Quantum plasmons in graphene nanoribbons

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This thesis is submitted in partial fulfillment of the requirements to receive a Doctorate of Philosophy (PhD) at the Technical University of Denmark. The work herein was carried out between April 2015 and November 2018 in the Structured Electromagnetic Materials Group at the Department of Photonics Engineering. The project was supervised by Assoc. Prof. Martijn Wubs, Prof. Kristian S. Thygesen from the Department of Physics, and Prof. N. Asger Mortensen, now at University of Southern Denmark. It would not have been possible to carry out this work without the funding from the Danish Council for Independent Research–Natural Sciences (DFF Grant No. 1323-00087) and from DTU’s Department of Photonics Engineering.

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Lastly, but most importantly, I cannot express my gratitude towards my family enough: My daughter Lisa, who always puts a smile on my face, and ensures that I get up early in the morning. My wife Anne, you have been strong, patient, overbearing, and absolutely wonderful. And finally, the baby girl on her way. She reminds me of wonderful things in the future.

Kongens Lyngby, November 18, 2018

Kåre Obel Wedel
In this thesis, the plasmons of graphene nanoribbons are studied in detail using quantum mechanical tight-binding calculations combined with linear response in the random phase approximation. Plasmonics is a highly active research area that shows promise in a broad range of technological applications. One of the main interests stems from the ability of the plasmons to confine light below the diffraction limit. Technological advances in nanofabrication – making structures on the nanoscale – and in the synthesis of two-dimensional materials have enabled the fabrication of a vast range of experimental structures. To understand the plasmons at these tiny length scales, modeling of quantum mechanical effects has become increasingly important.

For the two high-symmetry ribbon geometries – the armchair ribbon and the zigzag ribbon – the results presented are interpreted using insight from the Dirac model, which gives analytical expressions for the band structures. On the electron-structure level, comparisons between the Dirac model, the tight-binding method, and the even more detailed Density Functional Theory (DFT), are made, illustrating the value of analytical models for understanding numerical results. The plasmon calculations on narrow ribbons show strong dependence on the atomic configuration at the ribbon edges, showing the importance of an atomistic modeling approach. Scale invariant plasmon energies are expected from the Dirac model, and are shown to emerge from the tight-binding calculations when the modeled ribbons are made wider and wider. Treating the higher-order plasmons as standing waves, a so-called Fabry-Pérot model, we calculate non-trivial reflection phases and effective width corrections for the two ribbon types. Furthermore, we find prominent short-range oscillations of the induced charges of the plasmons. An effect that can be explained with our analysis of the wave functions.


LIST OF PAPERS

Paper I

Emergent scale invariance of nonclassical plasmons in graphene nanoribbons.

Paper II

Edge-dependent reflection and inherited fine structure of higher-order plasmons in graphene nanoribbons.

Paper III

All-graphene edge contacts: Electrical resistance of graphene T-junctions.

Paper III was written during the curse of my PhD studies, but the chief part of the scientific work was performed in relation to my Master’s Thesis prior to the PhD. It is included here for completeness, but not mentioned in the rest of the thesis.
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In 1884, Edwin A. Abbott wrote the novel *Flatland – A Romance of Many Dimensions*. The stage is set in an entirely two-dimensional world where the “author” A Square eventually discovers the third dimension and even speculates about the existence of higher-order dimensions. In our real, three-dimensional world, the epiphany has been pointing in the opposite direction. While living in a 3D world, we have found Flatland – an entire world of 2D materials has been discovered during the last decade after Andre Geim and Konstantin Novoselov in 2004 managed to isolate the world’s first 2D material, graphene [1], using something as ordinary as scotch tape and graphite – the “lead” in pencils. For that effort, they were awarded the Nobel Prize in Physics in 2010, an unusual quick decision for the committee in a field where waiting more than 20 years between the discovery and the prize is not uncommon [2]. Since the discovery, interest in graphene has grown rapidly to the point where a staggering 0.5% of the 2017 papers on Web of Science had a title that included the word “graphene” as seen in Figure 1.1. For a material that is no more than one atom thick, graphene is surprisingly opaque. It absorbs more than 2% of the light and can actually be detected with an optical microscope [3, 4] – a property properly not unimportant to the rapid adoption and development in the scientific world. In Fig. 1.1, we also see how the interest in other 2D materials – here the class of transition metal dichalcogenides (TMDCs) – has surged.¹ Many more classes and materials are already known – more than 50 experimentally [5] – and large computational studies have been made in order to predict new 2D materials and their properties [5–7], resulting in databases that now includes many hundred possibly stable materials. Besides the semi-metallic graphene, the collection includes anything from metallic to semiconducting and insulating materials.

The immense scientific interest in the 2D world is not without reason: 2D materials are, at least in one dimension, the smallest structures we can ever hope to produce.

¹It may not have the same abundant presence in the titles as graphene, but it is, all things considered, not as catchy a name either.
CHAPTER 1. INTRODUCTION

Figure 1.1: The fraction of papers with “graphene” or “transition metal dichalcogenide” (TMDC) in the title for each year, illustrating the growing interest in graphene and other 2D materials.

are tunable, flexible, and allow for atomically precise interfaces through construction of so-called heterostructures – horizontal stacks of different types of 2D materials held together by van der Waals forces [8]. Graphene, together with other 2D materials, have been predicted to be disruptively useful in many fields, from battery-applications, to nano-electronics, and bio-sensing [9, 10].

