Specific features of electric charge screening in few-layer graphene films

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Abstract

We present a nonlinear Thomas–Fermi theory which describes the electric charge screening in a system including two charged substrate layers separated by a few-layered graphene film. We show that by increasing the charge at the interfaces, the system can be turned from the weak screening regime where the whole film responds to the external charge to the strong screening regime where the external charge is screened by a surface charge distribution confined to the bounding graphene layers. The transition from weak to strong screening is shown to turn on relatively quickly, and it occurs when the applied external charge/external field reaches a certain crossover magnitude. The possibilities for experimental observation of the predicted crossover are discussed.

The past decade has seen a proliferation of interest in experimental and theoretical studies of graphene. The interest mainly stems from the striking properties of graphene, including tunable carrier type and density and exceptionally high carrier mobility. A very significant advantage of graphene is its inherent two-dimensionality which makes graphene-derived nanomaterials a promising family for applications in building nanoelectronic devices with planar device architectures [1–3]. Such applications require fabrication of few-layer graphene (FLG) film supported by/placed in between insulating substrate layers. Correspondingly, the effects of the substrate on the electronic properties of the FLG must be thoroughly analyzed. Some theoretical and experimental work concerning this issue already exists (see, e.g., [4–8]). However, further studies are necessary to obtain a better quantitative understanding of these effects.

In this work, we contribute to these studies by theoretically analyzing the charge exchange and electrostatic potential spatial distribution in a system that consists of an FLG film sandwiched in between two charged substrate layers. We assume that \( z \) denotes the coordinate perpendicular to the graphene layers in the FLG, which occupies the space where \( 0 < z < D \). The number of layers is supposed to be large enough to satisfy the condition \( d \ll D \), where \( d \) is the distance between adjacent layers in the film. At the interfaces between the FLG and the substrates \((z = 0, D, \text{respectively})\) the substrates are characterized by the areal charge densities \( \sigma_{1s} \) at \( z = 0 \) and \( \sigma_{2s} \) at \( z = D \). Also, we introduce charge carrier densities \( \sigma_i \) corresponding to the graphene layers in the FLG. The index \( i \) takes on values from 1 to \( N \) (\( N \) being the total number of layers in the stack). For convenience, in further analysis we assume that all the above mentioned charge carrier densities may take on either positive or negative values depending on the nature of the charge carriers associated with a certain layer. We attribute positive values to the areal densities of holes and negative ones to those of electrons, respectively.

Due to the specific form of the dispersion relation for the charge carriers in a single graphene sheet, their quantum-mechanical kinetic energy per unit area is proportional to the areal charge carrier density to the power of \( 3/2 \). For the \( i \)th graphene layer included in the pack, the kinetic energy per unit area of substrate is given by the expression

\[
K_i = \frac{2}{3} \sqrt{\pi} \hbar v_F |\sigma_i|^{3/2},
\]

where \( v_F \) is the Fermi velocity of the charge carriers. We remark that this expression differs from the well known result...
The charge distribution in the FLG is determined by the competition between the kinetic energy of the charge carriers and their interactions with the self-consistent electrostatic potential. This may be described employing a nonlinear Thomas–Fermi theory for the charge carriers in the continuum potential. This may be described employing a nonlinear and their interactions with the self-consistent electrostatic potential. At the same time, one must keep in mind that the Thomas–Fermi theory does not treat the effects of quantum coherence between nearby graphene layers, and it applies in the absence of interlayer tunneling. Therefore, the Thomas–Fermi approach may be used only if we assume that the adjacent graphene sheets are decoupled. This assumption is justified when the local Fermi energies are sufficiently far from the charge neutrality point and their shifts significantly exceed the hopping amplitudes characterizing the interlayer tunneling [8]. This requires the distances between the adjacent layers in the FLG to be large enough to prevent tunneling of charge carriers. Also, the Thomas–Fermi approach could be employed if the considered graphene pack belonged to the family of rotationally faulted FLG. In these systems the crystalline lattices of adjacent graphene sheets are misoriented (twisted) at random angles with respect to each other, as established in several recent experiments [9–13]. Twisted graphene multilayers exhibit only weak manifestations of interlayer hybridization and interlayer tunneling of charge carriers. Previously, Thomas–Fermi models were successfully used to describe the electrostatic interactions in graphite intercalate compounds [14, 15] as well as to analyze the intrinsic screening in graphene multilayers [8].

