Scattering of electrons in graphene by clusters of impurities

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I. INTRODUCTION

Graphene currently attracts intense attention as a novel strictly two-dimensional (2D) system with unique electronic properties that are interesting with respect to both basic physics and potential applications (for review, see Refs. 1–3). It was shown already in the early reports on graphene that charge carriers in this material exhibited a remarkably high mobility \( \mu \) such that submicron mean-free paths were routinely achievable and an order-of-magnitude higher \( \mu \) were observed for suspended graphene samples.\(^5,6\) Away from the neutrality point, the conductivity of graphene is weakly temperature dependent and approximately proportional to the carrier concentration \( n \).\(^7,8\) Despite extensive experimental and theoretical efforts, there is still no consensus about the scattering mechanism limiting \( \mu \) in graphene on a substrate. Charged impurities are probably the simplest and thus the most natural candidate,\(^9–11\) and this conjecture is in agreement with the experiments in which potassium atoms were deposited on graphene at cryogenic temperatures.\(^12\) However, room-temperature experiments with gaseous adsorbates such as NO\(_2\) have showed only a weak dependence of \( \mu \) on charged impurity concentration.\(^13\) The latter observation agrees with several reports of only modest changes observed in \( \mu \) after thermal annealing of sparsely doped samples. Furthermore, recent experiments\(^14\) did not find any significant dependence of \( \mu \) on immersing graphene devices in high-\( \kappa \) media such as ethanol and water (dielectric constants of \( \kappa \approx 25 \) and 80, respectively) but this also disagrees with another report\(^15\) in which two monolayers of ice increased \( \mu \) in graphene by \( \approx 30\% \). Because of the experimental controversy, alternative mechanisms such as scattering on frozen ripples\(^16\) and resonant impurities\(^17,18\) were discussed.

Regardless of the experimental debate about the dominant scattering mechanism, the case of graphene covered with adsorbates at elevated temperatures\(^19\) generally requires more careful consideration since there is a vast literature which shows the formation of clusters of different metals on the surface of graphite.\(^19–24\) These atoms easily diffuse on graphite’s surface overcoming only relatively low barriers and tend to form clusters. Potassium atoms on graphite arrange themselves into the so-called \( p(2 \times 2) \) structure with a K-K spacing of 0.492 nm, that is, roughly, 3.5 nearest-neighbor carbon-carbon distances.\(^25\) However, in the case of graphite, this usually happens only at low temperatures and high coverage by adsorbates.\(^22\) For low-doping concentrations such as those used in typical experiments on graphene, adsorbates on graphite are randomly dispersed and, at elevated temperatures, evaporate from its surface, except for such materials as, for example, Au, that forms stable clusters on graphite.

From the surface science perspective, graphene is different from graphite, and we expect that clusters can be more easily formed on graphene and be stable at high temperatures. Indeed, it was shown experimentally\(^26\) that graphene binds such molecules as NO\(_2\), NH\(_3\), and H\(_2\)O, etc. even at room temperature. In the case of graphite, they can attach only below liquid-nitrogen temperatures.\(^22\) The reason for the stronger attachment remains unclear but could be due to the presence of ripples on graphene.\(^26\) According to both experiments and theory,\(^26\) ripples can bind even atomic hydrogen that is unstable on a flat surface on both graphene and graphite.

We believe that once attached to graphene (and this certainly happens for various gases even at room temperature), adsorbates should tend to cluster, much more so than for the case of graphite’s surface. First, ripples would obviously force them to move from the valleys onto the hills which favor the adsorption. Second, there exists an additional long-range attraction due to Casimir-type interaction mediated by Dirac fermions,\(^27\) which is absent for graphite.

On the basis of the above consideration that agrees with what is now known about graphene adsorbates, both theoretically and experimentally, it is important to consider how such clustering of adsorbates can influence the electronic properties of graphene. In this paper, we analyze the scattering of Dirac fermions by clusters of charged impurities and...
show that for the same doping level such a disorder results in significantly lower resistivity. This model reconciles the doping experiments at cryogenic\textsuperscript{12} and ambient\textsuperscript{13} conditions, as low temperatures prevent surface diffusion and, therefore, clustering of adsorbates.

Section II presents the model to be studied. Section III contains the main results. We discuss in Sec. IV possible extensions of the model. The main conclusions are described in Sec. V.

II. MODEL

Let us first assume that the charged impurities inside the cluster are ordered, occupying positions over the centers of carbon hexagons, as in the \textit{p}(2 \times 2) structure mentioned above.\textsuperscript{22} In such a situation the impurities do not break the sublattice symmetry and cannot lead therefore to the gap opening. The main effect is therefore merely a local doping of graphene, that is, shift of its chemical potential, similar to what happens for graphene on the top of metals.\textsuperscript{28} Another effect, that is, the residual unscreened Coulomb potential, of the cluster as a whole, \( \sim 1/r \), far from the cluster, will be discussed further.

