Dominant source of disorder in graphene: charged impurities or ripples?

Zheyong Fan, Andreas Uppstu and Ari Harju

1 School of Mathematics and Physics, Bohai University, Jinzhou 121000, People’s Republic of China
2 COMP Centre of Excellence, Department of Applied Physics, Aalto University, Helsinki, Finland

E-mail: zheyong.fan@aalto.fi

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Abstract

Experimentally produced graphene sheets exhibit a wide range of mobility values. Both extrinsic charged impurities and intrinsic ripples (corrugations) have been suggested to induce long-range disorder in graphene and could be a candidate for the dominant source of disorder. Here, using large-scale molecular dynamics and quantum transport simulations, we find that the hopping disorder and the gauge and scalar potentials induced by the ripples are short-ranged, in strong contrast with predictions by continuous models, and the transport fingerprints of the ripple disorder are very different from those of charged impurities. We conclude that charged impurities are the dominant source of disorder in most graphene samples, whereas scattering by ripples is mainly relevant in the high carrier density limit of ultraclean graphene samples (with a charged impurity concentration less than about 10 ppm) at room and higher temperatures. Our finding is valuable to theoretical modelling of transport properties of not only graphene, but also other two-dimensional materials, as the thermal ripples are universal.

1. Introduction

Although the electronic and transport properties of graphene have been extensively studied [1–4], a fundamental question of what the dominant disorder limiting the carrier mobility is has not been definitely answered. In addition of theoretical importance, it is vital for graphene-based applications. Major features of electronic transport in graphene include [5] a non-universal conductivity at the charge neutrality point, a density-independent mobility [5, 6], and the formation of ‘electron–hole puddles’ [7, 8]. None of these features can be explained by short-range disorder that can suppress the conductivity even below the so-called minimum conductivity $4e^2/\pi h$, via weak [9] and strong localization [10–12], as observed in graphene that has been either irradiated [13], hydrogenated [14], or exposed to ozone [15]. It is thus most likely that long-range disorder dominates in graphene. However, the origin of the long-range disorder is widely debated.

There are two major candidates for the long-range disorder: extrinsic charged impurities and intrinsic ripples. Early theoretical works using the Drude–Boltzmann approach with charged impurities [16, 17] found good agreement with experimental data [5]. One the other hand, ripples, observed in several experiments [18, 19], may also be a major source of disorder [20, 21]. There are experiments [22, 23] that challenge the viewpoint that charged impurities are the dominant scatterers, and theoretical proposals that electron–hole puddles can be induced by the intrinsic ripples [24–26] and that the random strain fluctuations resulting from the ripples play an important or even a dominant role in affecting the transport properties of graphene [27–30]. The theoretical works regarding rippled graphene have assumed a continuous model [31] of long-range diagonal or off-diagonal disorder. The long-range nature of the disorder induced by the ripples has not been justified a priori, however. In a recent experimental work [32], a strong local correlation between doping and topography in graphene on a metallic substrate, as predicted theoretically [24–26], was observed, but the amplitude of the doping was nearly two orders of magnitude larger than that expected from the theory.

The aim of this paper is to clarify the dominant disorder limiting the graphene mobility. Omitting the continuous model for the ripples, we perform large-scale molecular dynamics (MD) simulations to obtain realistic graphene ripple configurations, from which we extract the electronic Hamiltonian of large-scale gra-
phene sheets using an accurate tight-binding description that we apply for electronic transport simulations. Importantly, we find that the hopping integrals and hence the induced gauge and scalar potentials fluctuate randomly from site to site, forming short-ranged disorder, in strong contrast with the previously used models. The resulting transport properties of this disorder are found to be very different from those of the long-ranged disorder induced by charged impurities. Our results indicate that the charged impurities play a major role of limiting the mobility, apart from a large-carrier-density regime in ultraclean graphene at high temperatures.

