# Effect of weak disorder on the density of states in graphene

Balázs Dóra\*

Max-Planck-Institut für Physik Komplexer Systeme, Nöthnitzer Strasse 38, 01187 Dresden, Germany

Klaus Ziegler

Institut für Physik, Universität Augsburg, D-86135 Augsburg, Germany

Peter Thalmeier

Max-Planck-Institut für Chemische Physik fester Stoffe, 01187 Dresden, Germany (Received 27 November 2007; published 14 March 2008)

The effect of weak potential and bond disorder on the density of states of graphene is studied. By comparing the self-consistent noncrossing approximation on the honeycomb lattice with perturbation theory on the Dirac fermions, we conclude that the linear density of states of pure graphene changes to a nonuniversal power law whose exponent depends on the strength of disorder like  $1-4g/\sqrt{3}\pi t^2$ , with g the variance of the Gaussian disorder and t the hopping integral. This can result in a significant suppression of the exponent of the density of states in the weak-disorder limit. We argue that even a nonlinear density of states can result in a conductivity that is proportional to the number of charge carriers, in accordance with experimental findings.

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## I. INTRODUCTION

Graphene is a single sheet of carbon atoms with a honeycomb lattice, exhibiting interesting transport properties.<sup>1–10</sup> These are ultimately connected to the low-energy quasiparticles of graphene, i.e., two-dimensional Dirac fermions. Its conductivity depends linearly on the carrier density and reaches a universal value in the limit of vanishing carrier density.<sup>1,2</sup> The former has been explained by the presence of charged impurities, while the latter does not allow a charged disorder.<sup>11,12</sup> Alternative explanations based on scattering on lattice corrugations or by resonant scatterers are also available.<sup>8,13,14</sup> Moreover, in the presence of a magnetic field, the half-integer quantum Hall effect is explained in terms of the unusual Landau quantization and by the existence of zero energy Landau level.<sup>2,3</sup>

The density of states in pure graphene is linear around the particle-hole symmetric filling (called the Dirac point) and vanishes at the Dirac point. This is a common feature in both the lattice description and in the continuum. In addition, the lattice model also shows a logarithmic singularity at the hopping energy, which is absent in the continuum or Dirac description.

When disorder is present, the emerging picture is blurred. Field-theoretical approaches to related models (quasiparticles in a *d*-wave superconductor) predict a power law vanishing with nonuniversal<sup>15</sup> or universal<sup>16</sup> exponent or a diverging<sup>15</sup> density of states, depending on the type and strength of disorder. Away from the Dirac point, a power law with positive nonuniversal exponent is also supported by numerical diagonalization of finite size systems.<sup>17,18</sup> At and near the Dirac point, the behavior of the density of states is less clear. Some approaches favor a finite density of states (DOS) at the Dirac point,<sup>19</sup> whereas others predict a vanishing DOS<sup>15,16</sup> or an infinite DOS.<sup>20</sup> There is some agreement that away from the Dirac point and for a weak disorder, the DOS behaves like a power law with positive exponent

$$\rho(E) \sim \rho_0 |E|^{\gamma} \quad (\gamma > 0). \tag{1}$$

The purpose of the present paper is to investigate how a nonuniversal (therefore, disorder dependent) power-law exponent (found numerically in Refs. 17 and 18) can emerge for a weak disorder (compared to the bandwidth) and what are the physical consequences. We determine the exponent based on the comparison of the self-consistent noncrossing approximation on the honeycomb lattice and of the perturbative treatment of the Dirac Hamiltonian. The exponent decreases linearly with disorder. Then, using this generally nonlinear density of states, we evaluate the conductivity away from the Dirac point by using the Einstein relation. We show that based on the specific form of the diffusion coefficient, this can result in a conductivity, depending linearly on the carrier concentration,<sup>1</sup> and in a mobility, decreasing with increasing disorder. These are in accord with a recent experiment on K adsorbed graphene.<sup>21</sup> By varying the K doping time, the impurity strength was controlled. The conductivity away from the Dirac point still depends linearly on the charge carrier concentration, but its slope, the mobility, decreases steadily with doping time.

Our results apply to other systems with Dirac fermions such as the organic conductor<sup>22</sup>  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub>.

