Density dependent exchange contribution to $\partial \mu/\partial n$ and compressibility in graphene

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(Dated: January 17, 2022)

We calculate $\partial \mu/\partial n$ (where $\mu =$ chemical potential and $n =$ electron density), which is associated with the compressibility, in graphene as a function of $n$, within the Hartree-Fock approximation. The exchange-driven Dirac-point logarithmic singularity in the quasiparticle velocity of intrinsic graphene disappears in the extrinsic case. The calculated renormalized $\partial \mu/\partial n$ in extrinsic graphene on SiO2 has the same $n^{-\frac{1}{2}}$ density dependence but is 20% larger than the inverse bare density of states, a relatively weak effect compared to the corresponding parabolic-band case. We predict that the renormalization effect can be enhanced to about 50% by changing the graphene substrate.

PACS numbers: 81.05.Uw, 71.70.Gm; 71.10.-w; 71.18.+y

The band structure of graphene (a single layer of carbon atoms), by dint of its honeycomb lattice, has linear dispersions near the $\mathcal{K}$ and $\mathcal{K}'$ points (“Dirac points”) of the Brillouin zone. Recent developments in techniques for fabricating conducting graphene layers have thus provided the physics community with a unique opportunity to study an interacting two-dimensional (2D) massless Dirac fermion system using table-top experimental equipment. This has led to a veritable explosion of both experimental and theoretical activity in this field.\[1]\]

Around the Dirac points (which we take to be the zero of energy), the kinetic energy for a “bare” electron (see below) is $\varepsilon_{k,s}(0) = s v_0 |k|$, where $k$ is the wavevector with respect to the Dirac point, and $s = +1$ and $-1$ for the conduction and valence bands, respectively. The electron chemical potential $\mu$, which in intrinsic graphene is at zero, can be shifted up or down by doping and/or application of external gate voltages, with a concommitant change in the electron density. This paper reports the calculation of $\partial \mu/\partial n$, which is related to the electronic compressibility, in extrinsic graphene at temperature $T = 0$ as a function of the density $n$. [In this paper, unless otherwise indicated, partial derivatives are at constant area and $T = 0$, and $n$ refers exclusively to the free carrier density (i.e., the difference in electron density from that of intrinsic graphene) in the gated graphene, which we take to be substantially less ($|n| \sim 10^{12}$ cm$^{-2}$) than the intrinsic electron density $n_{cv} (> 10^{15}$ cm$^{-2}$) filling up the valence band.] We obtain $\mu(n)$ by evaluating the electron self-energy within the Hartree-Fock approximation (HFA). The HFA is a good approximation up to reasonably high values of $r_s$ ($\sim$ the ratio of the average carrier potential to kinetic energy) in parabolic-band semiconductors, and we expect it to also give reliable results in graphene, where $r_s < 1$.

It is useful (and conceptually meaningful) to divide 2D graphene into three different systems depending on the band filling: bare or empty, a theoretical abstraction of just one electron in the graphene honeycomb lattice as appropriate for the single-particle band-structure calculation with both valence and conduction bands completely (and unphysically) empty, or equivalently, the unphysical situation where the interaction between the electrons is turned off; intrinsic, i.e., the undoped and ungated situation, which is a zero-gap semiconductor with a completely full (empty) valence (conduction) band and chemical potential $\mu (= E_F)$, since we are at $T = 0$ precisely at the Dirac point; extrinsic, i.e., gated/doped graphene with a tunable 2D free carrier density $n$ of electrons (holes) in the conduction (valence) band, with $\mu$ being above (below) zero, i.e. in the conduction (valence) band. Note that only the empty system can be characterized by the bare, noninteracting parameters (e.g., velocity $v_0$, density of states $D_0$) with both intrinsic and extrinsic graphene being characterized by renormalized parameters. We emphasize that the bare graphene parameters, being unphysical abstractions, cannot be experimentally determined.

