

\[ F_s = \frac{2Z^2e^2}{\pi v} \int_0^\infty dq e^{-2qz_0} \int_0^{qv} d\omega \frac{\omega}{\sqrt{q^2v^2 - \omega^2}} \left[ \frac{1}{\epsilon(q, \omega)} \right] \]

Image force

\[ F_i = \frac{2Z^2e^2}{\pi} \int_0^\infty dq e^{-2qz_0} \int_0^{qv} d\omega \frac{d\omega}{\sqrt{q^2v^2 - \omega^2}} \mathfrak{Im} \left[ \frac{1}{\epsilon(q, \omega)} - 1 \right] \]
Loss Function $-\Im \{1/\epsilon(q, \omega)\}$ for graphene and 2DEG

- **Inter-band single-particle excitations**
- **Intra-band single-particle excitations**

2D electron gas (2DEG) with paraboloc band
Stopping and image forces on a point charge moving over epitaxial graphene on SiC and 2DEG (Ag on Si)

Stopping force vs. speed

Image force (normalized) vs. distance
Wake effect due to charge moving at speed $v = 4v_F$ and distance $z_0 = 20 \, \text{Å}$ from free graphene & 2DEG with doping equilibrium density $n = 10^{13} \, \text{cm}^{-2}$

Fermi wavenumber in graphene:

$$k_F = \sqrt{\pi n}$$
HREEL spectra for graphene on a substrate

K.F. Allison et al., Nanotechnology 21 (2010) 134017

Total energy loss:

\[ E_{\text{loss}} = - \int_{-\infty}^{\infty} dt \int d^2r \int_{-\infty}^{\infty} dz \rho_{\text{ext}}(r, z, t) \frac{\partial}{\partial t} \Phi_{\text{ind}}(r, z, t) \]

\[ = \int_{0}^{\infty} d\omega \int_{-\frac{q}{2\pi}}^{\frac{q}{2\pi}} \frac{d^2q}{2\pi^2} |S(q, \omega)|^2 \Im \left[ \frac{1}{\epsilon(q, \omega)} \right] \]  

Loss function

Projectile structure factor:

\[ S(q, \omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \int d^2r e^{-iq \cdot r} \int_{-\infty}^{\infty} dz e^{-q |z|} \rho_{\text{ext}}(r, z, t) \]

\[ \epsilon(q, \omega) = \left[ 1 - \frac{\epsilon_{\text{surf}}(q, \omega) - 1}{\epsilon_{\text{surf}}(q, \omega) + 1} e^{-2qh} \right]^{-1} + \frac{2\pi e^2}{q} \chi_{\text{gr}}(q, \omega) \]

Surface dielectric function:

\[ \epsilon_{\text{surf}}(q, \omega) = \left[ \frac{q}{\pi} \int_{-\infty}^{\infty} dq_z \frac{dq_z}{(q^2 + q_z^2) \epsilon_{\text{sub}} \left( \sqrt{q^2 + q_z^2}, \omega \right)} \right]^{-1} \]
Plasmon coupling with substrate phonon

$$
\epsilon(q, \omega) \approx 1 + \epsilon_{\text{sub}}(\omega) - \frac{e^2}{\hbar} \frac{v_F q}{\omega^2} \sqrt{\pi n} = 0
$$

$$
\epsilon_{\text{sub}}(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \frac{\omega_{1\text{TO}}^2}{\omega_{1\text{TO}}^2 - \omega^2}
$$
**Stopping and image forces** on projectile moving over graphene on SiC: effects of **substrate phonons**

CEPAS proceedings
EEL spectra for free-standing $N$-layer graphene


\[ P(\omega) = \frac{4e^2}{\pi v^2} \int_0^{q_{\text{max}}} dq \frac{q^2}{\left[q^2 + \left(\frac{\omega}{v}\right)^2\right]^2} \Im \left\{ V(q)\chi(q, \omega) \sum_{n=1}^{N} \sum_{n'=1}^{N} e^{-i(n-1)d\omega/v} \left(M^{-1}\right)_{nn'} e^{i(n'-1)d\omega/v} \right\} \]

\[ M_{nn'}(q, \omega) = \delta_{nn'} + (1 - \delta_{nn'}) V(q)\chi(q, \omega) e^{-qd|n'-n|} \]

\[ \chi(q, \omega) = \chi_0(q, \omega) / \left[1 + V(q)\chi_0(q, \omega)\right], \quad V(q) = 2\pi e^2/q \]
Two-fluid, 2D hydrodynamic model for $\sigma$ and $\pi$ electrons: used in single-wall carbon nanotube experiment: Kramberger et al., Phys. Rev. Lett. 100 (2008) 196803


$$\chi_0(q, \omega) = \frac{n^0_\pi q^2 / m^*_\pi}{s^2_\pi q^2 + \omega^2_\pi r - \omega(\omega + i\gamma_\pi)} + \frac{n^0_\sigma q^2 / m^*_\sigma}{s^2_\sigma q^2 + \omega^2_\sigma r - \omega(\omega + i\gamma_\sigma)}$$

Experimental EEL spectra

Plasmon dispersions vs $k$ with angular mode $m$ for nanotube radius $a = 7 \text{ Å}$

$$q^2 \rightarrow \frac{m^2}{a^2} + k^2$$
EELS for free-standing graphite \((N >> 1)\)


\[ P(\omega) \approx N \frac{4e^2}{\pi v^2} \int_0^{q_{\text{max}}} \frac{dq q^2}{\left[ q^2 + \left( \frac{\omega}{v} \right)^2 \right]^2} \left\{ \frac{V(q)\chi_0(q, \omega)}{1 + \frac{\sinh(qd)}{\cosh(qd) - \cos(\omega d/v)} V(q)\chi_0(q, \omega)} \right\} \]
Outlook

• Electronic energy loss and image interaction important for charged particle interactions with C-nanostructures: energy deposition & transport

• Plasmon excitations in HREELS and EELS: full theory needed for dielectric response of both $\sigma$ and $\pi$ electrons

• Ion charge states during scattering need to be considered

• Effects of dielectric environment, particularly substrate phonons

• Concept of friction and screening or mobile ions in aqueous solution
Thank you for your attention