## **II. HONEYCOMB DISPERSION**

We start with the Hamiltonian describing quasiparticles on the honeycomb lattice, given  $by^{6,23}$ 

$$H_0 = h_1 \sigma_1 + h_2 \sigma_2, \tag{2}$$

where  $\sigma_j$ 's are the Pauli matrices, representing the two sublattices. Here,

$$h_1 = -t \sum_{j=1}^{3} \cos(\mathbf{a}_j \mathbf{k}), \quad h_2 = -t \sum_{j=1}^{3} \sin(\mathbf{a}_j \mathbf{k}),$$
 (3)

with  $\mathbf{a}_1 = a(-\sqrt{3}/2, 1/2)$ ,  $\mathbf{a}_2 = a(0, -1)$ , and  $\mathbf{a}_3 = a(\sqrt{3}/2, 1/2)$  pointing toward nearest neighbors on the honeycomb lattice,



FIG. 1. (Color online) A small fragment of the honeycomb lattice is shown. The thick red lines denote the unidirectional bond disorder; on-site disorder acts on the lattice points.

*a* is the lattice constant, and *t* is the hopping integral. The resulting honeycomb dispersion is given by  $\pm \sqrt{h_1^2 + h_2^2}$ , which vanishes at six points in the Brillouin zone. To take scattering into account, we consider the mutual coexistence of both Gaussian potential (on-site) disorder (with matrix element  $V_{o,r}$ , satisfying  $\langle V_{o,r} \rangle = 0$  and variance  $\langle V_{o,r}V_{o,r'} \rangle = g_o \delta_{rr'}$ ) and bond disorder in only one direction (in addition to the uniform hopping with matrix element  $V_{b,r}$ , satisfying  $\langle V_{b,r} \rangle = g_b \delta_{rr'}$ ), which is thought to describe

reliably the more complicated case of disorder on all bonds,<sup>24</sup> and is shown in Fig. 1. In graphene, ripples can represent the main source of disorder and are approximated by random nearest-neighbor hopping rates, while potential disorder might only be relevant close to the Dirac point.<sup>25</sup> The corresponding term in the Hamiltonian is

$$V = V_{o,r}\sigma_0 + V_{b,r}\sigma_1, \tag{4}$$

which results in  $H=H_0+V$ .

Without magnetic field, the self-energy for the Green's function, which takes all noncrossing diagrams to every order into account (noncrossing approximation, NCA), can be found self-consistently from<sup>26</sup>

$$\Sigma(i\omega_n) = \frac{1}{\frac{1 - (g_o + g_b)G^2}{[(g_o + g_b) - (g_o - g_b)^2 G^2]G} - G},$$
(5)

where  $i\omega_n$  is the fermionic Matsubara frequency and

$$G = G_0[i\omega_n - \Sigma(i\omega_n)].$$
(6)

Here,  $G_0$  is the unperturbed local Green's function on the honeycomb lattice, given by

$$G_0(z) = \frac{A_c}{(2\pi)^2} \int \frac{z d^2 k}{z^2 - t^2 [4\cos(\sqrt{3}k_x/2)\cos(3k_y/2) + 2\cos(\sqrt{3}k_x) + 3]},$$
(7)

where  $A_c = 3\sqrt{3}a^2/2$  is the area of the unit cell, and the integral runs over the hexagonal Brillouin zone with corners given by the condition  $h_1^2 + h_2^2 = 0$ . This can further be brought to a closed form using the results of Ref. 27. On the other hand, in the continuum representation, using the Dirac Hamiltonian, the above Green's function simplifies to

$$G_0(z) = \frac{2A_c\sigma_0}{(2\pi)^2} \int \frac{d^2k}{z + v(k_x\sigma_1 + k_y\sigma_2)} = -\frac{A_c z\sigma_0}{2\pi v^2} \ln\left(1 - \frac{\lambda^2}{z^2}\right),$$
(8)

and v=3ta/2. The cutoff  $\lambda$  can be found by requiring the number of states in the Brillouin zone to be preserved in the Dirac case as well. This leads to  $\lambda = \sqrt{\pi\sqrt{3}t}$ . Another possible choice relies on the comparison of the low frequency parts of the Green's function in the lattice and in the continuum limit, which reveals the presence of  $\ln(\omega/3t)$  terms. This leads to  $\lambda=3t$ , which coincides with the real bandwidth on the lattice. We are going to use this form in the following. The difference of the variances becomes important when calculating the second order correction (in variance) to the self-energy. It is clear from Eq. (5) that the same self-energy is found for pure potential or unidirectional bond disorder. The effect of their coexistence is strongest when they possess the same variance. From this, the density of states follows as