Within the Thomas–Fermi approach, the energy of the charge carriers in the FLG pack includes the kinetic term $K$ and the term $U_{\text{int}}$ given by equation (5) one may transform the integral equation (1) to a nonlinear differential equation of second order for the function $f(z)$,

$$
\frac{d^2 f}{dz^2} = \frac{2\tilde{\beta}}{d^2}f^2(z),
$$

with the boundary conditions

$$
\frac{df}{dz}|_{z=0} = -\tilde{\beta}\sigma_0 \text{sign}(\sigma_0),
\quad \frac{df}{dz}|_{z=D} = \tilde{\beta}\sigma_0 \text{sign}(\sigma_0).
$$

One may note that the function $f(z)$ has a negative slope at $z = 0$ and a positive slope at $z = D$ and these slopes are equal in magnitude. Also, one may expect the charge carrier density $\sigma(z)$ to take on values that are equal in magnitude and opposite in sign at the interfaces ($\sigma(0) = -\sigma(D)$). This gives grounds to conclude that the function $f(z)$ reaches its minimum in the middle of the film at $z = D/2$, whereas $\sigma(z)$ should increase/decrease over the whole interval $0 < z < D$ depending on the sign of $\sigma_0$. When $\sigma_0 > 0$, $\sigma(0)$ should take on a negative value to balance the charge on the substrate,
which means that $\sigma(z)$ is an increasing function. On the contrary, $\sigma(z)$ should monotonically decrease over the interval $0 < z < D$ if $\sigma_0 < 0$. At the middle point ($z = D/2$), $\sigma(z)$ becomes zero, and the derivative $df/dz$ satisfies the following relation:

$$\frac{df}{dz}\bigg|_{z=D/2-0} = -\frac{df}{dz}\bigg|_{z=D/2+0}. \quad (10)$$

One cannot analytically solve the differential equation (8) in a straightforward way. However, it has been shown (see [8]) that this equation is equivalent to a conservation law of the form

$$\frac{d}{dz} \left( \frac{1}{2} \left( \frac{df}{dz} \right)^2 - \frac{2\beta}{3d} f^3(z) \right) = 0. \quad (11)$$

Using this conservation law we obtain

$$\left( \frac{df}{dz} \right)^2 = \frac{4\beta}{3d} f^3(z) + C, \quad (12)$$

where the constant $C$ is determined by the boundary conditions. We start to analyze the solutions of equation (12) by splitting the original range $0 \leq z \leq D$ into halves and separately solving this equation for these halves. Employing the boundary conditions (9) and the relation (10) and introducing a dimensionless parameter $R$ defined by the expression

$$1 + R^3 = \frac{3\beta \sigma_0^2}{4f^3(0)} \quad (13)$$

we may present the solution of equation (12) as follows:

$$\begin{align*}
\frac{z}{D} &= \frac{1}{2} \int_0^1 \frac{du}{\sqrt{u^3 + R^3}}, & 0 \leq z \leq \frac{D}{2} \\
\frac{z}{D} &= \frac{1}{2} \left( 1 + \int_0^{f_0^2} \frac{du}{\sqrt{u^3 + R^3}} \right), & \frac{D}{2} < z \leq D. \quad (14)
\end{align*}$$

In these expressions, $r(z/D) = f(z)/f(0)$. Now, it is necessary to clarify the physical meaning of the parameter $R$ by relating it to certain characteristics describing properties of the considered system. Using equations (12) and (13) one may derive the following expression:

$$(1 + R^3)^{1/6} \int_0^1 \frac{du}{\sqrt{u^3 + R^3}} = \Gamma, \quad (16)$$

where

$$\Gamma = \left( \frac{\beta^2 |\sigma_0| D^3}{6d} \right)^{1/3}. \quad (17)$$

The newly introduced dimensionless parameter $\Gamma$ is determined by the thickness of the FLG pack, the distance between adjacent layers and the charge carrier density on the substrates $\sigma_0$. Also, and most importantly, it depends on the parameter $\tilde{\beta}$ which characterizes the Coulomb interactions between the graphene layers and the substrate as well as the interactions between different graphene sheets. All these characteristics are combined into the single control parameter, which determines the nature of the FLG screening. When the system is in a strong coupling regime dominated by its electrostatic energy ($\tilde{\beta} > 1$), the parameter $\Gamma$ may take on values significantly greater than 1. In the weak coupling regime, when the kinetic energy predominates ($\tilde{\beta} \ll 1$), the control parameter should become much smaller than 1. As follows from equation (16), within the extremely strong coupling limit ($\Gamma \gg 1$) the parameter $R$ is inversely proportional to $\Gamma^2$, and it takes on values close to zero. In this case we may approximate $f(0)$ as