2. Results and discussion

2.1. Disorder induced by thermal ripples in graphene

The MD simulations are performed using a code implemented on graphics processing units [33], with the optimized Tersoff potential [34] tailored for graphene systems. In the MD simulations, we start with flat graphene sheets and evolve the systems in the isothermal-isobaric ensemble, ending up with corrugated graphene sheets after a sufficiently long evolution time of a few nanoseconds. Typical MD-relaxed configurations of a square-shaped graphene flake containing \( N = 864 \text{,}000 \) atoms at 300 K are shown in the upper part of figure 1. The height fluctuations \( z(x, y) \) are of the order of a few angstroms, and the characteristic length of the ripple is of the order of 10 nm, both of which are comparable to experimental observations in suspended graphene [18]. Comparable height and length scales have also been observed in supported graphene [19], but the substrate surface corrugation might play a major role in determining the morphology of the supported graphene. The sample-size dependence of \( z(x, y) \) is consistent with that obtained by Monte Carlo simulations [35] and the temperature-dependence of \( z(x, y) \) agrees with earlier MD simulations [36]. Two configurations have marginal correlation when they are separated by about one nanosecond. This means that the ripples are dynamic rather than static. However, the presence of even a small \((<1\%)\) compressive prestrain can turn the dynamic ripples into static ones, which might be the case observed in the experiments [18]. Apart from out-of-plane deformation, there is also in-plane deformation, characterized by the fields \( u_x(x, y) \) and \( u_y(x, y) \), defined by the deviation of the corresponding \( x \) (the zigzag direction) and \( y \) (the armchair direction) coordinates from pristine graphene. Typical profiles of \( u_x(x, y) \) and \( u_y(x, y) \) are shown in the lower part of figure 1. The in-plane deformation fields have significantly smaller length and amplitude scales compared to those of the height fluctuations, but they are still crucial for determining the charge carrier disorder.

The fluctuating bond lengths of the rippled graphene lead to modified hopping integrals and gauge
The bond length dependence of the nearest-neighbour hopping integral \( t \) is obtained from a transferable tight-binding model developed by Porezag \textit{et al} \cite{37}, with the unperturbed value of \( t \) being chosen to be \( t_0 = -2.7 \text{ eV} \).

In the supplementary material \cite{3} (stacks.iop.org/TDM/4/025004/mmedia), we show that this tight-binding model is essentially equivalent to that proposed by Pereira and Castro Neto \cite{38} for strained graphene. The induced gauge potentials are given by

\[
\mathbf{A} = -\frac{\partial A_t}{\partial y} \mathbf{e}_y + \frac{\partial A_x}{\partial x} \mathbf{e}_x,
\]

where \( A_t \) and \( A_x \) are the gauge potentials in the \( t \) and \( x \) directions, respectively. The scalar potential, which corresponds to on-site potentials and is induced by local curvature and rehybridization effects, has been derived to be

\[
\phi \approx -\nabla^2 z \, \frac{a}{4 \sqrt{3}} \text{ eV}.
\]

The local curvature \( \nabla^2 z \) can be computed numerically using second-nearest-neighbour coordinates \cite{25}. Figure 2 shows the variations of \( t, A_t, A_x \), and \( \phi \) along a given line in a sample. It is clear that both the hopping integral and the induced gauge and scalar potentials have no long-range correlation. The short-range nature of the disorder results from the fact that the deformation fields are non-smooth functions of \( x \) and \( y \) at the atomic scale.

The above results are obtained by considering a single relaxed configuration at a fixed time. One may attempt to average out the short-range fluctuations by a time average of a set of consecutive configurations. According to our MD simulations, the global structure of a fully-relaxed rippled graphene flake does not change over a time scale which is comparable to that of the scattering time of electrons (about 1 ps). In view of this, we average over 500 consecutive configurations with an interval of 1 fs between two configurations. This results in smooth deformation fields, but the resulting hopping disorder and random gauge/scalar potentials also disappear; see figure 2. Therefore, one cannot obtain long-range disorder from the ripples even performing a thermal average. The vanishing of the hopping disorder and the resulting gauge potentials under thermal averaging can be understood intuitively, while the vanishing of the scalar potential (which is related to the local curvature) seems to be counter-intuitive. However, a closer inspection of the thermally-averaged configuration reveals that the in-plane deformation fields do not vanish. The non-vanishing in-plane deformation fields, together with the height fluctuations, result in a structure that is corrugated at the large length scale but has vanishing local curvature at the atomic scale.

Our atomistic model is in sharp contrast with continuous models, which assume a smooth height function \( z(x, y) \) and determine the in-plane deformation fields using equilibrium conditions, leading to long-ranged gauge and scalar fields.

The gauge potentials follow a Gaussian distribution, unlike the scalar potentials; see insets of figure 3. The strengths of the various kinds of disorder can be