$$\rho(\omega) = -\frac{1}{\pi} \text{Im } G(\omega + i\epsilon)$$
(9)

with  $\epsilon \rightarrow 0^+$ . Without disorder, we have the linear density of states  $\rho(\omega \ll t) = A_c |\omega|/2\pi v^2$ . At zero frequency, in the limit of weak disorder, the self-energy is obtained as

$$\Sigma(0) = -i\lambda \exp\left(-\frac{\pi v^2}{A_c(g_o + g_b)}\right),\tag{10}$$

which translates into a residual density of states as

$$\rho(0) = \frac{\lambda}{\pi(g_0 + g_b)} \exp\left(-\frac{\pi v^2}{A_c(g_o + g_b)}\right). \tag{11}$$

From this expression, a weak disorder is defined by the condition  $g_o + g_b \ll t^2$ . The exponential term indicates the highly nonperturbative nature of the density of states at the Dirac point: all orders of perturbation expansion vanish identically at  $\omega = 0$ . Similar results for the self-energy have been found by a more sophisticated analysis,<sup>25,28</sup> which showed similarities to the Kondo model, with  $|\Sigma(0)|$  playing the role of the Kondo scale. Renormalization group treatments<sup>25</sup> encounter singularities around the Kondo scale, which can be cured by going beyond the summation of the most divergent diagrams within the Boltzmann picture.<sup>28</sup> Therefore, approaching the



FIG. 2. (Color online) The density of states is shown in the left panel for pure on-site  $(g_b=0)$  or unidirectional bond  $(g_o=0)$  disorder (solid line) for  $(g_o+g_b)/t^2=0.1$ , 0.4, 0.8, and 1.6 with decreasing DOS at  $\omega=t$ . The red dashed line represents the coexisting bond and unidirectional bond disorder with  $g_0=g_b$ . The black dashed-dotted line denotes the free case with a linear density of states at low energies, exhibiting a logarithmic divergence at  $\omega=t$  in the pure limit. The right panel shows the residual density of states for on-site or unidirectional bond disorder (blue solid line) and their coexistence with  $g_0=g_b$  (red dashed line). The black dashed-dotted line denotes the approximate expression [Eq. (11)] for a weak disorder. For  $g_o+g_b \le 0.4t^2$ , the residual density of states is negligible.

Dirac point is equivalent to reaching the Kondo region, and perturbative treatments are valid above the Kondo scale, but fail around it.

From Eq. (5), it is evident that the interference of the mutual coexistence of both on-site and bond disorders should be most pronounced when  $g_o = g_b$ . The frequency dependence of the density of states on the honeycomb lattice can be obtained by the numerical solution of the self-consistency equation [Eq. (5)] and is shown in Fig. 2. For small frequency and disorder, there is hardly any difference between pure on-site or unidirectional bond disorder and their coexistence. However, at higher energies and disorder strength, they start to deviate from each other. At  $\omega = t$ , the weak logarithmic divergence is washed out with increasing disorder strength. Such features are absent from the Dirac description, which concentrates on the low-energy excitations. Interestingly, for a weak disorder, the residual DOS remains suppressed as suggested by Eq. (11), but the initial slope in frequency changes. In order to determine whether the exponent or its coefficient or both change with disorder, we perform a perturbation expansion in disorder strength using the Dirac Hamiltonian to quantify the resulting density of states, and we compare it to the numerical solution of the selfconsistent noncrossing approximation using the honeycomb dispersion.

#### **III. POWER-LAW EXPONENT**

The expansion of the one-particle Green's function in disorder at  $z=E+i\epsilon$  leads to

$$G(z) = G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + \dots, \qquad (12)$$

where  $V = V_{o,r}\sigma_0 + V_{b,r}\sigma_1$  describes both Gaussian potential and unidirectional bond disorder,  $G = (z - H_0 - V)^{-1}$  and  $G_0 = (z - H_0)^{-1}$ , and  $H_o = v(k_x\sigma_1 + k_y\sigma_2)$  is the Dirac Hamiltonian. After averaging over disorder, we get

$$\langle G_{rr} \rangle = G_{0;rr} + g \sum_{r'} G_{0;rr'} G_{0;r'r'} G_{0;r'r} + \dots$$
 (13)

with  $g=g_o+g_b$ . The Green's function  $G_0$  is translationally invariant and reads from Eq. (8) at real frequencies as

$$G_{0;rr} = \frac{A_c |E|}{2\pi v^2} \left\lfloor \ln\left(\frac{\lambda^2}{E^2} - 1\right) - i\pi \right\rfloor.$$
 (14)