In the absence of interaction, $\partial \mu/\partial n$ is just the inverse of the bare or non-interacting single-particle density of states at the Fermi level: $(\partial n/\partial \mu)_0 \equiv D_0(E_F) = \sqrt{g}(\sqrt{\pi} v_0)$, where $v_0$ is the bare graphene carrier velocity associated with the linear energy dispersion, and $g(=4)$ is the product of the spin ($g_s = 2$) and valley ($g_v = 2$) degeneracies of the graphene carriers. This implies that $\partial \mu/\partial n$ in graphene is a direct measurement of the thermodynamic Fermi velocity renormalization due to electron–electron interaction effects. (This should be distinguished from the quasiparticle Fermi velocity renormalization, as discussed later.) Our goal here is to theoretically calculate the renormalized $\partial \mu/\partial n$ in intrinsic and extrinsic graphene including exchange interaction effects, or equivalently in the HFA, which should be an excellent quantitative approximation in 2D graphene. Our calculated carrier density dependence of $\partial \mu/\partial n$ can be directly compared to experimental measurements in extrinsic graphene.
The exchange self energy is given by [2]

\[ \Sigma_{x,s}(k) = - \sum_{q\neq s'} n_F(\xi_{k-q,s'}) V_c(q) F_{s's}(k,k-q), \]

where \( s, s' = \pm 1 \) are the band indices, and since we assume \( T = 0 \), the fermi function \( n_F(\xi) = 0 \) or 1 for \( \xi \equiv \epsilon - \mu \) less than or greater than 0, respectively. \( V_c(q) = 2\pi e^2/(qs) \) is the bare coulomb potential (\( \kappa \) is the background dielectric constant in the graphene layer).

\[ F_{s's}(k,k') = (1 + ss'\cos\theta_{kk'})/2 \]

arises from the wavefunction overlap factor, where \( \theta_{kk'} \) is the angle between \( k \) and \( k' \). We assume that the valence band is cut off at the wavevector \( k_c \) with respect to the Dirac point. The ultra-violet regularization associated with the wavevector cut-off at \( k_c \) happens at a very large wavevector, comparable to the lattice wavevector; \( k_c \sim 1A^{-1} \). Within the HFA, \( \mu = \xi_{k_c,s} + \Sigma_{x,s,k}(F) \), where \( k_F = (4\pi|n|/g)^{2/3} \) is the Fermi wavevector.

We separate the exchange self-energy into contributions from the intrinsic electrons, \( \Sigma_{x}^{\text{int}} \), and the extrinsic carriers, \( \Sigma_{x}^{\text{ext}} \). That is, \( \Sigma_{x,s,k} = \Sigma_{x}^{\text{int}}(k) + \Sigma_{x}^{\text{ext}}(k) \), where

\[ \Sigma_{x}^{\text{int}}(k) = - \sum_{q} V_c(q) F_{s,-}(k,k-q); \]

\[ \Sigma_{x}^{\text{ext}}(k) = \sum_{s s' q} \delta n_F(\xi_{k-q,s'}) V_c(q) F_{s's}(k,k-q); \]

where \( \delta n_F(\xi_{k-q,s'}) = n_F(\xi_{k-q,s'}) - \frac{1}{2}(1-s') \) is the difference in the electron occupation from the intrinsic T = 0 case. Evaluating the integrals, we obtain

\[ \Sigma_{x}^{\text{int}}(k) = \frac{e^2 k_c}{\pi \kappa} \left[ - f \left( \frac{k}{k_c} \right) + s h \left( \frac{k}{k_c} \right) \right], \]

\[ \Sigma_{x}^{\text{ext}}(k) = \frac{e^2 k_F}{\pi \kappa} \left[ + f \left( \frac{k}{k_F} \right) - s h \left( \frac{k}{k_F} \right) \right], \]

where \( f(x) \) and \( h(x) \) are the complete elliptic integral of the first and second kinds, respectively [3]. Note that the \( T = 0 \) exchange self-energy for a regular parabolic-band two-dimensional electron gas (2DEG) is [3] \( \Sigma_{x}^{\text{ext}}(k) = \frac{2e^2 k_F}{\pi \kappa} f \left( \frac{k}{k_F} \right) \). At \( T = 0 \), \( \Sigma_x(k) \) does not depend on the band-structure away from the Fermi surface (since \( n_F \) is either 1 or 0 for \( \xi < 0 \) and \( \xi > 0 \) respectively, independent of the details of the band-structure) and therefore the only difference between \( \Sigma_x(k) \) for the parabolic-band case and and the intraband contribution for graphene is the difference in the wavefunction overlap factor \( F_{s's}(k,k') \).

This accounts for presence of the \( f(k/k_F) \) in both the \( T = 0 \) expressions for \( \Sigma_{x}^{\text{ext}}(k) \) and \( \Sigma_{x}^{\text{int}}(k) \).