$$f(0) \approx f_0 = \left( \frac{3d}{4} \beta^2 \sigma_0^2 \right)^{1/3}. \quad (18)$$

Within the weak coupling regime ($\Gamma \ll 1$) $R \approx \Gamma^{-1}$. Substituting this approximation into the expression for $f(0)$, we find

$$f(0) \approx \tilde{\beta} |\sigma_0| D/4. \quad (19)$$

Comparing these asymptotic expressions, we see that in the weak coupling limit the ratio $f(0)/f_0$ takes on small values of the same order as $\Gamma$. This means that the FLG charge carrier densities induced at the interfaces by the substrate charge carrier density $\sigma_0$ are significantly greater when the Coulomb interactions in the considered system are strong enough for the inequality $\Gamma > 1$ to be satisfied. For a general case, the dependence of $R$ on $\Gamma$ as given by equation (16) is presented in figure 1. One may observe that the crossover between the weak ($\Gamma \ll 1$) and strong ($\Gamma \gg 1$) coupling regimes occurs at $R \sim 1$.

The charge carrier density in the FLG is simply related to the function $r(z/d)$. Assuming for certainty that $\sigma_0 > 0$ we...
The renormalized electrostatic potential $\Phi(z)$ is closely related to the electrostatic potential:

$$e\Phi(z) = -\beta z \sigma_0 \text{sign}[\sigma(z)]$$

$$-\beta \text{sign}[\sigma(z)] \int_0^D \frac{dz'}{d} \sigma(z')|z-z'|$$

is simply related to the function $f(z)$. Comparing this expression and equation (7) we obtain

$$e\Phi(z) = \tilde{\mu} - f(z).$$

Assuming for certainty that $\Phi(0) = 0$ we easily find the corresponding value of the chemical potential $\tilde{\mu}$. Substituting the result into equation (23) we obtain the following expression for the dimensionless quantity $e\Phi(z)/f_0$ which is closely related to the electrostatic potential:

$$\frac{e\Phi(z)}{f_0} = \frac{1 + \text{sign}[z - \frac{D}{2}] r \left( \frac{z}{D} \right)}{(1 + R^3)^{1/3}}.$$

The profile of the electrostatic potential strongly depends on the coupling regime. When the electrostatic interactions in the system are weak ($\Gamma \ll 1$), we may employ the approximations (21) for the function $r(z/D)$. In this case the electrostatic potential has a linear profile and the potential difference across the film equals

$$\Phi(D) - \Phi(0) \equiv \Delta \Phi = \frac{e D \sigma_0}{4\varepsilon_0}.$$

So, when the Coulomb interactions are weak, the considered system behaves as a parallel-plate capacitor, and the FLG takes on the part of a dielectric material filling the space between the plates and characterized by the dielectric constant $\kappa = 2$.

However, when the parameter $\Gamma$ increases the approximation given by equation (25) ceases to be valid. In the general case the electrostatic potential difference is given by the expression

$$\Phi(D) - \Phi(0) \equiv \Delta \Phi = \frac{3y}{e} \frac{f_0}{(1 + R^3)^{1/3}},$$

and it exhibits a nonlinear dependence on $\sigma_0$. Within the strong coupling limit ($R \ll 1$) the potential difference between the interfaces $\Delta \Phi$ is proportional to $\sigma_0^{2/3}$, so one may consider the system as a capacitor whose differential capacitance $C$ varies as $\Delta \Phi$ changes, being proportional to $(\Delta \Phi)^{1/2}$. The electrostatic potential profiles are presented in the left panel of figure 3. In weak coupling the potential increases nearly linearly as we move into the FLG film. The stronger the coupling is the more pronounced the potential change is in the vicinities of the interfaces. One may expect that in the limit of very strong coupling ($R \ll 1$) almost the whole potential drop should occur near the interfaces leaving the potential nearly constant in the main body of the film.

