Vacuum Polarization and Screening of Supercritical Impurities in Graphene

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Screening of charge impurities in graphene is analyzed using the exact solution for vacuum polarization obtained from the massless Dirac-Kepler problem. For the impurity charge below certain critical value no density perturbation is found away from the impurity, in agreement with the linear response theory result. For supercritical charge, however, the polarization distribution is shown to have a power law profile, leading to screening of the excess charge at large distances. The Dirac-Kepler scattering states give rise to standing wave oscillations in the local density of states which appear and become prominent in the supercritical regime.

Massless Dirac excitations in graphene[1] provide an interesting realization of quantum electrodynamics (QED) in dimension two[2]. Because of zero mass and strong interactions, characterized by a large “fine structure constant” \( \alpha = \frac{e^2}{\hbar v_F} \approx 2.5 \), where \( v_F \approx 10^6 \) m/s is the Fermi velocity, this material breaks away from the perturbative QED paradigm. One of the phenomena fundamental in QED, expected to become ultrastrong in graphene, is “vacuum polarization” induced by charge impurities. Scattering on charge impurities features prominently in transport properties of graphene, where it is believed to be the leading factor limiting electron mobility[3,4,5], providing an explanation for the conductivity[6] linear in the carrier concentration. Although the problem of Coulomb scattering by charge impurities received a lot of attention[3,4,5,7,8,9], the key question of screening of the impurity potential outside the weak coupling regime has not been adequately addressed[3,4].

Here we present an accurate nonperturbative treatment of this problem based on the vacuum polarization found from the exact solution of the 2d Dirac-Kepler problem. There are two qualitatively different regimes emerging from this solution, which are somewhat analogous to those known in QED of heavy and superheavy atoms[11]. The Coulomb potential of subcritical charge (2) within the annulus \( \rho_1 < \rho < \rho_2 \) equals \( \delta Z = -N \beta^2 \ln(\rho_2/\rho_1) \), which leads to the RG equation

\[
\gamma = \frac{\beta^2}{4}, \quad \beta > \beta_c.
\]

Integrating the flow (3) we find that it terminates at a distance \( \rho_* = \rho_0 \exp(\frac{N e^2}{\pi \alpha \hbar v_F} \cosh^{-1}(2 \beta)) \) where \( \beta \) reaches the critical value \( \beta_c \). In contrast to screening in metals, here the polarization build-up brings the net charge down to the critical value \( \beta_c \), that remains unscreened at larger distances \( \rho \gtrsim \rho_* \). The RG treatment is applicable when the RG flow is slow, i.e., when the right-hand side of Eq. (3) is small. Thus the RG framework is adequate near the criticality, \( \beta \approx \beta_c \), where \( \gamma \) is small, even in the case of strong coupling, \( e^2/\alpha \hbar v_F \sim 1 \), and the predicted termination of screening at large \( \rho \) is universal.

Our treatment of vacuum polarization relies on the exact solution of the Dirac-Kepler problem from which we
extract scattering phases and use them in the Friedel sum rule framework to evaluate the screening charge. The phases are found to behave differently for $\beta < \beta_c$ and $\beta > \beta_c$. In the first case, the essential part of the phase is $\beta \ln k \rho$, while in the second case it is $\beta \ln k \rho - \gamma \ln \beta \ln k r_0$. It is important to realize that the term $\beta \ln k \rho$ is the same for all angular momentum channels. Such a contribution to the phase, as Ref. [12] insightfully remarks, arises from quasiclassical dynamics at large distances, and thus has nothing to do with scattering. In agreement with this, we find that it does not contribute to polarization at finite $\rho$, while the term $-\gamma \ln \beta \ln k r_0$ gives rise to the power law in $\rho$.

Now we turn to the analysis of the massless Dirac equation in dimension two in a central potential $V(\rho)$:

$$\hbar v_F \begin{pmatrix} 0 & -i \partial_x - \partial_y \\ -i \partial_x + \partial_y & 0 \end{pmatrix} \psi = (\varepsilon - V(\rho)) \psi.$$  (4)