First, we examine the intrinsic self-energy, \( \Sigma_{x}^{\text{int}}(k) \), which is independent of the carrier density \( n \). Since we are interested in the states around the Dirac point, the argument of the functions \( f \) and \( h \) in Eq. (3a), \( k/k_c \ll 1 \). For small \( x \), \( f(x) = E(x) \approx \frac{x}{2} - O(x^2) \), and \( h(x) \approx x(\frac{1}{8} \log(\frac{1}{8}) - \frac{3}{8}) + O(x^3) \) (in Eq. (4), the integrand \( y^3 [K(y) - E(y) - \frac{3}{8}y^2] \sim y \) as \( y \to 0 \), and therefore the integral \( \sim x^2 \) for small \( x \). Therefore,

\[ \Sigma_{x}^{\text{int}}(k) = \frac{e^2}{\kappa} \left\{ - \frac{k_c}{2} + s \frac{k}{4} \left[ \log \left( \frac{4k_c}{k} \right) - \frac{1}{2} + O \left( \frac{k}{k_c} \right) \right] \right\}, \]

The term \(-e^2 k_c/(2\kappa)\) in Eq. (6) simply shifts energy zero and can be ignored. The other terms renormalize the quasiparticle velocity. Ignoring terms of order \( k/k_c \), the renormalized quasiparticle velocity is [4, 7]

\[ v_{\text{int}}(k) = \frac{\partial [e_{\text{ext}}(0) + \Sigma_{x}^{\text{int}}(k)\}]}{\hbar \partial k} = v_0 \left[ 1 + r_{\text{ext}}(0) \frac{1}{4} \log \left( \frac{k_c}{k} \right) \right], \]

where \( k_c = 4e^{-\frac{1}{2}} k_c \approx 0.9k_c \) and \( r_{\text{ext}}(0) = e^2/(\hbar k v_0) \). Experimental measurements of the quasiparticle velocity in intrinsic graphene will yield \( v_{\text{int}} \) (in the absence of phonon coupling), and not the bare velocity \( v_0 \), which applies only for the unrealistic situation of a completely empty valence-band. This situation is analogous to the quantum electrodynamics calculation of the self-energy of a bare electron. The bare electron charge and mass of the theory are never observed. Instead, experimentally one sees the scale-dependent renormalized charge and mass, which include effects of the electron self-energy. The logarithmic dependence of the intrinsic graphene velocity is probably difficult to observe because of the smallness of the prefactor \( r_{\text{ext}}(0)/4 \approx 0.2 \) for graphene mounted on a SiO2 substrate with one side exposed to air (hence, the effective \( \kappa \) in the graphene layer is the average of the \( \kappa \) of air and SiO2, \( \approx 2.5 \)). To see clearly the logarithmic dependence in Eq. (7), \( k \) must be varied over a fairly wide range. Furthermore, the logarithmic divergence in \( v_{\text{int}}(k) \) at \( k \to 0 \) occurs only in the intrinsic graphene, and not in the extrinsic case.

In extrinsic graphene, \( k_F \neq 0 \). For \( k/k_F \ll 1 \), the small \( x \) expansions for \( f(x) \) and \( h(x) \) in Eq. (3a) yield

\[ \Sigma_{x}^{\text{ext}}(k) = \frac{e^2}{\kappa} \left\{ + \frac{k_F}{2} + s \frac{k}{4} \left[ \log \left( \frac{4k_F}{k} \right) - \frac{1}{2} + O \left( \frac{k}{k_F} \right) \right] \right\}, \]

(8)

(where \( \mp \) is for \( \mu \geq 0 \)). The log \( (k) \) term in \( \Sigma_{x}^{\text{ext}}(k \to 0) \) cancels the equivalent term in \( \Sigma_{x}^{\text{int}}(k \to 0) \), so the sum, \( \Sigma_{x,s}(k) = \Sigma_{x}^{\text{ext}}(k) + \Sigma_{x}^{\text{int}}(k) \), has a finite derivative at
k = 0, and the renormalized velocity in the extrinsic case, \( v_{\text{ext}}(k = 0) = v_0 \left[1 + \frac{\pi^2}{4} \log \left(\frac{k}{k_F}\right)\right]\), has no \( k \to 0 \) logarithmic divergence.