This implies

$$\langle G_{rr} \rangle = G_{0;rr} + g(G_0^2)_{rr} G_{0;rr} + o(g^2)$$
  
=  $G_{0;rr} [1 + g(G_0^2)_{rr}] + o(g^2).$  (15)

Moreover, we have, with Eq. (14),

$$(G_0^2)_{rr} = \frac{A_c}{(2\pi)^2} \int \frac{d^2k}{[z+v(k_x\sigma_1+k_y\sigma_2)]^2}$$
$$= -\frac{\partial G_{0;rr}}{\partial z}$$
$$= \frac{A_c}{2\pi v^2} \left[ \ln\left(1-\frac{\lambda^2}{z^2}\right) - \frac{2\lambda^2}{z^2-\lambda^2} \right] \sigma_0$$
$$\approx \frac{A_c}{2\pi v^2} \left[ -2\ln\left(\frac{|E|}{\lambda}\right) - i\pi \right] \sigma_0$$
(16)

for  $\lambda \gg |E| \gg \epsilon$ . Therefore, we obtain

$$\langle G_{rr} \rangle = G_{0;rr} \left[ 1 - \frac{A_c g}{\pi v^2} \ln\left(\frac{|E|}{\lambda}\right) - \frac{igA_c}{2v^2} \right] + o(g^2). \quad (17)$$

From this, the density of states follows as

$$\rho(E) = -\frac{1}{\pi} \operatorname{Im} \langle G_{rr} \rangle = \frac{A_c E}{2\pi v^2} \left[ 1 - \frac{2gA_c}{\pi v^2} \ln\left(\frac{E}{\lambda}\right) \right]. \quad (18)$$

If we further assume that: (i) the density of states as a function of E satisfies a power law (inspired by Refs. 16–18) and (ii) the disorder strength g is small, we can formally consider



FIG. 3. (Color online) The low-energy density of states is shown in the left panel for  $(g_o + g_b)/t^2 = 0.004$ , 0.1, 0.2, 0.3, 0.4, and 0.5 from bottom to top, for pure on-site  $(g_b=0)$  or unidirectional bond  $(g_o=0)$  disorder at positive energies (blue solid line), and for their coexistence at negative energies at  $g_o = g_b$  (red dashed line). The black dashed-dotted line denotes the power-law fit as  $\rho(\omega) = \rho_0 + 2\rho_1(\omega/t)^{\gamma}$ . The green vertical dotted line separates the two parts. The right panel visualizes the exponents as a function of the variance of the disorder  $(g_o+g_b)$  for on-site or bond disorder (blue solid line) and their coexistence  $(g_o=g_b)$ . The black dashed-dotted line denotes the result of perturbation theory:  $\gamma = 1 - 4(g_o + g_b)/\sqrt{3}\pi t^2$ . As can be seen, the agreement is excellent in the limit of weak disorder. Note that g denotes the variance of the disorder.

Eq. (18) as the lowest order expansion in disorder and sum it up to a scaling form as

$$\rho(E) = \frac{A_c \lambda}{2\pi v^2} \left(\frac{E}{\lambda}\right)^{1 - (2gA_c/\pi v^2)}.$$
(19)

Hence, this suggests that the linear density of states of pure graphene changes into a nonuniversal power law depending on the strength of the disorder as  $\gamma = 1 - (4g/\pi\sqrt{3t^2})$ . Note that the exponent does not depend on the ambiguous cutoff  $\lambda$ . We mention that Eq. (18) might suggest closed forms other than Eq. (19). By using the renormalization group procedure to select the most divergent diagrams at a given order g (similar to parquet summation in the Kondo problem), one can sum it up as a geometrical series.<sup>25,29</sup> However, the resulting expression contains a singularity around  $|\Sigma(0)|$  [Eq. (10) plays the role of the Kondo temperature here], and is valid at high energies compared to  $|\Sigma(0)|$  as Eq. (18). To avoid such problems, we use a different scaling function, suggested by the results of Refs. 16–18. A similar relation between the Kondo problem and disordered graphene has been highlighted in Ref. 28 with a Kondo scale in Eq. (10).

