Quantum capacitance and compressibility of graphene: The role of Coulomb interactions

Yu.E. Lozovik,1,2,3,4 † A.A. Sokolik,1,2 † and A.D. Zabolotskiy1,3

1 Institute for Spectroscopy, Russian Academy of Sciences, 142190 Troitsk, Moscow, Russia
2 MIEM at National Research University HSE, 109028 Moscow, Russia
3 All-Russia Research Institute of Mathematics, 127055 Moscow, Russia
4 Moscow Institute of Physics and Technology, 141700 Dolgoprudny, Moscow region, Russia

Many-body effects on quantum capacitance, compressibility, renormalized Fermi velocity, kinetic and interaction energies of massless Dirac electrons in graphene, induced by the Coulomb interactions, are analyzed theoretically in the first-order, Hartree-Fock and random phase approximations. Recent experimental data on quantum capacitance and renormalized Fermi velocity are analyzed and compared with the theory. The bare Fermi velocity and the effective dielectric constants are obtained from the experimental data. A combined effect of Coulomb interactions and Gaussian fluctuations of disorder potential is considered.

PACS numbers: 73.22.Pr, 71.10.-w, 71.45.Gm, 73.21.-b

I. INTRODUCTION

Discovery of graphene, a two-dimensional carbon material with effectively massless electrons, stimulated new fundamental and applied studies in solid state physics [1–3]. In recent years, a considerable attention has been attracted by the problem of compressibility and quantum capacitance of graphene, which is connected both with the fundamental aspects of the physics of Coulomb-interacting gas of massless electrons and with possible applications of graphene in electronics and energy storage technologies.

In the early experiments [4, 5] on graphene electron compressibility, the results consistent with the model of non-interacting Dirac electron gas were reported. Linear dispersion and chirality of graphene electrons were proposed as a possible cause of the apparent absence of electron interactions signatures [5].

The recent experiments [6, 7] on measuring the electron compressibility or quantum capacitance in high-quality graphene samples revealed signatures of electron interactions, in consistency with the many-body calculations [8–13] of these quantities. The observed interaction-induced effects are closely related to the logarithmic renormalization of the electron Fermi velocity in graphene in vicinity of the charge neutrality point (CNP), which was observed by different experimental groups [14–18] and considered in theoretical literature (see [19], the reviews [20–22] and cited literature in [23]).

Random potential, arising in real graphene samples due to charged impurities and corrugations, manifests itself in formation of electron-hole puddles [21, 22] and qualitatively changes graphene physics at low carrier densities near CNP. The disorder has been proposed to be the source of observed nonvanishing compressibility and quantum capacitance of graphene at CNP [8, 22–29]. The model of Gaussian fluctuations of the disorder potential was successfully used to describe the experimentally measured dependencies of compressibility and quantum capacitance on electron density [23, 25–29]. Random phase approximation with polarizability, modified by disorder, was used to calculate the compressibility in [12].

In the present article, we perform a theoretical study of the quantum capacitance and related properties of graphene in the presence of Coulomb interactions in the first-order approximation (FOA), Hartree-Fock approximation (HFA) and random phase approximation (RPA). In order to obtain the bare Fermi velocity $v_F$, we analyze the recent experimental data on quantum capacitance and renormalized Fermi velocity [6–8, 18]. Influence of Coulomb interactions on quantum capacitance, renormalized Fermi velocity (see Sec. [III] for its definition) as well as kinetic and interaction energies of electron gas in graphene is studied in FOA, HFA and RPA. A combined effect of Coulomb interaction and disorder on these quantities is studied within the model of the Gaussian fluctuating electrostatic potential.