Introducing polar coordinates $x + iy = \rho e^{i \varphi}$, we separate angular harmonics of the two-component wave function $\psi$, and seek the solution in the form [20]

$$\psi(\rho, \varphi) = \begin{pmatrix} w(\rho) + v(\rho) \\ (w(\rho) - v(\rho)) e^{i \varphi} \end{pmatrix} e^{i m \varphi} e^{i k \rho},$$  (5)

with integer angular quantum number $m$. The terms $w$ and $v$ represent the incoming and outgoing waves. The parameters $s$ and $k$ are determined by the behavior at small and large $\rho$. For $V(\rho) = Ze^2 / \rho$, we find

$$s = \sqrt{(m + \frac{1}{2})^2 - \beta^2}, \quad k = -\frac{\varepsilon}{\hbar v_F},$$  (6)

where $\beta$ is the dimensionless coupling [14]. (The minus sign in [12] is chosen to make $k > 0$ in the Fermi sea.) The solution [3] behaves differently for $|\beta| < |m + \frac{1}{2}|$, when the exponent $s$ is real, and $|\beta| > |m + \frac{1}{2}|$, when $s$ becomes complex imaginary.

The ansatz [3], substituted into Dirac equation, yields coupled equations for the functions $w(\rho)$ and $v(\rho)$:

$$\rho \partial_\rho w + (s + i \beta - 2ik \rho) w - (m + \frac{1}{2}) v = 0,$$  (7)

$$\rho \partial_\rho v + (s - i \beta) v - (m + \frac{1}{2}) w = 0.$$  (8)

We eliminate $w$ and, after introducing a new independent variable $z = -2ik \rho$, obtain a hypergeometric equation

$$z v'' + (2s + 1 - z) v' - (s - i \beta) v = 0.$$  (9)

The solution regular at $z = 0$ is given by the confluent hypergeometric function [13]\

$$v(z) = A \Gamma_1 F_1 (s - i \beta, 2s + 1, z),$$  (10)

$$w(z) = A \frac{s - i \beta}{m + \frac{1}{2}} \Gamma_1 F_1 (s + 1 - i \beta, 2s + 1, z),$$  (11)

where $A$ is a normalization factor. The expression for $w$ was obtained using Eq. [5] and an identity for $\Gamma_1 F_1$ [14].

The solution [5], [10], [11] of the Dirac-Kepler problem, regular at $\rho = 0$, can be used to evaluate the polarization charge in the subcritical case $|\beta| < 1/2$. This can be done most easily using the scattering phases, given by the behavior of $w$ and $v$ at large $\rho$. Using the asymptotic form of the functions $\Gamma_1 F_1$, we find

$$v(\rho) = \frac{\lambda e^{i \beta \ln(2k \rho)}}{(2k \rho)^{s}}, \quad w(\rho) = \frac{\lambda^* e^{-i \beta \ln(2k \rho)} e^{-2ik \rho}}{(2k \rho)^s},$$  (12)

where the parameter $\lambda$ depends on $m$ and $\beta$ but not on $k$. From [12] we see that $\rho^{s - \frac{1}{2}} w(\rho) \exp(i k \rho)$ and $\rho^{s - \frac{1}{2}} v(\rho) \exp(i k \rho)$ indeed describe the incoming and the outgoing waves, characterized by relative phase

$$v/w = e^{2ik \rho \delta_m(k) + 2ik \rho}, \quad \delta_m(k) = \beta \ln(2k \rho) + \arg \lambda.$$  (13)

The log dependence in Eq. [13] is typical for the phase coming from 1/r Coulomb tail [12).

The scattering phases $\delta_m(k)$ can be used to find the polarization charge pulled on the origin. However, a straightforward application of the Friedel sum rule [10], [17], involving phases evaluated at the Fermi level, encounters a difficulty due to the position and energy dependence of the phases in Eq. [13]. Since this may indicate that the polarization is distributed rather than localized at $\rho = 0$, we proceed with caution.

To evaluate the excess particle number $Q_{pol}(\rho)$ in the interval $0 \leq \rho' < \rho$, we note that the states with wavelength greater than $\rho$, i.e. $|k| \lesssim 1/\rho$, contribute negligibly to $Q_{pol}(\rho)$. Thus we can write the sum rule [10], [17] as

$$Q_{pol}(\rho) \approx -\frac{N}{\pi} \sum_m \delta_m(k \sim 1/\rho),$$  (14)

where the minus sign corresponds to that in Eq. [6]. Conveniently, the expressions [13] for $\delta_m(k)$, valid at $k \rho \gtrsim 1$, can be used to evaluate [14]. However, since $\delta_m(k)$ depend on the product $k \rho$, they yield a $\rho$-independent result for $Q_{pol}(\rho)$. We therefore conclude that the polarization charge is concentrated on the lattice scale $\rho \approx r_0$.

