Adsorbate-limited conductivity of graphene

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Outline

- Chemical disorder – experimental evidence

- Modelling

- Transport:
  - kinetic theory
  - quantum corrections
  - localization
Effects of pollution: experiments


• Shifted effective Dirac point
• Conductance asymmetric

[Solid State Communications 146, 351-355 (2008)]
Effects of pollution: experiments

Systematic current annealing

(data courtesy of Amelia Barreiro, Barcelona)
Selective adsorption (T. J. Echtermeyer et al. 2007)
Hydrogenated graphene

General considerations

*Disorder in conventional conductors:* Time reversal symmetry preserved / broken?

*Graphene:* Valley index preserved / broken? Chirality preserved / broken?

In particular:
Long ranged vs short-ranged
Coulomb vs defect scattering
*Ionic vs chemisorbed adsorbates*
Aim: Adsorbate-specific theory for chemisorption
Tight-binding description

\[ H = v_0 (\xi k_x \sigma_x + k_y \sigma_y), \quad v_0 = \frac{3}{2} \gamma_0 a \]

Wallace 1946
Tight-binding description

\[
H_0 = -\gamma_0 \sum_{nm} c_m^+ c_n
\]

\[
H_i = \varepsilon_i d_i^+ d_i - \gamma_i [d_i^+ c_h + c_h^+ d_i]
\]

Parameters can be fit from DFT (here: Siesta)

\[\begin{align*}
H^+ & : \varepsilon_i = 0.66 \gamma_0, \quad \gamma_i = 2.2 \gamma_0 \\
\text{OH}^- & : \varepsilon_i = -2.90 \gamma_0, \quad \gamma_i = 2.3 \gamma_0
\end{align*}\]
outside the gap

in the gap
Scattering rate off a single adsorbate

Self energy (exact): \[ H_i = \frac{\gamma_i^2}{E - \varepsilon_i} c_h^+ c_h \]

Green’s function (exact): \[ G = G_0 + G_0 \frac{\gamma_i^2}{E - \varepsilon_i - g_0} P_i G_0 \]
\[ g_0 = P_i G_0 P_i^T = R(E) - i\pi\nu_0(E) \]

Scattering rate (Fermi golden rule) \[ \tau_k^{-1} = \frac{2\pi}{\hbar} \frac{1}{N} \nu_0 |t_i|^2 \]

Using dos on adsorbate \[ \tau_k^{-1} = \frac{2\pi}{\hbar} \frac{1}{N} \nu_i \gamma_i^2 \]
Renormalisation of the resonance

\[
\tau_k^{-1} = \frac{2\pi}{\hbar} \frac{1}{N} \gamma_i \nu_i \gamma_i^2
\]

dos on adsorbate

\[
\frac{\gamma_i^2 \nu_0(E)}{[E - \epsilon_i - \gamma_i^2 R(E)]^2 + \pi \gamma_i^2 \nu_0(E)^2}
\]

Strong coupling: resonance $\rightarrow$ Dirac point
Renormalisation of the resonance

\[
\tau_k^{-1} = \frac{2\pi}{\hbar} \frac{1}{N} \nu_i \gamma_i^2
\]

dos on adsorbate

\[
\frac{\gamma_i^2 \nu_0(E)}{[E - \epsilon_i - \gamma_i^2 R(E)]^2 + [\pi \gamma_i^2 \nu_0(E)]^2}
\]

Origin: level repulsion

(2\textsuperscript{nd} order perturbation theory: \( \frac{\gamma_i^2}{E_i - E} \))
Randomly placed adsorbates

\[ \tau^{-1} = \frac{2\pi}{\hbar} n_i \nu_0 |t_i|^2 \]

\[ \sigma = e^2 D \nu_0 \]

\[ D = \frac{\langle \nu_k \rangle_{E_F}}{2\langle \nu_k^{-1} \rangle_{E_F}} \tau \]

\[ A = (3\sqrt{3}/4)a^2 \]
Comparison to numerics

Fixed width nanoribbon

Averaged over width
Additional Coulomb scattering

\[ x = \frac{2\pi}{\beta} \frac{n_i}{n_f} \]: relative amounts of disorder

\[ \tau_i^{-1} = n_i \beta \frac{\gamma^2}{\hbar |\varepsilon|} \]

\[ \sigma_i = \frac{2\pi \sqrt{3}}{n_i \beta} \frac{g_s e^2}{h} n_e \]
Additional Coulomb scattering

Additional scattering

\[ \tau_i^{-1} = n_i / \beta \frac{\gamma^2}{\hbar |\varepsilon|} , \]

\[ \sigma_i = \frac{2\pi \sqrt{3}}{n_i \beta} \frac{g_s e^2}{h} n_e \]

4x10^{12} \text{ cm}^{-2}

\[ x = (2\pi / \beta)(n_i / n_l) : \text{relative amounts of disorder} \]
hydrogenated graphene...


