Many-body effects in graphene

Mikhail Katsnelson
Introduction: Graphene and massless Dirac fermions

Realistic interelectron interactions in graphene: mapping on pi-band and on effective Hubbard model

Is freely suspended graphene semimetal or excitonic insulator?

Screening and optical properties

Non-Fermi-liquid behavior in weak interaction regime

Many-body renormalization of ballistic conductivity at the neutrality point
Carbon, an elemental solid

Diamond

Graphite

Crystal lattices

Fullerenes

Nanotubes

Graphene
Mother of all graphitic forms

Fullerenes  Nanotubes  Graphite
Why graphene is interesting?

Till 2004: a way to understand graphite, nanotubes, fullerenes + theoretical interest (Dirac point Wallace 1947, McClure 1956…)

Do we theoreticians need experimentalists?! – Yes!!! (Klein tunneling, supercritical charge, ripples, new wave equation – bilayer, new type of transport…)

1. Applications (modern electronics is 2D, bulk is ballast)
2. Prototype membrane (new drosophila for 2D statistical mechanics)
3. CERN on the desk (mimic high energy physics)
Honeycomb lattice

Two equivalent sublattices, A and B (pseudospin)
Massless Dirac fermions

$sp^2$ hybridization, $\pi$ bands crossing the neutrality point

Neglecting intervalley scattering: massless Dirac fermions

Symmetry protected ($T$ and $I$)

Massless relativistic particles (light cones)

FIG. 2: (color online) Band structure of a single graphene layer. Solid red lines are $\sigma$ bands and dotted blue lines are $\pi$ bands.
Spectrum near $K (K')$ points is linear. Conical cross-points: provided by symmetry and thus robust property.
If Umklapp-processes K-K’ are neglected: 2D Dirac massless fermions with the Hamiltonian

\[
H = -i\hbar c^* \begin{pmatrix}
0 & \frac{\partial}{\partial x} - i \frac{\partial}{\partial y} \\
\frac{\partial}{\partial x} + i \frac{\partial}{\partial y} & 0
\end{pmatrix}
\]

\[\hbar c^* = \frac{\sqrt{3}}{2} \gamma_0 a\]

“Spin indices” label sublattices A and B rather than real spin
Massless Dirac fermions in condensed matter physics

1. d-wave superconductors
2. Vortices in superconductors and in superfluid helium-3
3. Topological insulators
4. Graphene

Gap in high-Tc cuprates

Electronic structure on surface of Bi$_2$Se$_3$
**Strength of Coulomb interactions in graphene**

Wehling, Şaşıoğlu, Friedrich, Lichtenstein, MIK & Blügel, PRL106, 236805 (2011)

**Generalized Hubbard model for π-bands only**

\[
\hat{H}_0 = -t \sum_{\langle i,j \rangle, \sigma} c_{i,\sigma}^\dagger c_{j,\sigma} - t' \sum_{\langle\langle i,j \rangle\rangle, \sigma} c_{i,\sigma}^\dagger c_{j,\sigma} + U_{00} \sum_i n_{i,\uparrow} n_{i,\downarrow} + \frac{1}{2} \sum_{i \neq j, \sigma, \sigma'} U_{ij} n_{i,\sigma} n_{j,\sigma'}
\]

All electrons except π contribute to screening of the Coulomb interactions (constrained RPA)

\[
P(r,r';\omega) = \sum_i \sum_j \psi_i(r) \psi_j^*(r') \psi_j^*(r) \psi_i(r')
\]

\[
\times \left\{ \frac{1}{\omega - \varepsilon_j + \varepsilon_i + i0^+} - \frac{1}{\omega + \varepsilon_j - \varepsilon_i - i0^+} \right\}
\]

π bands (blue) crossing Fermi level

σ bands (green) at higher energies

Polarization function
Strength of Coulomb interactions in graphene II

Static cRPA dielectric function of graphene in momentum space

Graphene vs graphite

<table>
<thead>
<tr>
<th></th>
<th>graphene</th>
<th>graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>bare</td>
<td>cRPA</td>
</tr>
<tr>
<td>$U_{00}^{A}$ (eV)</td>
<td>17.0</td>
<td>9.3</td>
</tr>
<tr>
<td>$U_{00}^{B}$ (eV)</td>
<td>17.0</td>
<td>9.3</td>
</tr>
<tr>
<td>$U_{01}$ (eV)</td>
<td>8.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>
Effective Hubbard model for graphene

Schüler, Rösner, Wehling, Lichtenstein & MIK, PRL 111, 036601 (2013)

Long-range Coulomb interaction is crucially important for graphene but not everywhere, e.g., for magnetism effective Hubbard model should be OK. How to build it?