To independently verify the conclusion about polarization at $\beta < 1/2$ concentrated at $\rho \lesssim r_0$ we evaluated it directly using the eigenstates given by Eqs. [5], [10], [11]. This calculation involves an energy cutoff introduced at the bottom of graphene band, corresponding to $k \approx r_0^{-1}$. We found nonvanishing contribution to polarization charge only on the cutoff scale, leading to an expression $n_{pol}(\rho) = -q_0 \delta_0(\rho)$ (the second term in Eq. [7]). This form of polarization charge can be independently justified by the RPA method [4], [9], giving $q_0 = \frac{2}{3} \beta$. Our numerical results at $0 < |\beta| \lesssim 1$, presented in Fig. II yield a very similar dependence, nearly linear at $|\beta| < \frac{1}{2}$, independently confirming the above analysis.

The behavior of the scattering phase and of the polarization charge changes when the potential strength $|\beta|$ exceeds $|m + \frac{1}{2}|$ for one or several values of $m$. For such
supercritical $\beta$ Eq. (10) is not the only possible solution. Adding another solution of the equation (9), we write the function $v(z)$ in the form

$$v(z) = A_1 F_1(i(\gamma - \beta), 1 + 2i\gamma, z) + B z^{-2i\gamma} F_1(-i(\gamma + \beta), 1 - 2i\gamma, z),$$

where $\gamma = \text{Im} s = \sqrt{\beta^2 - (m + \frac{1}{2})^2}$, and $z = -2ik\rho$. With the help of the relation (14) we find

$$w(z) = -i A \eta_1 F_1(1 + i\gamma - i\beta, 1 + 2i\gamma, z) - i(B/\eta) z^{-2i\gamma} F_1(1 - i\gamma - i\beta, 1 - 2i\gamma, z),$$

where $\eta = \sqrt{\beta - \gamma}$. ($\eta \eta_1 = \frac{1}{\sqrt{2}}$).

To find the relation between $A$ and $B$ we consider our solution at small distances, $\rho \approx r_0 \ll 1/k$:

$$v(\rho) \approx A + Be^{-\gamma e^{-2i\rho}\ln(2k\rho)},$$

$$w(\rho) \approx -i A \eta - i(B/\eta) e^{-\gamma e^{-2i\rho}\ln(2k\rho)}.$$ (18)

Without loss of generality we use the boundary condition $\psi_2(\rho = r_0) = 0$, which enforces zero wavefunction on one of the graphene lattice sites. (Similar boundary condition was used to describe graphene zigzag edge in the Dirac equation framework [13, 14]). Solving the equation $v(r_0) = w(r_0)$, we find the relation

$$B = e^{i\chi(k)} \eta e^{\gamma A}, \quad e^{i\chi(k)} = -i\frac{1 - i\eta}{1 + i\eta} e^{2i\gamma \ln 2kr_0}.$$ (19)

The product $kr_0$ is very small for typical $k$, making the phase factor $e^{i\chi(k)}$ a rapidly oscillating function of $k$.

To better understand the role of the second solution, let us take another look at the subcritical case, $|\beta| < |m + \frac{1}{2}|$, when the parameter $s$, Eq. (19), is real. In this case, two independent solutions are still provided by Eqs. (15), (16), whereby $i\gamma$ is replaced by $s$. Applying the boundary conditions the same way as above, instead of (19) we find $B/A \propto (2kr_0)^{2s} \ll 1$, which indicates that the second solution plays no role in the subcritical case.

To link $\chi(k)$, Eq. (19), to the scattering phase, we write our solution for $v(\rho)$, $w(\rho)$ at large distances $\rho k \gg 1$, again using the asymptotic expression for $F_1$ [15],

$$\frac{v}{w} = \frac{g_{\beta,\gamma} + e^{\pi e^{-\gamma} \eta g_{\beta,\gamma}} e^{2ik\rho e^{i\beta} \ln(2k\rho)}}{e^{-\gamma} g_{\beta,\gamma} + e^{\gamma} g_{\beta,\gamma}},$$ (20)

where $g_{\beta,\gamma} = \Gamma(1 + 2i\gamma) \Gamma(1 + i\gamma + i\beta)$. We note that (20) automatically satisfies the current conservation requirement $|v| = |w|$. The relative phase of $v$ and $w$, defined as in Eq. (13), thus equals

$$\delta_n(k) = \theta(k) + \beta \ln 2k\rho + \arg g_{\beta,\gamma},$$ (21)

where

$$\theta(k) = \arg \left[ e^{-\frac{1}{2} \chi(k)} + ae^{\frac{1}{2} \chi(k)} \right], \quad a = e^{-\pi e^{-\gamma} \eta g_{\beta,\gamma}} g_{\beta,\gamma}.$$ (22)