3.8 \times 10^{12} \text{ cm}^{-2}
Fundamentally, the asymmetry with respect to $E_D$ arises from the position of a dispersionless hydrogen acceptor level, which is not centered at $E_D$ as for carbon vacancies (in a treatment without second neighbor hopping [16]) but instead $\sim 200$ meV above $E_D$ [4,9,20]. This state, although weak, is observed by comparing ARPES for the clean and disordered sample obtained far from the $\pi$ bands [Fig. 2(e)]; it imposes another particle-hole symmetry breaking factor discussed later.
Quantum corrections

Random potential with TRS → described by 5 parameters:

- $\alpha_0$ (preserves all rotation ($C_{6v}$) symmetries)
- $\beta_z, \gamma_z$ (preserve $C_{3v}$ symmetry)
- $\beta_\perp, \gamma_\perp$ (preserve no symmetry)

$\beta_{z,\perp}$: induce intervalley scattering

$$\sigma = \frac{g_s e^2}{\hbar \pi^2} \left( \frac{\alpha_0}{2} + \beta_\perp + \gamma_\perp + \frac{3}{2} \beta_z + \frac{3}{2} \gamma_z \right)^{-1}$$

adsorbate scattering:

$$\alpha_0 = \gamma_z = \beta_\perp / 2 = \frac{A_c n_i |t_0(\varepsilon_F)|^2}{2\pi \langle v_k \varepsilon_F \rangle / \langle v_k^{-1} \varepsilon_F \rangle}, \quad \beta_z = \gamma_\perp = 0$$

- $\beta_\perp \gtrsim$ others indicates negative quantum corrections to $\sigma$.  

[McCann et al., PRL 97, 146805 (2006)]
Test: increase adsorbate concentration
Renormalization group

- resum corrections into renormalized parameters $\tilde{a}_0$ etc.
- here: follow formulation in abovementioned parameters
  [Ostrovsky, Gorny and Mirlin, PRB 74, 235443 (2006)]
- flow equations

\[
\begin{align*}
\dot{a}_0 &= 2a_0(a_0 + \beta_\perp + \gamma_\perp + \beta_z + \gamma_z) + \beta_\perp \beta_z + 2\gamma_\perp \gamma_z, \\
\dot{\beta}_\perp &= 4(a_0 \beta_z + \beta_\perp \gamma_\perp + \beta_z \gamma_z), \\
\dot{\beta}_z &= 2(a_0 \beta_\perp - \beta_z a_0 + \beta_\perp \gamma_z + \beta_z \gamma_z), \\
\dot{\gamma}_\perp &= 4a_0 \gamma_z + \beta_\perp^2 + \beta_z^2, \\
\dot{\gamma}_z &= 2\gamma_z(-a_0 - \beta_\perp + \beta_z + \gamma_\perp - \gamma_z) + 2a_0 \gamma_\perp + \beta_\perp \beta_z, \\
\dot{\epsilon} &= \epsilon(1 + a_0 + \beta_\perp + \gamma_\perp + \beta_z + \gamma_z),
\end{align*}
\]
- $\dot{X} \equiv dX/d\ln(L/a)$.
- integrate until $\epsilon$ reaches cutoff (bandwidth)
  (running length $L$ from $a$ to $\sim \lambda_F$)
Comparison to numerics

renormalization group

transport computations

(a)

(b)
Towards strong localization

Scaling theory: large systems should be insulating

Hydrogenated graphene

D. C. Elias et al
Science 323, 610 (2009)
Towards strong localization

Here:
Quasi-1d Nanoribbon
Onsite potential $V_0$, coverage $p$
exponential decay of conductance $g \sim \exp(-L/\xi)$

- Localization length $\xi$ can become very large
- Transient regime: ‘ballistic’ minimal conductivity
- Both happens away from the nominal Dirac point
average effect of adsorbates

Effective Dirac point shifted to

\[ \bar{V} = V_0 p \]

 Localization length diverges at effective Dirac point

\[ \xi = \frac{\pi \sqrt{3}}{4} \frac{t^3 W}{p(1-p) V_0^2 \rho^2 (\mu - \bar{V})} N_p, \]

Effective potential step induces evanescent modes

-> intrinsic pseudodiffusive regime
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Transport in graphene w/adsorbed molecules

- chemistry-dependent energy-dependent scattering
- strong coupling shifts resonance towards Dirac point
- transport asymmetric about Dirac point
- small impurity concentration: kinetic theory
- cumulative effect of many impurities: quantum corrections towards localization
- RG (quantitative agreement in perturbative regime)

- disorder-induced pseudodiffusion and localization

See also: PRL 101, 196803 (2008), PRB 79, 195413 (2009)