We compare this expression to the numerical solution of the self-consistent noncrossing approximation in Fig. 3. To extract the exponent, we fit the data with  $\rho(E)$  $=\rho_0+2\rho_1(|E|/t)^{\gamma}$  and extract  $\rho_{0,1}$  and the exponent  $\gamma$ . As can be seen in the left panel, the power-law fits are excellent in an extended frequency window up to t/4. This suggests that this effect should also be observable experimentally as well. The obtained value of  $\rho_0$  is negligibly small, as follows from Eq. (11). From the fits, we deduce the exponent and its coefficient, which is shown in the right panel. It agrees well with the result of perturbation theory [Eq. (19)] in the limit of weak disorder. The suppression of the exponent is significant and can be as big as 30%-35% around  $(g_o+g_b)/t^2 \sim 0.4$ . A similar phenomenon has been observed for Dirac fermions on a square lattice in the presence of random hopping,<sup>17,18</sup> where disordered systems were studied by exact diagonalization. The decreasing exponent with disorder agrees with our results.

Similar structures in the density of states have been revealed around isolated impurities<sup>30</sup> as well as in the case of (non-Gaussian) substitutional potential disorder using the coherent potential approximation.<sup>31,32</sup>

# IV. CONDUCTIVITY FOR NONLINEAR DENSITY OF STATES

Now we turn to the discussion of the conductivity in graphene. A possible starting point is the generalized Einstein relation, which is a generally valid relation of nonequilibrium statistical mechanics, first derived by Kubo.<sup>33–35</sup> It states that the conductivity

$$\sigma = e^2 \rho D, \qquad (20)$$

where  $\rho$  is the density of states and *D* is the diffusion coefficient, both at the Fermi energy  $E_F$ . Assuming a general power-law density of states, as found above, we have  $\rho(E) = \rho_1(E/\lambda)^{\gamma}$ . In the weak-disorder limit and away from the Dirac point E=0, we can safely neglect any tiny residual value. Moreover, the diffusion coefficient in this case is of the form  $D=D_1E$ , which is validated from the Boltzmann approach in the presence of charged impurities.<sup>11</sup> On the other hand, at the Dirac point, there is an exponentially small density of states and a finite nonzero diffusion coefficient  $D \propto g/\rho$  in the presence of uncorrelated bond disorder<sup>36</sup> such that the conductivity is of order 1 in units of  $e^2/h$ .

Recently, the validity of the Boltzmann equation for twodimensional Dirac fermions was discussed in detail,<sup>28</sup> which took into account Zitterbewegung corrections. Our approach starts from the generally valid expression for  $\sigma$  given by the Einstein relation Eq. (20), which avoids certain ambiguities hidden in the Kubo or Landauer formulation.<sup>37</sup> So far, we have determined the density of states away from the Dirac point for impure graphene in accordance with exact diagonalization studies, taking into account interband transitions due to impurity scattering as well, which might correspond to Zitterbewegung. Then we have used the diffusion coefficient obtained from the Boltzmann approach<sup>11</sup> without a further justification of  $D_1$ . The aim of our semiphenomenological approach for the conductivity is only to reach a qualitative understanding, and not a complete derivation from microscopic analysis.

The self-consistent noncrossing approximation is expected to give reliable results in the case of a weak disorder, as was shown in Ref. 25 by a direct comparison with the more sophisticated renormalization group analysis. Moreover, numerically exact studies on the DOS<sup>17,18</sup> also reported about a similar evolution of the slope of the DOS at low energies and the rounding of the van Hove singularity at  $\omega = t$ . On the other hand, corrections to the noncrossing approximation may play a role in the minimal conductivity at the Dirac point. This is indicated by the fact that the twoparticle Green's function decays exponentially in the noncrossing approximation, whereas it has a power law according to the saddle-point integration.<sup>36</sup>

In the following, however, we will concentrate on the regime away from the Dirac point. Putting these results together, we find

$$\sigma = e^2 \rho_1 D_1 \frac{E_F^{\gamma+1}}{\lambda^{\gamma}}.$$
 (21)