We show that both HFA and RPA are in close agreement with the experiments at $v_F \approx 0.9 \times 10^6$ m/s, although HFA requires much larger effective dielectric constants of surrounding media to simulate the screening, lacking in this approximation. The influence of Coulomb interactions on the electron gas properties has two major features: the exchange effects push the Fermi velocity to higher values and the quantum capacitance to the lower values; the correlations effects partly compensate the exchange ones. The renormalized Fermi velocity is enhanced up to 50% at lowest achievable densities near CNP and on 10–20% away from CNP. The quantum capacitance typically reduces by 10–15%, although it can be described in the non-interacting model with $v_F \approx 1.1 \times 10^6$ m/s. In the presence of the disorder, a nonzero quantum capacitance appears at CNP, in agree-
II. THEORETICAL MODELS

We start with the description of an electron gas in graphene in terms of a grand canonical ensemble when temperature $T$, chemical potential $\mu$ and area of the system $S$ are the controlling parameters. Physically this corresponds to a flake of graphene, brought in contact with a conductor, specifying $\mu$. At these conditions, the system tends to an equilibrium, where the thermodynamic potential $\Omega = E - T\mathcal{S} - \mu N$ attains the minimum ($E$ and $\mathcal{S}$ are the internal energy and entropy of the electron gas, $N$ is the mean number of electrons in the system). The electron surface density, or concentration, $n = N/S$, is given by

$$n = -\frac{1}{S} \frac{\partial \Omega}{\partial \mu}. \tag{1}$$

Compressibility $\kappa$ and quantum capacitance per unit area $C_Q$ can be calculated as:

$$\kappa = \frac{1}{n^2} \frac{dn}{d\mu}, \quad C_Q = e^2 \frac{dn}{d\mu} \tag{2}$$

(sometimes the quantity $d\mu/dn$ is referred to as inverse compressibility $\frac{1}{\kappa}$).

In the noninteracting system, the thermodynamic potential $\Omega_0$ in the $T \to 0$ limit is:

$$\Omega_0 = g \sum_{p\gamma} (\epsilon_{p\gamma} - \mu) f(\epsilon_{p\gamma}), \tag{3}$$

where $\epsilon_{p\gamma} = \gamma_v|p|$ is a one-particle energy of an electron in graphene with the momentum $p$ in the conduction or valence band at $\gamma = \pm 1$ respectively; $v_F$ is the bare Fermi velocity; $g = 4$ is the degeneracy factor over spin and valleys; and $f(\epsilon) = \Theta(\mu - \epsilon)$ is the occupation number for a state with energy $\epsilon$ at $T \to 0$, where $\Theta(x)$ is the unit step function.

The electron density in the noninteracting graphene is determined through (1) and (3) as:

$$n_0(\mu) = \text{sgn}(\mu) \frac{\hbar v_F^2}{4\pi^2} \tag{4}$$

($\hbar \equiv 1$). Here $\mu$ is measured from CNP, and $n$ is measured from the background electron density of the filled valence band; thus $n$ is positive or negative in, respectively, electron- or hole-doped graphene.
The Hartree-Fock approximation, providing more accurate results than FOA, can be obtained by “dressing” the electron Green functions in Fig. 1a with the exchange self-energy parts. Unfortunately, as is known [34], one cannot simply replace the bare Green functions in the closed diagrams by the Hartree-Fock ones, because this would result in overcounting of the diagrams. In fact, in order to obtain HFA, starting from the grand canonical ensemble, we need to calculate the infinite series of diagrams with the bare Green functions, depicted in Fig. 2, with each diagram having a numerical prefactor, dependent on its symmetry.

To overcome this difficulty, we can calculate $\Omega$ by means of the Luttinger-Ward functional [40], where all excess diagrams, appearing in the “overcounted” thermodynamic potential, are exactly compensated by a simple means of the Luttinger-Ward functional [40], where all dependence on its symmetry.

The occupation numbers $\delta \Omega_{\text{HF}} = g \sum_{p'\gamma} \left( \epsilon_{p'\gamma} + \frac{\Sigma_{p'\gamma}^{(\text{HF})}}{2} - \mu \right) f(\epsilon_{p'\gamma} + \Sigma_{p'\gamma}^{(\text{HF})})$, (9)

where the Hartree-Fock self-energy is

$$\Sigma_{p'\gamma}^{(\text{HF})} = - \frac{1}{2} \sum_{p'\gamma} V_{p'pF} \gamma_{p'\gamma} f(\epsilon_{p'\gamma} + \Sigma_{p'\gamma}^{(\text{HF})})$$