One may increase the parameter $\Gamma$ and thus stimulate the switching to the regime of strong coupling in two ways. First, one can enhance $\sigma_0$ keeping $D$ fixed. This would be an appropriate analysis for experiments on a single FLG sample of a certain thickness where $\sigma_0$ is varied by varying the voltage applied across the system. Secondly, one may keep...
\( \sigma_0 \) fixed and increase the film thickness \( D \) by adding extra graphene sheets to the pack. We illustrate the effect of these two factors on the electrostatic potential change across the film in the right panel of the figure 3. The curves shown in this figure correspond to different values of \( D \). At small values of \( \sigma_0 \) all curves exhibit nearly linear dependences of \( \Delta \Phi \) on \( \sigma_0 \), which is typical for the weak coupling regime. As \( \sigma_0 \) increases the curves deviate from the corresponding straight lines, and this indicates the transition to the strong coupling regime. We observe that the greater \( D \) becomes the smaller \( \sigma_0 \) that is required to provide this transition. We remark that the slopes of the presented curves at \( \sigma_0 = 0 \) differ for different values of \( D \). The greatest value of \( D \) corresponds to the steepest slope, which obviously makes sense. As follows from equation (26), in the strong coupling regime (\( \Gamma \gg 1 \)) the electrostatic potential difference is close to \( \frac{3}{\pi} e f_0 \), and the first correction to this main approximation is proportional to \( D^{-6} \).

To further analyze the possibilities for experimental observations of the described features in the electric charge and electrostatic potential distribution in the FLG samples, one should take into account the direct contribution to the potential from the substrates. For certainty, we assume that the areal charge densities on the surfaces of the substrates appear due to the presence of ionized impurities in the substrate materials. The impurities are supposed to be uniformly distributed in the substrates with the volume density \( \rho_0 \). First, we consider the substrate layer adjoining the FLG at \( z = 0 \). Then the electrostatic potential inside the substrate layer obeys the Poisson equation, which in the considered case is reduced to the form

\[
\frac{d^2 \Phi_s}{dz^2} = -\frac{e}{\varepsilon_0} \rho_0.
\]

Setting \( \Phi_s = 0 \) at the depletion length \( L_D \) we obtain the solution of this equation, namely

\[
\Phi_s = -\frac{e \rho_0}{2 \varepsilon_0} (z + L_D)^2.
\]

Calculating the electric field at the interface \( z = 0 \) (\( E = -\partial \Phi_s / \partial z \)) and keeping in mind that \( E(0) = e \sigma_0 / \varepsilon_0 \) we find that \( L_D = \sigma_0 / \rho_0 \). Accordingly, the electrostatic potential \( \Phi_s \) at the interface equals

\[
\Phi_s(0) = -\frac{e \sigma_0^2}{2 \varepsilon_0 \rho_0}.
\]

The electrostatic potential associated with the substrate at the substrate/FLG interface at \( z = D \) can be estimated in a similar way. As a result, the total electrostatic potential difference including the contribution from the FLG as well as that from the substrate takes the form

\[
\Delta \Phi = \frac{3y}{e} \left( \frac{f_0}{(1 + R^2)^{1/3}} + \frac{e \sigma_0^2}{\varepsilon_0 \rho_0} \right).
\]

Within the low coupling limit the ratio of the terms in equation (30) is of the order of \( D \rho_0 / \sigma_0 \) (see equation (25)), therefore the first term predominates if \( \rho_0 > \sigma_0 / D \). If the Coulomb interactions are strong the FLG contribution dominates when

\[
\rho_0 > \left( \frac{4}{3d^2} \beta^2 \sigma_0^4 \right)^{1/3}.
\]

The expression for the total potential drop (30) must be changed if we allow for the predominating effect of surface/interface states. This seems to be a likely resolution with the culprit being some adsorbed species confined to the interfacial layer. This basically cuts off the depletion length \( L_D \) at the characteristic depth for the surface states \( d_s (d_s < L_D) \). Then \( \sigma_0 = \rho_0 d_s \) and the contribution from the substrates to the total potential drop takes the form \( e \sigma_0 d_s / \varepsilon_0 \). In this case, the predomination of the FLG contribution to the total potential drop becomes easier to reach. In the weak coupling regime the graphene contribution predominates when \( d_s < D \), which is usually the case. When the coupling is strong, one must require the inequality

\[
d_s < \left( \frac{3d^3}{4 \beta^2 \sigma_0} \right)^{1/3}
\]

to be satisfied to provide the prevalence of the graphene contribution to the potential drop.