\[3\] See Supplementary Material for more details of the tight-binding model, a demonstration of the robustness of the MD results, a demonstration of the statistical accuracy of the transport results, and a note regarding the ballistic-to-diffusive transition in rippled graphene.
quantified by their standard deviations: \( \Delta t \), \( \Delta A \), and \( \Delta \phi \). We find that \( \Delta t \) and \( \Delta A \) scale as \( \sim T^{1/2} \), while \( \Delta \phi \) scales as \( \sim T \); see the caption of figure 3 for explicit expressions. The \( T^{1/2} \)-scaling of \( \Delta t \) and \( \Delta A \) can be understood in terms of the equipartition theorem and the \( T \)-scaling of \( \Delta \phi \) is related to the second-order coordinate-dependence of the local curvature \( \nabla^2 z(x,y) \). The MD results are not expected to be accurate at very low temperatures, but they are assumed to be reasonably accurate above the Bloch–Grüneisen temperature \( T_{BG} \), which is of the order of 100 K [39], where the phonons follow a quasi-classical distribution. An important observation from our simulations is that the disorder strength is largely sample-independent. The disorder strengths shown in figure 3 correspond to a sample with \( N = 96 \, 000 \) atoms, but nearly identical results are obtained for other sample sizes as well. Also, for a given sample, the disorder strengths extracted from two uncorrelated configurations at different times points in a MD simulation are also nearly identical. In other words, the disorder induced by ripples can be well represented by that associated with a single relaxed sample. The results regarding the ripple-induced disorder also do not depend on the empirical potential used\(^4\).

### 2.2. Transport fingerprints of ripples and charged impurities

After having determined the effect of the ripples to the electronic structure, we can apply it for large-scale charge transport simulations. For these, we use a linear-scaling [\( O(N) \)] real-space Kubo–Greenwood method [40] developed for graphics processing units [41]. We will compare transport in rippled graphene with that in graphene with charged impurities. The Hamiltonian is described in both cases by a tight-binding model \( H = \sum_{i} U_{i}|i\rangle\langle i| + \sum_{ij} t_{ij}|i\rangle\langle j| \), where \( U_{i} \) is the on-site potential at site \( i \) and \( t_{ij} \) is the hopping integral between sites \( i \) and \( j \). For rippled graphene the nearest-neighbour hoppings \( t_{ij} \) are directly obtained from fully relaxed rippled configurations at fixed times in the MD simulations and the on-site potentials \( U_{i} \) take values determined by the scalar potential \( \phi(x,y) \). Although we included the scalar potential in our transport calculations, it is interesting to note that \( \Delta \phi \ll 3 \Delta t \) and thus the off-diagonal disorder \( \Delta t \) dominates the carrier scattering in rippled graphene. For the simulations of charged impurities, we use pure graphene hoppings \( t_{ij} = t_{0} \) and the local potential \( U_{i} \) is obtained from the standard model [42] of randomly distributed Gaussian correlated long-range on-site potentials, i.e. \( U_{i} = \sum_{k=1}^{N_{imp}} \epsilon_{k} \exp(-r_{ik}^{2}/\xi^{2}) \). Here, \( \epsilon_{k} \) is the strength of one of the \( N_{imp} \) impurity centres taking a value uniformly distributed in the interval \([-t_{0}/4, t_{0}/4]\), \( \xi \) is the effective range of the charged impurities, and \( r_{ik} \) is the distance between the \( i \)-th site to the \( k \)-th impurity centre. Impurity concentration is defined as \( n_{imp} = N_{imp}/N \), where \( N \) is the number of atoms in a simulated sample. A Hubbard mean field term accounting for electron–electron interactions could be added to the Hamiltonian, but it would not change the results significantly [43]. We use a large simulation cell of \( N = 5 \times 10^{8} \) atoms and average the

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\(^4\)See footnote 3.
results over several rippled configurations and charged defects realizations in the transport calculations\(^5\).

Figure 4 shows the conductivity \(\sigma\) calculated as a function of the carrier concentration \(n\) both in graphene with ripples and in graphene with charged impurities. The rippled sample at 300 K shows a clear saturation of the conductivity to a constant value\(^6\) at large \(n\). This is in strong contrast with results for charged defects showing unequivocal linear increase of the conductivity as a function of \(n\), for all the defect densities and potential ranges used. Using the Einstein relation of diffusion, the corresponding mean free path (MFP) \(l\) can be computed as \(l = 2\sigma/\epsilon^2\rho(E)v_F\), where \(v_F\) is the Fermi velocity, \(\rho(E) = 2E/\hbar^2v_F^2\) is the electron density of states (spin degeneracy included). Converting density of states to carrier density \(n(E) = E^2/\hbar^3v_F^2\), we get \(l = \sigma\hbar^{-1/2}/(e^2/\hbar)\). Therefore, the MFP resulting from ripples \(l_{ri}\) is proportional to \(n^{-1/2}\) and for charged defects \(l_{cd} \sim n^{1/2}\). The scaling of \(l_{ri}\) happens to be the same as that for electron–phonon scattering in the high-temperature regime obtained in [44]. This suggests that the temperature-induced random hopping disorder captures essential effects of the electron–phonon scattering. Indeed, based on the \(T^{1/2}\) scaling of \(\Delta t\) and Fermi’s golden rule, we have the inverse-temperature scalings, \(l_{ri} \sim T^{-1}\). Results for rippled graphene at a lower temperature of 150 K are also shown in figure 4 for comparison\(^7\). This trend is in good agreement with the linear increase of resistivity with increasing temperature from 50 K to 240 K in suspended graphene [45]. Actually, this linear scaling is found to be valid down to \(T = 0.2T_{BG}\) [39], where the Bloch–Grüneisen temperature \(T_{BG}\) is about 100 K [39] in the low-carrier-density regime. Based on our numerical results, we can also obtain a practical formula expressing the electron–phonon scattering MFP mediated by the ripples as a function of temperature and carrier density: \(l_{ri}(T, n) \approx 20(T/300\ K)^{-1/2}n^{-1/2}\). At \(T = 300\ K\), \(l_{ri}\) is about 200 nm at a moderate carrier density of \(n = 10^{10} \text{cm}^{-2}\), but can be 2 \(\mu\)m at a small carrier density of \(n = 10^{12} \text{cm}^{-2}\). This formula represents an upper limit of the electron MFP achievable in suspended graphene.