The occupation numbers $f(\epsilon_{p'\gamma} + \Sigma_{p'\gamma}^{(\text{HF})})$, entering into these equations, drop from 1 to 0 at the Fermi surface, where $p = p_F$, $\gamma = \text{sgn}(\mu)$. Applying (11) to (10) and subtracting the background electron density, we obtain the electron density in HFA:

$$n_{\text{HF}}(\mu) = g \sum_{p'\gamma} \left[ f(\epsilon_{p'\gamma} + \Sigma_{p'\gamma}^{(\text{HF})}) - \Theta(-\epsilon_{p'\gamma}) \right].$$

In fact, the expressions (10)–(11) depend on $p_F$, rather than on $\mu$, therefore it is more convenient to find the Fermi momentum $p_F$ from the equation

$$\mu = \epsilon_{p_F, \text{sgn}(n)} + \delta \Omega_{\text{HF}}$$

and then use Eq. (11), rewritten in the form:

$$n_{\text{HF}}(\mu) = g \sum_{p'\gamma} \frac{\epsilon_{p'\gamma}}{4\pi}.$$

Here we used the equality $\Sigma_{p'\gamma}^{(\text{HF})} = \Sigma_{p'\gamma}^{(1)}$, following from (7) and (12). Solving (12)–(13) and integrating $n_{\text{HF}}(\mu)$ according to (11), we can restore the thermodynamic potential in HFA.

The calculations in (9)–(13) may appear rather formal, especially in the light of similarity of (4) and (13), but they demonstrate the essential difference between the first-order and the Hartree-Fock approximations: the latter is self-consistent, which means that it actually takes into account an infinite series of Feynman diagrams (Fig. 2) and deals with the renormalized electron dispersion $\epsilon_{p\gamma} + \Sigma_{p\gamma}^{(\text{HF})}$ instead of $\epsilon_{p\gamma}$.

The random phase approximation for calculating $\Omega$ becomes asymptotically exact in the limit $g \to 0$ of large electron state degeneracy. It was also argued that RPA dominates in graphene because of taking into account all diagrams with infrared divergences [44]. Recently applicability of RPA has been confirmed by quick convergence of expansion in RPA-screened interaction [45]. The sum of diagrams for $\delta \Omega$ in this approximation, shown in Fig. 3 is (see also [11]):

$$\delta \Omega_{\text{RPA}} = \frac{1}{2} \sum_q \left\{ T \sum_{k_q} \ln \left[ 1 - V_q \Pi_q(i\omega_k) \right] - n V_q \right\},$$

where $\omega_k = 2\pi n^2 k$ are bosonic Matsubara frequencies. The polarizability of electron gas in graphene $\Pi_q(\omega)$ was calculated explicitly at real [46] and imaginary [11] frequencies.

It is useful to separate (14) into the first-order exchange part (5) and the correlation part $\delta \Omega_{\text{corr}}$. In order to obtain analytical results, we expand $\delta \Omega_{\text{corr}}$ in powers of $1/\Lambda$ up to $\Lambda^{-2}$:

$$\delta \Omega_{\text{corr}} = \left( \frac{1}{4} \epsilon^2 v_F \right) \left\{ a(\alpha_{gr}) \ln \Lambda + \frac{b(\alpha_{gr})}{\Lambda ^2} \right\},$$

where $\alpha_{gr} = ge^2/\epsilon v_F$. The functions $a(\alpha_{gr})$, $b(\alpha_{gr})$ and $c(\alpha_{gr})$, being smooth, can be easily tabulated and approximated in the physically accessible range $0 \leq \alpha_{gr} \leq \Lambda^{-2}$. 

![FIG. 2: The closed connected diagrams for $\delta \Omega$ in the Hartree-Fock approximation.](image1)

![FIG. 3: The closed connected diagrams for $\delta \Omega$ in the random phase approximation.](image2)
Venezuela and the author who is responsible for this analysis. The authors gratefully acknowledge support from the National Science Foundation, Grant No. 1052357.
The data on $v_F(n)$, presented in [8], demonstrate strong asymmetry and anomalous behavior near CNP, which are not commented by the authors. We suggest a possible explanation of this anomaly that some nonzero charge is present on graphene even at zero voltage due to impurities or parasitic external voltage. This excess charge appears as an integration constant in the right hand side of (13).