We have:

\[ H = - \sum_{i,j,\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_{i \neq j, \sigma, \sigma'} V_{ij} n_{i\sigma} n_{j\sigma'} \]

We want:

\[ H^* = - \sum_{i,j,\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U^* \sum_i n_{i\uparrow} n_{i\downarrow} \]
Effective Hubbard model for graphene II

The idea: Feynman-Peirels-Bogoliubov variational principle

\[ \Phi^* = \frac{1}{\beta} \ln Z^* \]

\[ Z^* = \text{Tr} \{ e^{-\beta H^*} \} \]

\[ \rho^* = \frac{1}{Z^*} e^{-\beta H^*} \]

\[ \langle \ldots \rangle^* \text{ denotes the Gibbs average over the trial system} \]

\[ \partial_{U^*} \Phi[U^*] = 0 \]

\[ U^* = U + \frac{1}{2} \sum_{i \neq j} V_{ij} \frac{\partial U^* \langle n_{i\sigma} n_{j\sigma'} \rangle^*}{\sum_l \partial U^* \langle n_l \uparrow n_l \downarrow \rangle^*} \]

The calculations are done by lattice QMC
Effective Hubbard model for graphene III

For translationally invariant system:

\[ U^* = U - \bar{V} \]

\[ \bar{V} = - \sum_{j \neq 0, \sigma'} V_{0j} \frac{\partial U^* \langle n_0\uparrow n_{j\sigma'} \rangle^*}{\partial U^* \langle n_0\uparrow n_0\downarrow \rangle^*} \]

Number of particle conservation:

\[ \sum_{j\sigma} \langle n_0\uparrow n_{j\sigma} \rangle^* = N/2 \]

A naive estimation:

\[ U^* = U - V_{01} \]

turns out to be amazingly good
Figure 2. (Color online) Derivatives of the correlation functions $\langle n_{0\uparrow}n_{j\downarrow}\rangle$ with respect to $U^*$ for graphene (16x16 unit cells) calculated with DQMC for inverse temperature $\beta = 9t$ and $U = 2t$. Each circle corresponds to one carbon atom. The shaded area depicts the region of nearly vanishing derivatives. The cutoff radius is $r_c$. The thick drawn circles indicate the lattice site with index $i = 0$.

Table I. First three rows: Coulomb matrix elements obtained with cRPA ($t_{\text{graphene}} = 2.80$ eV, $t_{\text{silicene}} = 1.14$ eV, $t_{\text{benzene}} = 2.54$ eV). Last three rows: Effective local Coulomb matrix elements with and without the approximation that electrons are only displaced to next neighbors and the factor by which the local Coulomb interaction is decreased.

<table>
<thead>
<tr>
<th></th>
<th>Graphene</th>
<th>Silicene</th>
<th>Benzene</th>
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<tbody>
<tr>
<td>$U/t$</td>
<td>3.63</td>
<td>4.19</td>
<td>3.96</td>
</tr>
<tr>
<td>$(V_{01},V_{02})/t$</td>
<td>2.03, 1.45</td>
<td>2.31, 1.72</td>
<td>2.83, 2.01</td>
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<tr>
<td>$(V_{03},V_{04})/t$</td>
<td>1.32, 1.14</td>
<td>1.55, 1.42</td>
<td>1.80</td>
</tr>
<tr>
<td>$U^*/t$</td>
<td>$1.6 \pm 0.2$</td>
<td>$2.0 \pm 0.3$</td>
<td>$1.2$</td>
</tr>
<tr>
<td>$(U - V_{01})/t$</td>
<td>1.6</td>
<td>1.9</td>
<td>1.1</td>
</tr>
<tr>
<td>$U^*/U$</td>
<td>$0.45 \pm 0.05$</td>
<td>$0.46 \pm 0.05$</td>
<td>0.3</td>
</tr>
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</table>

Decrease of effective $U$ roughly by a factor of 2
Semimetal-insulator phase transition

M. Ulybyshev, P. Buividovich, MIK & M. Polikarpov, PRL111, 056801 (2013)

Lattice QMC simulations; Hubbard-Stratonovich transformation:

18 by 18 sites, 20 time slices, $T = 0.5$ eV
(should be improved in future!)