The conductivity can be converted to mobility \(\mu\) using the Drude model \(\mu = \sigma/\rho\). Away from the charge neutrality point, the charged defects lead to a \(\mu_{cd}\) that is largely independent of \(n\), whereas \(\mu_{ri}\) for the rippled case shows a clear drop as a function of the carrier density. Quantitatively, the ripple-induced mobility is \(\mu_{ri} \approx 20(e^2/\hbar)(T/300\ K)^{-1/2}n^{-1/2}\). We can thus conclude that the thermal rippling of graphene does not result in similar transport properties as caused by the long-range scatterers. In contrast, the results for long-range charged defects are in good agreement with experimental findings [5, 6] for supported graphene.

The scaling of the mobility of graphene with charged impurities as a function of impurity density \(n_{imp}\) or range \(\xi\) is shown in figure 5. It is shown for a fixed charge carrier density of \(10^{12} \text{cm}^{-2}\) and for an average over \(2-4 \times 10^{12} \text{cm}^{-2}\), corresponding to a modest and a large carrier density, respectively. The dependence on the impurity density is inversely linear, whereas the mobility shows quantitatively a \(\sim \xi^{-2}\) dependence on the impurity range, which can be understood by the fact that the size of the disordered region scales as \(\sim \xi^2\). These scaling behaviours can be used to compare our findings with different experimental results.

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\(^5\)See footnote 3.

\(^6\)See footnote 3.

\(^7\)See footnote 3.
The mobility in rippled graphene at 300 K is about 3 m²/Vs when \( n = 10^{12} \text{ cm}^{-2} \), which is comparable to that in graphene with charged impurities at a concentration of \( n_{\text{imp}} = 10 \text{ ppm} \). According to the inverse dependence of \( \mu \) on \( n_{\text{imp}} \), one can infer that when \( n_{\text{imp}} \) is reduced to below 10 ppm, the thermal ripples would become the major source of disorder around and above room temperature. This, however, excludes ripples as the major source of disorder in graphene samples on substrate.

In suspended graphene, the dominant source of disorder may also not be ripples if there is a relatively high concentration of adsorbed charged impurities, the potential distribution of which could be imaged by low-energy electron holography [46]. A rapid increase of \( \mu \) has been observed by Newaz et al [47] in graphene samples suspended in liquids at room temperature when the dielectric constant \( \kappa \) of the surrounding media is increased from 1.9 to 4.3, which can be caused by a decrease of the charged impurity range \( \xi \). A further increase of \( \kappa \), however, brings \( \mu \) back to lower values, which was attributed to additional scattering caused by ions present in the polar liquid \( (\kappa > 5) \) [47]. The same mechanism may account for the insensitivity of the mobility to the dielectric environment of supported graphene as observed in earlier works [22, 23], which has challenged the dominant role of charged impurities in supported graphene.

3. Conclusions

To conclude, we have clarified the nature of the disorder induced by the thermal ripples in graphene and its transport fingerprints. Although the thermal corrugation of graphene is a long-wavelength phenomenon, the disorder caused by ripples affecting the charge carriers is rather counterintuitively very similar to that caused by short-range scatterers. The thermal ripples result in a constant conductivity (in the diffusive transport regime) as a function of the carrier density and a decreasing mobility, in disagreement with most experimental data. In contrast, charged impurities result in a linear conductivity as a function of the carrier density and a constant mobility (not too close to the charge neutrality point), which strongly correlates with most existing experimental data. However, it should be noted that the ripple-induced disorder can be significant at relatively high temperatures and at large carrier densities.

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