Assuming the additional charge density, equivalent to the electron density $\Delta n = -1.5 \times 10^6$ cm$^{-2}$ and recalculating the dependence $v_F^\ast(n)$, we managed to improve substantially agreement between the experiment [8] and our theoretical curves, shown in Fig. 5(a). The both approximations reproduce the experimental points fairly well.

In [18] a graphene sample, placed on a hBN layer on top of oxidized silicon, was studied with the scanning tunneling spectroscopy in magnetic field. The electron and hole renormalized Fermi velocities were extracted from Landau level energies at different points of the sample, appearing in electron and hole puddles. The authors fit the dependence $v_F^\ast(n)$ by an approximate RPA formula, using the effective background dielectric constant $\varepsilon = (1 + 5.3)/2 \approx 3.15$, which originates as a half-sum of the dielectric constants of air and hBN-SiO$_2$ substrate layer. Our fittings of the data from [18], based on this dielectric constant, are shown in Fig. 5(b).

The work [8] is focused mainly on electron-hole asymmetry, however measurements of the quantum capacitance were carried out there on high-quality graphene samples in the experimental setup, very similar to that in [6]. The results of the fitting, based on the hBN dielectric constant $\varepsilon = 4.5$, are shown in Fig. 6(a).

In the work [8] the inverse compressibility $\kappa^{-1}$ as a function of electron density was measured in graphene samples on SiO$_2$ substrate, covered by Y$_2$O$_3$ insulating layer. The data at $|n| < 0.3 \times 10^{12}$ cm$^{-2}$ were excluded from our analysis because of disturbing effects of disorder, appreciable at these concentrations.

The authors of [8] adopt $v_F = 0.957 \times 10^6$ m/s from [18] and use the effective dielectric constant $\varepsilon = (3.9+4.38) = 4.14$ to reproduce the measured $\kappa^{-1}$ with the first-order expression, similar to [19]. We replotted the data on $\kappa$ in terms of the quantum capacitance $C_Q$ (see [2]) and show our fits, based on $\varepsilon = 4.14$, in Fig. 6(b).

Comparing the values of $\varepsilon$ in Table I obtained from RPA and HFA analysis of the experimental data [6,8,18], we see that in the latter case $\varepsilon$ is larger by 4.5–5.5 (except the case of [7], where it is larger by 9.5 by unknown reason). This difference, however, exceeds that following from the simple estimate $\varepsilon_{\text{eff}} = \varepsilon + \pi g e^2/8v_F \approx \varepsilon + 3.46$, based on a static interband screening [17].

One can also note the anomalously high values of $v_F$, obtained by fitting the data from [8]. Even within the authors’ theoretical model, the best agreement with the experimental data is achieved at $v_F = 1.115 \times 10^6$ m/s, while the estimate $v_F = 0.957 \times 10^6$ m/s, taken in [8], provides the values of $\kappa^{-1}$, which are smaller than the experimental ones. Perhaps the source of this anomaly is underestimated classical capacitance, used to extract the compressibility from total capacitance.

Lastly, the quantum capacitance $C_Q$, in contrast to $v_F$, does not qualitatively change its dependence on $n$ when interactions are switched on (see Fig. 6(a) in the next section). As a consequence, the experimental points on $C_Q$ can be well described by the noninteracting dependence $C_Q = \varepsilon^2 g \sqrt{|n|} / \pi v_F^2$ with $v_F = 1.104 \times 10^6$ m/s, $\varepsilon = 4.5$ for [6] and $v_F = 1.496 \times 10^6$ m/s, $\varepsilon = 4.14$ for [8] (see Fig. 6).

IV. MANY-BODY EFFECTS OF COULOMB INTERACTIONS ON CHARACTERISTICS OF ELECTRON GAS

To calculate the quantum capacitance and the renormalized Fermi velocity of the electron gas in graphene, we choose the value $v_F \approx 0.9 \times 10^6$ m/s of the bare Fermi velocity, consistent with the most of the data in Table II. We also take three characteristic values of the background dielectric constant, controlling an interaction strength: $\varepsilon = 1$ (suspended graphene), $\varepsilon = 4.5$ (graphene, en-
capsulated in hBN) and $\varepsilon = 8$ (graphene in a strongly screening environment).