Fig. 1 shows \( \Sigma_{k}^{\text{ext}}(k) \) for graphene with \( \mu > 0 \) and, for comparison, \( \Sigma_{k}^{\text{pb}}(k) \). At \( k = k_F \) (and \( \mu > 0 \)),

\[
\Sigma_{k}^{\text{ext}}(k_F) = \frac{1}{2} \left[1 + s \left(C - \frac{1}{2}\right)\right] \Sigma_{k}^{\text{pb}}(k_F),
\]

where \( C \approx 0.916 \) is Catalan’s constant, and \( \Sigma_{k}^{\text{pb}}(k_F) = -\pi^2 k_F/(\pi \kappa) \). As in the case of \( \Sigma_{k}^{\text{ext}}(k) \) for graphene with \( \mu > 0 \) has a logarithmic divergence as \( k \to k_F \) from both the \( f(x) \) and \( h(x) \) terms in Eq. (3b). We expect that the logarithmic divergence in \( d \Sigma_{k}^{\text{ext}}(k_F)/dk \) will disappear when correlation effects are included, as in the case of the parabolic-band \( \Sigma_{k}^{\text{pb}} \). Note that this logarithmic divergence has no singular pathological effect on \( \partial \mu/\partial n \), the quantity of interest in this work, and is irrelevant for our purpose. The \( \Sigma_{k}^{\text{ext}} \) has a finite derivative at \( k = k_F \), because for an electron-doped sample there is no Fermi surface at \( k = k_F \) in the valence band.

We now discuss the effect of the exchange self-energy on \( \partial \mu/\partial n \). In a regular parabolic-band 2DEG with mass \( m \), \( \left(\frac{\partial \mu}{\partial n}\right)^{\text{pb}}_0 = \frac{2\hbar^2 e^2}{m g_0 \kappa} \) is density independent. When interactions are included this picture changes due to exchange and correlation effects of the Coulomb potential. Within the HFA, which neglects correlation effects, \( \left(\frac{\partial \mu}{\partial n}\right)^{\text{pb}}_0 \) is

\[
\left(\frac{\partial \mu}{\partial n}\right)^{\text{pb}}_0 \left(1 - \frac{\pi^2}{4} r_s^{\text{pb}}\right),
\]

where \( r_s^{\text{pb}} = \sqrt{2\varepsilon^2 m/(\kappa k_F)} \propto n^{-\frac{1}{2}} \).

Thus, \( \partial \mu/\partial n \) becomes negative at low enough densities. Measurements of \( \partial \mu/\partial n \) in two-dimensional electron and hole gases have confirmed this behavior. The observed change of sign in \( \partial \mu/\partial n \) comes mainly from the exchange contribution to the total energy. It is known that the correlation corrections to \( \partial \mu/\partial n \) beyond the HFA is not very large (\(< 20\%\) [9]), even at the reasonably large effective \( r_s \) (\(> 1\)) values at which the 2D semiconductor experiments have typically been carried out.

What is the contribution of exchange on \( \partial \mu/\partial n \) in graphene? Using \( k_F = \sqrt{\pi |n|} \), together with \( \mu_s(k_F) = \epsilon_{\text{F},s}^{(0)} + \Sigma_{k}^{\text{int}}(k_F) + \Sigma_{k}^{\text{ext}}(k_F) \), and Eq. (4) gives

\[
\frac{\partial \mu}{\partial n}_{\text{ext}} = \frac{\sqrt{\pi}}{2\sqrt{|n|}} \left[h v_0 + \frac{e^2}{\kappa} \left\{1 + \left(\frac{1}{4} \log \left(\frac{k}{k_F}\right) - C + \frac{1}{2}\right)\right\}\right]
\]

\[
= \left(\frac{\partial \mu}{\partial n}\right)_{\text{int}} \left[1 - \frac{C + \frac{1}{2}}{\pi} r_s^{\text{int}}\right],
\]