The last two terms of the phase (21) are identical in form to (13). They represent spherical wave “deformed” by the tail of Coulomb potential at large distances and, as we discussed above, give no contribution to polarization charge at finite $\rho$. The term $\theta(k)$, however, arising from the boundary condition at small $\rho$ via the phase $\chi = \arg(B/A)$, Eq. (19), makes the behavior completely different from that found for $|\beta| < |m + \frac{1}{2}|$. The phase $\theta(k)$ dependence on $k$, arising via the phase $\chi(k)$, is quite peculiar. To understand the relation $\theta$ vs. $\chi$, we find the winding number of $\theta(k)$ that depends on

$$|a| = \sqrt{\frac{e^{-2\gamma \chi(k)} - e^{-2\pi\gamma}}{e^{2\pi\gamma} - e^{-2\rho \gamma}}} = \begin{cases} < 1 & \text{if } \beta > 0, \\ > 1 & \text{if } \beta < 0. \end{cases}$$ (23)

(We recall that $0 < \gamma < |\beta|$.) The phase $\theta$ winding is thus controlled by the first term of (22) at $\beta > 0$ and by the second term at $\beta < 0$, allowing us to write it as

$$\theta(k) = -\text{sign} \beta \frac{\chi(k)}{2} + \Delta \theta(k),$$ (24)

where $\Delta \theta$ is an oscillatory periodic function of $\chi$.

It is instructive to compare the behavior of $\Delta \theta(k)$ at strongly overcritical and nearly critical $\beta$. For large $|\beta|$ we have $\gamma \approx |\beta|$ and $|a| \approx e^{-2\gamma \gamma}$, and thus the oscillatory part $\Delta \theta$ is exponentially small:

$$\Delta \theta(k) \approx \text{sign} \beta e^{-2\gamma \gamma} \sin(\arg a - \chi(k)).$$ (25)

In the opposite limit of nearly critical $\beta = \beta_c = \pm |m + \frac{1}{2}|$, we expand $|a|$ in $\gamma$, which is small in this case, to find

$$|a| = 1 - \xi, \quad \xi = \frac{2\pi \gamma}{1 - e^{-2\beta \gamma}} + O(\gamma^2).$$ (26)

In this case $\theta$, as a function of $\chi$, is a staircase

$$\theta = \frac{\xi}{2} - \arctan \left( \xi \tan \frac{\chi + \xi}{2} \right), \quad \zeta = \arg a,$$ (27)
with steps of height $\pi$, width $2\pi$, and corners rounded on the scale $\xi$. The staircase slope $-\frac{1}{\pi}$ sign $\beta$ corresponds to the first term in Eq. (22). The oscillatory part $\Delta n(\kappa)$ manifests itself in the local density of states around the impurity (see peak in the $\varepsilon < 0$ region in Fig.2 inset).

To analyze the contribution of the phase $\varphi(\kappa)$ to the polarization density, we suppress the periodic part $\Delta n$. Substituting it in the Friedel sum rule, Eq. (14), we find

$$Q_{\text{pol}}(\rho) = -N\frac{n_0(\kappa = 1/\rho)}{\pi} = -\pi \beta \gamma/N \ln \frac{\rho}{2\pi r_0} \quad (28)$$

From $n_{\text{pol}}(\rho) = \left(2\pi\rho\right)^{-1}dQ_{\text{pol}}/d\rho$, we find the polarization density (2). When the parameter $\beta$ is complex in more than one channel, one has to consider a sum

$$n_{\text{pol}}(\rho) = \frac{N \pi \gamma}{2\pi^2 \rho^2} \sum_{m + \frac{1}{2} < |\beta|} \sqrt{\beta^2 - (m + \frac{1}{2})^2} \quad (29)$$

For large $\beta \gg 1$, replacing the sum by an integral, we recover the expression $n_{\text{pol}}(\rho) = N \beta |\beta|/(4\pi \rho^2)$ found in [8] by the Thomas–Fermi method.