To get an additional insight into the results, we calculate the kinetic $E_{\text{kin}}$ and Coulomb interaction $E_{\text{int}}$ energies of the electron gas, which can be found on the basis of the grand canonical ensemble as: $E_{\text{kin}} = n_F(\partial \Omega / \partial n_F)$, $E_{\text{int}} = e^2(\partial \Omega / \partial e^2)$. These energies, calculated for ideal Dirac electron gas and for interacting gas in different approximations, are shown in Fig. 7. Quantum capacitance and renormalized Fermi velocity, calculated in the same manner, are shown in Fig. 8. FOA provides reasonable results only in a weak-interacting regime ($\varepsilon \gg 1$), thus its results are not shown at $\varepsilon = 1$. Even at $\varepsilon = 4.5$ it shows such artifacts as multiple-valuedness of $E_{\text{kin}}(n)$, $E_{\text{int}}(n)$, $\mu(n)$ and negative compressibility and $C_Q$ near CNP.

In contrast to a usual electron gas with negative exchange energy, the electron exchange self-energy in graphene is positive due to electron chirality. Therefore the exchange effects in graphene tend to increase $v_F^*$, as seen in Fig. 8(a) in FOA and HFA. As a consequence, $C_Q$ becomes smaller (Fig. 8(b)), because this quantity reflects an effective density of states, which decreases as $v_F^*$ increases (note that the interaction-induced change in $C_Q$ can be essentially diminished by a proper choice of the fitting parameter $v_F$ within the non-interacting model, as seen in Fig. 8).

For the same reason, the interaction energy $E_{\text{int}}$, consisting of exchange energies of individual electrons, is positive in FOA and HFA (Fig. 7(b)). The kinetic energy $E_{\text{kin}}$ decreases in FOA due to decreasing density (Fig. 7(a)). In HFA it does not change in comparison with the non-interacting regime at the same density, because the ground state wave function is the same Slater determinant in the both cases. Generally HFA provides more plausible and moderate results than FOA even at $\varepsilon \gg 1$, which indicates an importance of the self-consistent treatment of the interactions.

The difference between RPA and FOA results demonstrates the correlation effects. As is known, in the correlated electron liquid electrons tend to be located farther from each other in comparison with the mean field picture, thus the interaction energy decreases. At the same time, the kinetic energy increases because of this additional correlated motion. The both of these effects are seen in Fig. 8. From the other point of view, the correlations partly compensate the exchange effects.

**FIG. 7:** Kinetic (a) and interaction (b) energies of electron gas in graphene, calculated as functions of electron density $n$ at different dielectric constants $\varepsilon$ in the noninteracting regime (dotted line) and in the first-order (dash-dotted line), Hartree-Fock (dashed line) and random phase (solid line) approximations.

**FIG. 8:** Quantum capacitance $C_Q$ (a) and renormalized Fermi velocity $v_F^*$ (b), calculated as functions of electron density $n$ at different dielectric constants $\varepsilon$ in the noninteracting regime (dotted line) and in the first-order (dash-dotted line), Hartree-Fock (dashed line) and random phase (solid line) approximations.

**FIG. 9:** The same quantities as in Fig. 8 calculated as functions of the average electron density $\langle n \rangle$ in the Gaussian disorder potential with the spread $s = 50$ meV.
V. DISORDER

A random disorder potential $V(r)$, arising in graphene sample due to substrate charge impurities and corrugations, leads to formation of a spatially varying electron density pattern, emerging as electron and hole puddles near CNP. Typical size of the puddles, observed in recent experiments, is 10–20 nm. Thus the local density approximation, proposed and used to calculate compressibility and quantum capacitance of disordered graphene, is applicable at carrier densities $|n| > 10^{11} \text{ cm}^{-2}$, where $p_F^{-1} \lesssim 15 \text{ nm}$. In this approximation we assume that the local chemical potential $\mu_{\text{loc}}(r)$ is established in each region of graphene sample in such a way so that the total electrochemical potential $\mu = V(r) + \mu_{\text{loc}}(r)$ is constant throughout the sample. Following [23, 29, 31, 33], we assume the Gaussian distribution of areas such regions:

$$\rho(V) = \frac{1}{\sqrt{2\pi}s} e^{-V^2/2s^2}.$$  \hspace{1cm} (20)