We start with the simplest model, that is, the scattering of the charge carriers by a closed region where the chemical potential has been modified. For simplicity, we assume a circular cluster. The problem of scattering of the 2D massless Dirac electrons by the circularly symmetric potential well has been considered in Refs. 17 and 29--33. The model parameters are the Fermi energy and Fermi wave vector outside the cluster, \( e_F \) and \( k_F \), the change in chemical potential inside the cluster, \( V \), the Fermi velocity, \( v_F \), and the radius of the cluster, \( R \). We take \( h = 1 \) in the following. The differential cross section can be written in terms of Bessel functions, whose dimensionless arguments are \( \phi_{\text{in}} = k_F R \) and \( \phi_{\text{out}} = (k_F + V/v_F)R \). We assume that the cluster is heavily doped so that \( \phi_{\text{in}} \gg \phi_{\text{out}} \). The charge induced inside the cluster is estimated as \( \pi V R^2 \), \( \phi_{\text{out}} \). We will neglect the intervalley scattering, which is justified if the boundaries of the cluster are smooth on the atomic scale, and \( R \gg a \), where \( a \) is the lattice constant.

III. RESULTS

The scattering cross section reads\textsuperscript{17,29--33}

\[
\sigma(\theta) = \frac{4}{\pi} \left| f(\theta) \right|^2 = \sum_{n=-\infty}^{n=\infty} \sum_{m=-n}^{m=n} R_n e^{i n \theta},
\]

\[
R_n = - \frac{J_n(\phi_{\text{out}})J_{n+1}(\phi_{\text{in}}) - J_{n+1}(\phi_{\text{out}})J_n(\phi_{\text{in}})}{J_{n+1}(\phi_{\text{out}})J_{n+1}(\phi_{\text{in}}) - J_n(\phi_{\text{out}})J_{n+1}(\phi_{\text{in}})}.
\]

Note that since \( R_0 = R_{-1} = 0 \), the back-scattering amplitude vanishes, \( f(\theta = \pi) = 0 \) which is the consequence of the pseudospin conservation at the “chiral” scattering related with the Klein paradox.\textsuperscript{34}

The cross section shows two regimes depending on whether \( \phi_{\text{out}} = k_F R \ll 1 \) or \( \phi_{\text{out}} \gg 1 \). In the first case, the cluster is small compared to the Fermi wavelength. The cluster per-
FIG. 3. (Color online) Classical trajectories of an electron scattered by a circular cluster. 50 internal reflections are shown. The impact angle, $\theta$, of the incoming trajectories is $\theta = \pi/4$. Left: $V = E_F$. Right: $V = 10E_F$.

and the cross section can be approximated as

$$\sigma(\theta) = \frac{\pi}{\kappa_F^2} \int_{-\pi}^{\pi} \sin \left( \frac{\theta}{\kappa_F} \right)^2 \frac{d\theta}{\kappa_F}$$  \hspace{1cm} (5)

The elastic electron mean-free path, $l$, is given approximately by

$$l \sim \frac{1}{n_c \sigma_t}$$  \hspace{1cm} (6)

where $n_c$ is the cluster concentration. At low carrier densities, $k_F R < 1$, the Born approximation gives

$$\sigma_t \propto k_F^2 \left( \frac{V}{v_F R} \right)^2$$  \hspace{1cm} (7)

and $\sigma_t$ is proportional to the density of states and to the square of the potential. At high densities, $k_F R \gg 1$, one can use Eq. (5). The conductivity is estimated as

$$\sigma = \frac{e^2}{h} k_F \rho \sim k_F^2 \left( \frac{V}{v_F R} \right)^2$$  \hspace{1cm} (8)

We expect the oscillations of the cross section shown in Fig. 2 to be averaged out in clusters with less symmetric shapes. The parameter $k_F R$ reaches the value $k_F R \approx 10^{-12}$ for $R = 20$ nm and charge density $\rho = 2 \times 10^{13}$ cm$^{-2}$. Interestingly, for the regime $\phi_{out} \gg 1$ the total cross section $\sigma_{tot}$ distinguished from $\sigma_t$ by the absence of the factor $\sin \theta$ in Eq. (5) is larger than $\sigma_t$ by a factor $k_F R$. The total cross section is related with the single-particle decoherence time which determines, e.g., Dingle temperature in the Shubnikov–de Haas oscillations.

The elastic mean-free path depends on the cluster density and carrier concentration, $\rho$. For $n_c = 10^{10}$ cm$^{-2}$ and $\rho = 5 \times 10^{13}$ cm$^{-2}$ we obtain $l = 1/(n_c \sigma_t) = 200$ nm.