Neutrality point: $\mu = 0$

No sign problem (e-h symmetry)!
Semimetal-insulator phase transition II

The effect of screening by σ-bonds is essential. At our distances a factor 1.4

(1) Introduce the mass term $m$
(2) Chiral condensate $\Delta n$, difference in occupation number between A and B sublattices
(3) Introduce external dielectric constant (due to substrate) $\varepsilon$
Semimetal-insulator phase transition III

We are on semimetal side (screening by $\sigma$ bonds is crucial) but not too far from the transition point $\varepsilon \approx 0.7$

Exciton fluctuations may be important

FIG. 2: The dependence of the chiral condensate (11) on $\varepsilon$ and on $m$ (in the inset) for the $18 \times 18$ lattice with $N_t = 20$ and $\delta = 0.1$ eV$^{-1}$. For $\varepsilon = 1.0$ we show the results obtained on the $24 \times 24$ lattice with $N_t = 40$, $\delta = 0.05$ eV$^{-1}$. 
Effect of vacancies/adatoms: QMC

M. Ulybyshev & MIK, PRL 114, 246801 (2015)

Random missing sites equally distributed in two sublattices

AFM state with very strong exchange interactions
Effect of vacancies/adatoms II

For vacancies: clearly contradict experiments


Model of empty sites gives too strong antiferromagnetic exchange
Effect of vacancies/adatoms III

For fluorinated graphene: mostly no local moments (or very high AFM coupling between them)

Spin-half paramagnetism in graphene induced by point defects

R. R. Nair¹, M. Sepioni¹, I-Ling Tsai¹, O. Lehtinen², J. Keinonen², A. V. Krasheninnikov²,³, T. Thomson¹, A. K. Geim¹ and I. V. Grigorieva¹*

both scarce and controversial¹³-¹⁶. Here we show that point defects in graphene—(1) fluorine adatoms in concentrations x gradually increasing to stoichiometric fluorographene CFₓ₋ₓ=1.0 (ref. 17) and (2) irradiation defects (vacancies)—carry magnetic moments with spin 1/2. Both types of defect lead to notable paramagnetism but no magnetic ordering could be detected down to liquid helium temperatures. The induced paramagnetism dominates graphene’s low-temperature magnetic properties, despite the fact that the maximum response we could achieve was limited to one moment per approximately 1,000 carbon atoms. This limitation is explained by For vacancies: quite strong distortion, buckling etc., other electron states are involved
Quite noticeable gap in impurity band and much larger in K point for freely suspended graphene with 5% defects.
Renormalization of Fermi velocity

Coulomb interaction of 2D massless fermions
Zero doping (Fermi level at the Dirac point)
Logarithmic renormalization of the Fermi velocity due to Fock contribution

\[ \hat{H}_F = \sum \sum \psi^\dagger_{\alpha \chi}(\vec{k}) h_{\alpha \beta}(\vec{k}) \psi_{\beta}(\vec{k}) \]

\[ h_{\alpha \beta}(\vec{k}) = -2\pi e^2 \sum \frac{\rho_{\beta \alpha}(\vec{k}')}{|\vec{k} - \vec{k}'|} \]

\[ \rho_{\beta \alpha}(\vec{k}) = \langle \psi_{\tilde{k} \alpha}^\dagger \psi_{\tilde{k} \beta} \rangle \]

\[ \delta v_F = \frac{e^2}{4\hbar} \ln \left( \frac{\Lambda}{k_F} \right) \]

\( \Lambda \propto 1/a \) is the ultraviolet cut-off due to inapplicability of Dirac model at large wave vectors
**Renormalization of Fermi velocity II**

Many-body effects in graphene beyond the Dirac model with Coulomb interaction

N. Yu. Astrakhantsev, V. V. Braguta, and M. I. Katsnelson

Graphene on hBN, Coulomb interaction

\[ \frac{\nu_F^R(T)}{\nu_F^0} = \left(1 + A \log \left[ \frac{\Lambda}{\mu} \right] \right) \]

\[ A = 0.096, \ \Lambda = 3.2 \text{ eV} \]

Effect of screening is quite important

FIG. 11. (Color online) The renormalization factor for the Fermi velocity as a function of the temperature for graphene on hBN for Coulomb and screened at small distance Coulomb interactions [23].
Renormalization of Fermi velocity III


\[ \frac{1}{C} = \frac{1}{C_G} + \frac{1}{C_Q} \]

\[ C_Q = S e^2 \frac{dn}{d\mu} \]

Fitting

\[ v_F(\mu) = v_F(\mu_0) \left(1 + \frac{1}{4} \frac{\alpha}{\epsilon(v_F/c)} \log \left[ \frac{\mu_0}{\mu} \right] \right) \]

\[ = v_F(\mu_0) \left(1 + A \log \left[ \frac{\mu_0}{\mu} \right] \right), \]

\[ v_F(\mu_0) = 0.85 \times 10^6 \text{ m/s}, \quad \mu_0 = 3.2 \text{ eV} \]

\[ \epsilon \approx 8, \text{ and } A = 0.081 \]