Thus the experimentally observed electron density in graphene sample can be calculated as a spatial average of the local densities $n(\mu_{\text{loc}}) = n(\mu - V)$:

$$\langle n(\mu) \rangle = \int \rho(V)n(\mu - V) \, dV.$$ \hspace{1cm} (21)

The spread $s$ in [21] can be related to an average charge carrier density $|n|$ at $T \to 0$, calculated from (21)–(20) at CNP: $\langle |n| \rangle = s^2/\pi v_F^2$. The values of $s$, reported in the experiments with graphene on SiO$_2$ [1-3, 10, 21, 23, 26, 28, 29] and other substrates [22, 27], or calculated from the corresponding residual carrier density, range from 10 to 130 meV. Therefore we assume $s = 50 \text{ meV}$ for a typical disorder strength. Similar values are considered in theoretical works [30, 34].

The quantum capacitance and renormalized Fermi velocity, calculated with taking into account disorder by replacing $n(\mu)$ in (2) and (17) with $\langle n(\mu) \rangle$, are shown in Fig. 5. The major effect of the disorder on $C_Q$ is its smearing, leading to appearance of a nonzero $C_Q$ at CNP, where $C_Q = 0$ in the clean limit (see Fig. 5(a)). At the same time, $v_F^* \approx \sqrt{n}$ implies $\langle n \rangle \propto n^{1/2}$, so that $v_F^* \propto |\mu|^{1/2} \propto \langle |n| \rangle^{1/2}$. Perhaps this can explain the anomalous dip of $v_F^*$ at CNP, observed in [3].

VI. CONCLUSIONS

We have considered the many-body effects of Coulomb interactions on observable quantities of graphene as quantum capacitance $C_Q$, compressibility $\kappa$ and renormalized (thermodynamic) Fermi velocity $v_F^*$. Three approximations (FOA, HFA and RPA) are analyzed and applied for massless Dirac electrons. The recent experimental data on $v_F^* \approx 0.9 \times 10^6\text{ m/s}$ was obtained as the result of the least square fitting. The same experimental data can be described by HFA as well, but with larger values of the background dielectric constant that simulates the screening, absent in this approximation.

Our main conclusions, concerning the influence of Coulomb interactions on $C_Q$, $v_F^*$ and kinetic and interaction energies of the electron gas in graphene, are the following:

a) Kinetic energy increases in RPA in the presence of interactions due to correlated motion of electrons.

b) Interaction energy is positive due to positive exchange energy (as opposed to usual electron gas) [48], while it somewhat reduces in RPA due to the correlations, which partly compensate the exchange.

c) The very demonstrative effect of the interactions is the renormalization of $v_F^*$ to higher values, most prominent near CNP. In RPA, $v_F^*$ increases by 50% at lowest achievable carrier densities $n \sim 10^9\text{ cm}^{-2}$ and on 10–20% at moderate densities $n \sim 10^{11–10^{12}}\text{ cm}^{-2}$.

d) The quantum capacitance $C_Q$ decreases in the presence of interactions by 10–15% due to effective reduction of the density of states at higher $v_F^*$. However, generally it changes only quantitatively, retaining the same form $C_Q \propto \sqrt{n}$ as in the noninteracting model. That is why experimentally measured $C_Q$ and $\kappa$ are often successfully described in the noninteracting model [4, 23, 24, 26, 28, 29, 31, 33, 51], but with the higher Fermi velocity $v_F^* \approx 1.1 \times 10^6\text{ m/s}$.

The considered theoretical models can be easily generalized to take into account a disorder fluctuating potential in the local density approximation. Calculations of $C_Q$ in the model of Gaussian fluctuations with the typical spread 50 meV show a formation of nonzero $C_Q$ at CNP, in agreement with the experiments. On the contrary, $v_F^*$ acquires a dip at CNP, which can even override the logarithmic interaction-induced peak.

Finally we can note that the studies of graphene quantum capacitance are important for its electronic applications, because $C_Q$ dominates in the case of ultrathin oxide layer between graphene and a gate (see, e.g., [51–53]). In this case an additional screening by the metallic gate electrode can essentially affect the many-body corrections to $C_Q$, as considered in [49].

The work of A.D.Z. was supported by RFBR, and the work of Y.E.L. and A.A.S. was supported by the HSE Basic Research Program.