The results of this work can be summarized as follows. Since a single graphene sheet is semimetallic one may expect the screening length in an FLG film placed between two charged substrates (or exposed to an external electric field in some other way) to be large. In consequence, any electric charge donated to the film would be distributed over all the graphene layers, and the electrostatic potential inside the film would have a linear spatial profile. However, these conclusions remain valid only within the weak coupling regime (\( \Gamma \ll 1 \)), when the Coulomb interactions between the graphene sheets as well as between the film and the substrates are smaller than the kinetic energy of the charge carriers.

By increasing the areal carrier density on the substrates and/or making the FLG sample more densely packed by reducing the ratio \( d / D \), one may carry out a transition to the strong coupling regime (\( \Gamma > 1 \)). Within this regime, the FLG
exhibits a metallic-like behavior, so that the induced electric charge becomes concentrated near the surfaces of the FLG film, and the electrostatic potential inside the film acquires a nonlinear spatial profile. The transition from the weak to the strong coupling regime turns on relatively quickly at a crossover value of the external areal charge density \( \sigma_0 \) (or at a crossover value of the external electric field). The obtained results ignore the effects of hybridization between adjacent graphene sheets. Therefore, these results can be applied either to loosely packed FLG samples (where interlayer tunnelings are prevented by a sufficient layer separation) or to twisted graphene where interlayer tunneling is hindered due to the rotational misorientation of the crystalline lattices.

Finally, we estimate the parameters characterizing the considered system to show that the strong coupling regime where the graphene sheets exhibit a metallic-like behavior can be reached in realistic experiments. A typical value of the parameter \( \gamma \) is 6.5 eV Å, which gives for the dimensionless constant \( \beta \) a value of the order of ten, namely \( \beta = 9.5 \). Then, assuming that \( d \) takes on a value close to the interlayer spacing in graphite (\( d \approx 3.347 \) Å), the crossover value of the parameter \( \Gamma' \) (\( \Gamma' = 1 \)) occurs at \( 0.5\sigma_0 \approx 3d/2\beta^2D^3 \approx 6.5 \times 10^{-2}/D^3 \). This areal density has dimensions of Å\(^{-2}\) if the FLG thickness is expressed in Å. The minimum value of \( D \) cannot be smaller than \( d \), so \( 1/2\sigma_0 \) needs only to exceed \( \approx 2 \times 10^{-3} \) Å\(^{-2}\) to provide the switching of the system to the strong coupling regime. We remark that for \( D > d \) this crossover value for \( \sigma_0 \) may be one or even two orders of magnitude smaller. Certainly, such values of the areal charge carrier densities at the surfaces of substrates are within the experimentally accessible range. However, the specific features originating from the special properties of graphene can be manifested only provided that the contributions from the substrates to the total electrostatic potential distribution in the system are small compared to the contribution from the FLG. As follows from equations (30) and (31), this occurs when the volume density of charged impurities uniformly distributed in the substrates \( \rho_0 \sim 10^{20} \) cm\(^{-3}\) (assuming that \( 1/2\sigma_0 \sim 10^{-3} \) Å\(^{-2}\)), which is quite large. One may obtain smaller and more realistic values for \( \rho_0 \) by reducing \( \sigma_0 \). However, in this way one may find oneself beyond the strong coupling regime which is the most interesting for observation. The situation is much better in the case when the areal charge densities at the substrate surfaces appear due to the effect of surface states with the characteristic depth \( d_0 \). Using equation (32), we may estimate \( d_0 \sim 1 \) nm at \( 1/2\sigma_0 \sim 10^{-3} \) Å\(^{-2}\). This is quite reasonable. The substrate only starts to dominate if the characteristic depth \( d \) becomes significantly larger than the one estimated above. Therefore, the specific effects originating from the particular charge carrier spectrum in graphene which were discussed in this work are likely to be accessible for experimental observations.

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