Fig. 2. Quantum capacitance of graphene. (A) Differential capacitance in zero \( B \). Blue symbols are experimental data; green and red curves are the best fits with constant and renormalized \( v_F \), respectively. This particular device has \( d \sim 27 \text{ nm} \) and \( S \sim 250 \mu \text{m}^2 \). (B) Same data replotted in terms of \( v_F \) and carrier concentration \( n \); color coding as in A.
Optics

Single-particle result for the Dirac Fermions:

\[ P = \frac{W_a}{W_i} = \frac{\pi e^2}{\hbar c} = \pi \alpha \]

Fine Structure Constant Defines Visual Transparency of Graphene

R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, A. K. Geim

6 JUNE 2008 VOL 320 SCIENCE

No corrections within accuracy 3%
Do we expect renormalization? A controversial issue

For short-range interaction one expects no renormalization

Phenomelonogical theory of Fermi liquid:


Microscopic theory for Hubbard model:


For Coulomb interaction graphene is not Fermi liquid

$\alpha_{\text{eff}}$ logarithmically dependent on frequency

$\frac{\sigma(\omega)}{\sigma_0} = 1 + C \alpha_{\text{eff}} + O(\alpha_{\text{eff}}^2)$

Various ways of regularization gives $C = 0.01$, or $C=0.26$
Numerically: almost no renormalization in semimetal phase and strong renormalization in AFM insulator phase.
Static screening

Quantum Monte Carlo study of electrostatic potential in graphene

N. Yu. Astrakhantsev, V. V. Braguta, M. I. Katsnelson, A. A. Nikolaev, and M. V. Ulybyshev

RPA (lowest order) result:

\[ \epsilon = 1 + \frac{\pi}{2} \alpha_{\text{eff}} \]

No small parameters, how good is it?

Second-order result:

\[ \alpha_{\text{eff}} = \alpha \cdot c / v_F \sim 300 / 137 \sim 2.2 \]


Corrections are significant!
Monte Carlo simulations: put two point charges, calculate effective interaction energy,

Zero-temperature results
Perturbative (RPA) result fits very well the QMC despite the absence of any explicit small parameter

<table>
<thead>
<tr>
<th>$r/a$</th>
<th>$\varepsilon(r)$</th>
<th>$\varepsilon_{1\text{loop}}(r)$</th>
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</thead>
<tbody>
<tr>
<td>0.00</td>
<td>2.24 $\pm$ 0.02</td>
<td>2.19</td>
</tr>
<tr>
<td>1.00</td>
<td>2.83 $\pm$ 0.08</td>
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<tr>
<td>1.73</td>
<td>3.45 $\pm$ 0.21</td>
<td>3.49</td>
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<tr>
<td>2.00</td>
<td>3.33 $\pm$ 0.23</td>
<td>3.63</td>
</tr>
<tr>
<td>2.65</td>
<td>3.86 $\pm$ 0.49</td>
<td>4.05</td>
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<td>3.00</td>
<td>3.89 $\pm$ 0.66</td>
<td>4.11</td>
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<td>3.46</td>
<td>3.97 $\pm$ 0.88</td>
<td>4.22</td>
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<tr>
<td>3.61</td>
<td>3.84 $\pm$ 0.80</td>
<td>4.26</td>
</tr>
<tr>
<td>4.00</td>
<td>4.01 $\pm$ 1.15</td>
<td>4.35</td>
</tr>
</tbody>
</table>
Quantum-Limited Resistivity

no temperature dependence in the peak between 3 and 80K

$E = 0$

zero-gap semiconductor

Novoselov et al, Nature 2005

$\rho_{\text{max}}$ (h/4e$^2$)

$\mu$ (cm$^2$/Vs)

15 devices
Transport via evanescent waves

Conductance = $e^2/h \text{ Tr } T$ per valley per spin

$T$ is the transmission probability matrix

The wave functions of massless Dirac fermions at zero energy:

$$
\psi_\pm(x, y) = f(x \pm iy)
$$

Boundary conditions determine the functions $f$
Transport via evanescent waves II

\[ f(y + L_y) = f(y) \]

Edge states near the top and bottom of the sample

New type of electron transport: via evanescent waves – different from both ballistic and diffusive

\[ \psi_\pm(x, y) = \exp\left[ \frac{2\pi n}{L_y} (x \pm iy) \right] \quad n = 0, \pm 1, \pm 2, \ldots \]
Transport via evanescent waves III