This can be simplified further by expressing the total number of charge carriers participating in electric transport as

$$n = \int_{0}^{E_{F}} \rho(E) dE = \rho_{1} \frac{E_{F}^{\gamma+1}}{(\gamma+1)\lambda^{\gamma}}.$$
 (22)

By inserting this back to Eq. (21), we can read off the conductivity as

$$\sigma = e^2 D_1 (\gamma + 1) n. \tag{23}$$

From this we can draw several conclusions. First, it predicts that away from the Dirac point, where our approach predicts a general power-law density of states, the conductivity varies linearly with the density of charge carriers, in agreement with experiments.<sup>1</sup> Second, the mobility of the carriers, which is the coefficient of the *n* linear term in the conductivity, behaves as

$$\mu = e \left( 2 - \frac{4g}{\pi\sqrt{3}t^2} \right) D_1, \tag{24}$$

where we used our approximate expression for the exponent in the density of states [Eq. (19)]. This means that with increasing disorder (g), the mobility decreases steadily, in agreement with recent experiments on K adsorbed graphene.<sup>21</sup> There, the graphene sample was doped by K, representing a source of charged impurities. Nevertheless, these centers also distort the local electronic environment and act as bond and potential disorder as well. The observed conductivity varied linearly with the carrier concentration n, similar to Eq. (23). Moreover, the mobility (the slope of the n linear term) decreased steadily with the doping time (and, hence, the impurity concentration), which, in our picture, corresponds to a reduction of the exponent  $\gamma$  as well as the mobility [Eq. (24)].

To study the properties close to the Dirac point, we have to go beyond the perturbative regime. Then we realize that the density of states does not vanish at E=0. As an approximation, we add a small contribution near the Dirac point

$$\rho(E) = \rho_0 \delta_{\eta}(E) + \rho_1 \left(\frac{E}{\lambda}\right)^{\gamma},$$

in the form of a soft Dirac delta function

$$\delta_{\eta}(E) = \frac{1}{\pi} \frac{\eta}{E^2 + \eta^2} \quad (\eta > 0).$$

This implies a particle density n, which does not vanish at the Dirac point, as follows:

$$n(E_F) = \int_0^{E_F} \rho(E) dE \approx \rho_0 + \frac{\rho_1}{(\gamma+1)\lambda^{\gamma}} E_F^{\gamma+1}.$$
 (25)

Moreover, the diffusion coefficient does not diverge or vanish at the Dirac point<sup>24,36</sup> such that we can assume

$$D(E) = D_0 \delta_\eta(E) + D_1 E.$$

From the Einstein relation, we get the conductivity which provides an interpolation between a behavior linear in n away from the Dirac point and a minimal conductivity at the Dirac point as follows:

$$\sigma \sim \frac{e^2}{h} \begin{cases} D_0 \rho_0 \delta_\eta^2(E_F) & \text{for } E_F \sim 0\\ D_1 \rho_1 E_F^{\gamma+1} / \lambda^{\gamma} \sim (1+\gamma)n & \text{for } E_F \gg 0 \end{cases} \quad . \tag{26}$$

This, together with Eq. (25), implies for  $E_F \gg 0$  the same behavior as in Eq. (23) with the mobility of Eq. (24). The value of the minimal conductivity can be adjusted by choosing the parameter  $\eta$  properly. Therefore, Eq. (26) provides us with a qualitative understanding of the conductivity in graphene for arbitrary carrier density.

## **V. CONCLUSIONS**

We have studied the effect of weak on-site and bond disorders on the density of states and conductivity of graphene. By using the honeycomb dispersion, we determine the selfenergy due to disorder in the self-consistent noncrossing approximation. The density of states at the Dirac point is filled in for arbitrarily weak disorder. We investigate the possibility of observing nonlinear density of states away from the Dirac point, motivated by numerical studies on disordered Dirac fermionic systems. By comparing the results of noncrossing approximation on the honeycomb lattice to perturbation theory in the Dirac case, we conclude that a disorder dependent exponent can account for the evaluated density of states. The exponent decreases linearly with the variance for weak impurities. Then, by using the obtained power-law DOS, we evaluate the conductivity away from the Dirac point through the Einstein relation. We find that this causes the conductivity to depend linearly on the carrier concentration by assuming that the diffusion coefficient is linear in energy<sup>11</sup> and that the mobility decreases steadily with increasing disorder. These can also be relevant for other systems with Dirac fermions.<sup>22</sup>

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\*dora@pks.mpg.de

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