We have neglected so far the long-range part of the Coulomb potential induced by the cluster. This potential will modify the scattering cross section for electron wavelengths $k_F^2 \sim R$. The cross section will depend on the carrier concentration as $\sigma_{tot} \propto k_F^2$ instead of the dependence given by Eq. (8). However, since the scattering cross section is proportional, in Born approximation, to the charge square and to the first power of the charge concentration, the clusterization will lead to the suppression of this contribution to the resistivity by a factor of order of number of atoms in cluster in comparison with the case of chaotically distributed impurities.

IV. BEYOND THE SIMPLIFIED MODEL

Our model of completely ordered impurities inside the cluster is oversimplified. However, if disorder inside the cluster is relatively weak so that the local mean-free path $l$
becomes stronger one reaches at some moment the Mott here as the mean-free path of the infinite-disordered system be to reduce the oscillations of the transport cross section as expressed in terms of the new reflection amplitudes [cf. Eq. (1)].

To see potential consequences of this local reconstruction of the sublattice equivalence and lead to the local gap opening. We also neglect, for simplicity, the shift of the electronic structure, one can extend the model to the case of large neutral clusters due to a shift of the chemical potential. Similar boundary conditions were discussed in Ref. 43. We assume that the mass, $\Delta$, is only finite inside the cluster. We also neglect, for simplicity, the shift of the chemical potential. The cross section in such model is expressed in terms of the new reflection amplitudes [cf. Eq. (1)],

\[ R_n = -\frac{ia_n(kFR)I_{n+1}(kR) - a_{n+1}(kFR)I_n(kR)}{ia_n(kFR)I_{n+1}(kR) - a_{n+1}(kFR)I_n(kR)} \]

\[ \kappa = \sqrt{\Delta^2 - (E_F + V)^2} \]

where $I_n(x)$ is a modified Bessel function, which is zero at the origin and grows exponentially as $x \rightarrow \infty$.

We have also calculated the cross section including a staggered potential, $\Delta$. The main effect of a mass term seems to be to reduce the oscillations of the transport cross section as a function of angle. If the mass term is large enough, the effect should be qualitatively the same as for the strong disorder, that is, the transport cross section will be of the order of $R$, as for a nontransparent obstacle in optics. The changes induced by a mass term in the differential cross section are shown in Fig. 5.

\[ \sigma(\theta) \]

\[ \frac{\pi}{2} \quad \frac{\pi}{2} \theta \]

**V. CONCLUSIONS**

Let us summarize the main results of our consideration. (i) The transport cross section of charge carriers in graphene by large neutral clusters due to a shift of the chemical potential inside the cluster becomes independent of the cluster size, $R$, and shift in chemical potential, $V$, for $k_FR \gg 1$, except for an oscillatory function. This can be viewed as a consequence of the Klein tunneling: electrons can always tunnel into the cluster, irrespective of the value of $V$. The oscillatory function is, most likely, replaced by its average for clusters with irregular shapes, as one can assume by analogy with the geometric optics. (ii) The total scattering cross section, obtained by integrating $\sigma(\theta)$ over angles, is proportional to $R$ for $k_FR \gg 1$, as it should. In this regime $\sigma_{tot}/\sigma_r \approx k_FR$ which, in principle, can be observed by the comparison of the mean-free path with the Dingle temperature if this scattering mechanism is dominant. For all other scattering mechanisms considered before, including charged impurities, $\sigma_{tot}/\sigma_r \approx n_q^{1/2}$, with a numerical factor of order of 1. (iii) The transport cross section is proportional to $k_FR$. Hence, scattering by charged impurities leads to the same correction to the transport cross section. (iv) The formation of clusters is a process favored by high atomic diffusion. Hence, we expect that by annealing the samples used in Ref. 12 above 100 K, the mobility will increase toward the values measured before doping by potassium. (v) The correlation observed in Ref. 45 between the shift of the Dirac point and the electron mobility for different adsorbates as a function of adsorbate concentration is consistent with the formation of clusters. The effective charge, $q_i$, transferred from the adsorbate atom to the graphene layer varies for different adsorbates. For elements that transfer to graphene an amount of charge much less than one-electron charge, such as Pt, the scattering cross section $31$ goes as $q_i^2$. The shift of the Dirac point should be proportional to $E_Dq_i^n$, where $n_i$ is the concentration of the adsorbate. The change in mobility should scale, on the other hand, as $\mu_i^{-1} \propto n_q^{1/2}$, for adsorbates such that $q_i^{-1} < n_q^{-1}$, $q_i^{-1} = n_q^{-1}$. Hence, different adsorbates should show different ratios $\mu_i^{-1}/E_Dq_i^n$. A ratio that varies weakly for different adsorbates is more consistent with the existence of clusters, each of which transfers to graphene a few free-electron charges independent of the type of adsorbate and size of the cluster.

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