Leads from doped graphene

\[ T_n = |t(k_y)|^2 = \frac{\cos^2 \phi}{\cosh^2(k_y L_x) - \sin^2 \phi} \]

\[ \sin \phi = k_y / k_F \]

\[ T r T = \sum_{n=-\infty}^{\infty} \frac{1}{\cosh^2(k_y L_x)} \approx \frac{L_y}{\pi L_x} \]

Conductivity per channel:

\[ e^2 / (\pi h) \]

The problem of “missing pi(e)” – may be, no problem
Many-body renormalization

F. Guinea & MIK, PRL 112, 116604 (2014)


Overlap of the wave functions are suppressed by overlap of the wave functions of environment (then, averaging over the environment)

Transport via evanescent waves is tunneling

Nonlocal self-interaction

e-h pairs as thermal bath
Many-body renormalization II

Correction to the effective tunneling action

\[ \delta S = \frac{1}{2} \int_{-\infty}^{+\infty} d\tau \int_0^\beta d\tau' \int_{-\infty}^{+\infty} dq \int_{-\infty}^{+\infty} d\omega \, e^{iq[x(\tau)-x(\tau')-\omega|\tau-\tau'|]} W(q, \omega) \]

Screened Coulomb interaction

\[ W(q, \omega) = \frac{\nu_q}{\epsilon(q,\omega)} \]

Bare Coulomb interaction

\[ \nu_q \approx \begin{cases} -\frac{2e^2}{\epsilon_0} \log(qL_y) & qL_y \ll 1 \\ \frac{2\pi e^2}{\epsilon_0 qL_y} & 1 \ll qL_y \end{cases} \]

For undoped graphene

\[ \epsilon(q, \omega) = 1 + \nu_q \chi_{1D}(q, \omega) \]

\[ \chi_{1D}(q, \omega) \approx L_y \chi_{2D}(q, \omega) \approx L_y \frac{q^2}{4 \sqrt{v_F^2 q^2 - \omega^2}} \]
Many-body interaction III

Suppression of tunneling probability

\[ T(k_y) \approx T_0(k_y) e^{-\delta S} \]

\[ \delta S_G \approx \frac{L_x}{8\pi L_y} \frac{\alpha^2}{4\sqrt{2} + \alpha} \log \left( \frac{L_x}{a} \right) \]

for isolated graphene

In the presence of metallic layer:

\[ g = k_F \ell \]

\[ \chi_{1D}^M (q, \omega) \approx \begin{cases} \frac{u_{1D} D q^2}{i\omega + D q^2} & q \leq \ell^{-1} \\ \frac{u_{1D} v_F^M q}{i\omega + v_F^M q} & \ell^{-1} \leq q \leq k_F \end{cases} \]

\[ \delta S_M = \delta S_d + \delta S_b \approx \frac{L_x^2}{4\pi g \ell L_y} + \frac{L_x}{8\pi L_y} \log(g) \]
At finite temperatures the cut-off wave vector

\[ q_c \approx \text{Max}(L_x^{-1}, T / v_F) \]

Magnetic field effects on diffusion!

**FIG. 2.** Temperature dependence of the inverse conductance, normalized to the non interaction value, \( \sigma_0 = e^2 / (\pi h) \), for \( L_x = 4\mu \), \( L_y = 1\mu \). Red: Contribution from the graphene excitations, \( \delta S_G \), eq. 6. Blue: Contribution from a metallic layer, \( \delta S_M \), eq. 8. The two terms which describe the contribution from the metal, \( \delta S_d \) and \( \delta S_b \) are shown in the inset. Green: diffusive part, \( \delta S_d \) in eq. 8. Magenta: ballistic part, \( \delta S_b \) in eq. 8. The carrier density in the metal is \( n = 10^{11} \text{cm}^{-1} \), and the elastic mean free path is \( \ell = 100\text{nm} \).
A recent experiment

Insulating Behavior at the Neutrality Point in Single-Layer Graphene

F. Amet, J. R. Williams, K. Watanabe, T. Taniguchi, and D. Goldhaber-Gordon

Also, graphene on hBN

Power-law behavior with temperature

\[ g_{CNP} \propto T^\alpha \text{ with } \alpha \approx 0.48 \pm 0.05 \]
Conclusions

Nonlocal interaction, no small parameters, still a lot of open questions

Main collaborators

A. Geim, K. Novoselov  (Manchester)
F. Guinea  (Madrid & Manchester)
A. Lichtenstein  (Hamburg)
T. Wehling  (Bremen)
M. Ulybyshev  (Regensburg)
V. Braguta, N. Astrakhantsev  (Moscow)

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