For supercritical $\beta > \frac{1}{2}$, as discussed above, the scattering phase becomes sensitive to the physics at small distances, $\rho \approx r_0$. This leads to pronounced interference of the incoming and outgoing waves, which is manifest in the local density of states (LDOS),

$$n_{\text{pol}}(\rho) = \frac{N \pi \gamma}{2\pi^2 \rho^2} \sum_{m + \frac{1}{2} < |\beta|} \sqrt{\beta^2 - (m + \frac{1}{2})^2} \quad (29)$$

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The standing waves in LDOS (30) at $\beta > \frac{1}{2}$ are different from Friedel oscillations, since $\kappa F = 0$ in our case (Fermi level at the Dirac point). As illustrated in Fig.2, their spatial period scales inversely with energy, so that the maxima occur at $k_{\text{sc}} \rho = (n + \frac{1}{2})\pi$, which is similar to the oscillations in LDOS studied in carbon nanotubes [19]. As in Ref. [19], the energy-dependent spatial period can be used to obtain direct information about Fermi velocity $v_F$ in graphene.

The spatial structure predicted around supercritical Coulomb impurities, which extends up to the vacuum polarization cloud size $\rho_*$, will be affected by finite temperature $T \gtrsim T_\ast = h v_F/\rho_*$, and also by carrier doping away from neutrality by $\delta n \gtrsim \rho_0^{-2}$ strong enough to induce screening at distances less than $\rho_*$.

To summarize, we found that the excess charge $\beta - \frac{1}{2}$ of supercritical impurities in graphene is fully screened by the Dirac vacuum polarization. The large screening cloud size and the standing wave oscillations predicted within it can be directly probed by STM technique. The sharp departure from linear screening for supercritical impurities represents an interesting example of nonlinear screening that can be realized in graphene. Our estimates for the critical charge, using $\kappa_{\text{FFA}} \approx 5$, yield an experimentally convenient value $Z_c \sim 1$, making experimental tests of these effects in graphene practical.

This work is supported by the DOE (contract DEAC 02-98 CH 10866), FOM (The Netherlands), NSF MRSEC (DMR 02132802) and NSF-NIRT DMR-0304019.

[1] A. K. Geim and K. S. Novoselov, Nat. Mater. 6, 183 (2007).
[2] J. González, F. Guinea, and M. A. H. Vozmediano, Nucl. Phys. B 424, 595 (1994); J. Low Temp. Phys. 99, 287 (1995)
[3] K. Nomura and A. H. MacDonald, Phys. Rev. Lett. 96, 256602 (2006).
[4] T. Ando, J. Phys. Soc. Japan 75, 074716 (2006).
[5] E. H. Hwang, S. Adam, and S. Das Sarma, Phys. Rev. Lett. 98, 186806 (2007).
[6] K. S. Novoselov et al., Nature 438, 197 (2005).
[7] D. P. DiVincenzo and E. J. Mele, Phys. Rev. B 29, 1685 (1984).
[8] M. I. Katsnelson, Phys. Rev. B 74, 201401(R) (2006).
[9] P. M. Ostrovsky, I. V. Gornyi, and A. D. Mirlin, Phys. Rev. B 74, 235443 (2006).
[10] I. Pomeranchuk and Y. Smorodinsky, J. Fiz. USSR 9, 97 (1945).
[11] Y. B. Zeldovich and V. S. Popov, Usp. Fiz. Nauk 105,
[12] L. D. Landau and E. M. Lifshitz, Quantum Mechanics, Chap. XVII, §135 (3rd ed., Pergamon, London 1977).

[13] M. Abramowitz and I. A. Stegun, Handbook of Mathematical Functions, (Dover, New York, 1964).

[14] \( z_1 F_1'(\alpha, \gamma, z) = \alpha (1 F_1(\alpha + 1, \gamma, z) - 1 F_1(\alpha, \gamma, z)) \), which follows from Eqs. (13.4.8), (13.4.4) of Ref. [13]

[15] \( 1 F_1(a, c; z) \approx \frac{\Gamma(c)}{(c - a) \Gamma(c - a)} (-z)^{-a} + \frac{\Gamma(c)}{(c - a) \Gamma(c - a)} e^{z} z^{a-c} \) for large \( |z| \) (see Eq.(13.5.1), Ref. [13])

[16] J. Friedel, Phil. Mag. 43, 153 (1952).

[17] D.-H. Lin, Phys. Rev. A 72, 012701 (2005); ibid. 73, 052113 (2006).

[18] D. A. Abanin, P. A. Lee, and L. S. Levitov, Solid State Comm. 143, 77 (2007)

[19] M. Ouyang, J.-L. Huang, and C. M. Lieber, Phys. Rev. Lett. 88, 066804 (2002).

[20] We use the ansatz \( \psi \propto \rho^{s-\frac{1}{2}} \), as appropriate for the 2d case, instead of \( \psi \propto \rho^{s-1} \) which is a convention in 3d.