where \( r_s^{\text{int}} = \frac{e^2}{(\kappa h v_F^2)} \) [here, \( v_F^0 \equiv v_{\text{int}}(k_F) \)] and \( (\partial \mu/\partial n)_{\text{int}} = \left(h v_F^{\text{int}}/\sqrt{\pi}\right)/(2\sqrt{|n|}) \) is the inverse of the density of states for intrinsic graphene. This shows that in extrinsic graphene, the exchange effect changes \( \partial \mu/\partial n \) from the bare value \( (\partial \mu/\partial n)_0 \), by a factor of \( r_s^{(0)} \left\lfloor\frac{1}{4} \log \left(\frac{k}{k_F}\right) - \pi^{-1}(C + \frac{1}{2})\right\rfloor \), or from the intrinsic value \( (\partial \mu/\partial n)_{\text{int}} \) by a factor of \( -\pi^{-1}(C + \frac{1}{2}) r_s^{\text{int}} \). Thus, \( (\partial \mu/\partial n)_{\text{ext}} \) is enhanced over \( (\partial \mu/\partial n)_0 \) by \( \approx 0.25 r_s^{(0)} \) \((n = 10^{12} \text{ cm}^{-2})\), but reduced from \( (\partial \mu/\partial n)_{\text{int}} \) by a factor of \( \approx -0.45 r_s^{\text{int}} \). If we take single-particle band-structure graphene velocity \( v_0 \approx 10^6 \text{ cm/s} \), we get \( r_s^{(0)} \approx 0.9 \) for SiO\(_2\) mounted graphene, giving an exchange enhancement of approximately 20% over the bare \( (\partial \mu/\partial n)_0 \); see Fig. 2(a). Estimating the change with respect to \( (\partial \mu/\partial n)_{\text{int}} \) is a little trickier because \( r_s^{\text{int}} \), which depends on the intrinsic graphene velocity \( v_F^0 \), is unknown since the intrinsic graphene velocity is at present unknown! An approximate way to estimate the intrinsic \( r_s^{\text{int}} \) is to change \( \kappa \to \kappa' \) where \( \kappa' \) is the effect of the background screening by the filled valence band [10], with \( \kappa' = 1 + \frac{\pi}{2} d_{gr} r_s^{(0)} \approx 2 \), which gives \( r_s^{\text{int}} \approx r_s^{(0)}/2 \), leading to around a 20% decrease of \( (\partial \mu/\partial n)_{\text{ext}} \) with respect to \( (\partial \mu/\partial n)_{\text{int}} \). The extrinsic \( \partial \mu/\partial n \) depends on \( \kappa \), as shown in Fig. 2(b), but unlike the parabolic band case, for experimentally relevant parameters \( (\partial \mu/\partial n)_{\text{ext}} \) does not change sign. By using freely suspended graphene (i.e., \( \kappa = 1 \)), the many body renormalization can be enhanced to around 50%.

In the literature, \( \partial \mu/\partial n \) is often associated with the term “compressibility,” defined as \( K \equiv -V^{-1}(\partial V/\partial P)_{T,N} \), where \( N \) is particle number, \( V \) is the system volume/area, \( P \equiv -(\partial F/\partial V)_{T,N} \) is the pressure, and \( F \) is the Helmholtz free energy. It can be shown that \( K^{-1} = n^2(\partial \mu/\partial n) \), where \( n = N/V \).

In experimental papers on the compressibility of electron gases, the quantity that is measured is not actually the compressibility (after all, experimentalists do not physically compress the electron gas and measure the change in pressure) but \( \partial \mu/\partial n \), which is then converted to \( K^{-1} \) by multiplication of \( n^2 \). In graphene, it is in fact ambiguous which \( n \) should be used — (a) the free carrier density or (b) the density of the electrons in the
The free carrier density plus to think of \( \frac{\partial \mu}{\partial n} \) as providing a measurement of the exchange contribution to the Fermi liquid parameter \( F_s \). We believe that correlation, neglected in our Hartree-Fock theory, would introduce only small quantitative corrections to our calculated results, particularly because of the relatively small values of \( r_s \) (< 1) in graphene. Thus, our Fock exchange approximation for graphene \( \frac{\partial \mu}{\partial n} \) should quantitatively be an excellent approximation. Disorder would also introduce only small quantitative corrections except at low extrinsic carrier densities \( \langle |n| \rangle \lesssim 5 \times 10^{11} \text{cm}^{-2} \) associated with the so-called “minimal graphene conductivity” regime, where random charged impurities in the substrate introduce inhomogeneous electron/hole puddles in the graphene layer which would lead to random spatial variations in \( \frac{\partial \mu}{\partial n} \) over 5 – 20 nm (10 – 100 meV) length (energy) scales. Finally, finite temperature would have little effect on our results because \( E_F > 1000 \text{K} \) in the usual density range of experimental interest \( \gtrsim 5 \times 10^{11} \text{cm}^{-2} \).

This work is supported by US-ONR and LPS-NSA.

Note added: After submission of this manuscript, we received a preprint reporting an experimental observation of the exchange contribution to \( \frac{\partial \mu}{\partial n} \) that is consistent with our theory.

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