As the title reveals, this thesis is not only about graphene, but also about plasmons. Historically, plasmons have mainly been studied in noble metals and are by no means a new invention. In fact, what we can call technological use of plasmons, will be familiar to most people as it is has been the basis for the coloring of stained glass windows since the Middle Ages [11]. Embedded in the glass are small metal particles, gold or silver for instance, that sustain localized surface plasmons at specific energies. Part of the light excites the plasmons and gets absorbed, while the remaining light passes through. This gives rise the beautiful colors in, for instance, the window from the Notre-Dame Cathedral in Paris shown in the right side of Fig. 1.2. The use of plasmons for coloring is still a highly active research area [12, 13], with the benefit, compared to the Middle Ages, that a theoretical understanding of the concept actually exists. A search in Google Books Ngram Viewer\(^2\) shows that the word plasmon does not occur until the beginning of the 20th century – see left panel of Fig. 1.2. After a small decline, the interest has been steadily increasing since the first microscopic description – in form of the random phase approximation – was given by Bohm and Pines [14–16] in a series of papers in the beginning of the 1950s. Classically, plasmons can be thought of as oscillations of a free electron cloud – like waves in a pond. This renders it possible

\(^2\)Google Books Ngram Viewer calculates the frequency of a word comparing to all written words in Google's massive text corpus in a given year.
to find the plasmons in, e.g., the extinction spectra of metal spheres, as was done by Mie [17] in 1908, and almost 20 years earlier by the Danish physicist Lorenz [18, 19]. Plasmons can couple with light to form plasmon-polaritons and concentrate the electromagnetic field deep below the diffraction limit [20, 21]. A feature that for instance makes it possible to do Surface Enhanced Raman Spectroscopy on a single molecule [22].

The work presented in this thesis lies in the intersection between the novel world of 2D materials and the century old plasmons – namely the subject of plasmons in graphene. Graphene plasmons have many advantages to conventional plasmons in metals, such as tunability [23–25], low loss [26] and stronger field confinement as iterated in a long list of review articles [27–35], and can among other things be used for sensing [36–38].

As is the case with transistors and computer chips, making devices smaller seem to be a universal goal. But as the nanometer-scale is approached – in plasmonics as well as electronics – classical theory breaks down and new properties emerge, such as nonlocal effects [39] and strictly quantum mechanical effects [40] – the “wave in a pond” picture is no longer sufficient. Using a plethora of methods, graphene nanoribbons – the geometry considered in the present work – can be produced in various widths, from a few to several hundred nanometers [41–43]. While not all fabrication methods allow for the same degree of accuracy, atomically precise ribbons, about 1 nm wide, have been demonstrated [44–46]. This thesis aims to understand some of the new plasmonic behaviors in graphene nanostructures, not with a specific technological aim, but as a small piece of the human knowledge. Graphene nanoribbon plasmons have been studied experimentally with both far field optical methods [47–50] and with near-field microscopies [51, 52], and have also been the subject of much theoretical attention [53–62]. Disks, triangles and bow-ties are among other nano-geometries that have been studied [63–66]. Graphene ribbons have two main types of edges, called the zigzag and the armchair edge, depending on how the atomic lattice is cut. These will be presented in more detail in Chap. 3.
understand the effect each of these two edge-types have on the plasmons. There have been some important contributions to this specific topic, both theoretically [48, 67–69], and recently also experimentally [70, 71]. The hope for this thesis is to provide not only a presentation of my own work, but also a more general overview of some of the underlying theories and methods used in the field.

1.1 Outline

In this thesis, I have chosen to include the published papers as an integral part of the structure by placing them in the middle of the text rather than in the back. This has the advantage of placing the main medium for scientific communication, namely the papers, as a key part of the thesis, but will inevitably challenge the possibility of getting a flow in the text. For the benefit of the reader, before each of the papers there will be an introduction as well as a guide to which parts of the papers that contain new information and which that overlap with the main text in the thesis.

With that in place, the outline is as follows.

Chapter 2 | Theory Explains the fundamentals behind the methods used in this thesis. The electron structure problem is treated in varying level of detail and the calculation of plasmons is presented. Band structure and plasmon dispersion results for infinite graphene are presented.

Chapter 3 | Applications to the ribbon geometry – Electronic structure and methods Shows the result of applying the Dirac theory to the ribbon geometry to find the band structure and the wave functions. These are compared with numerical results, some taken from Paper II, and some unpublished.

Chapter 4 | Response function with Dirac theory Contains unpublished endeavors on the response function within the Dirac model in ribbons. Presents analytical derivations of the conductivity contributions within this framework. Size dependent corrections to the bulk conductivity are presented.

Chapter 5 | Emergent scale invariance of nonclassical plasmons in graphene nanoribbons (Paper I) Introduces the results of Paper I, the entire paper, and additional information and discussion.

Chapter 6 | Edge-dependent reflection and inherited fine structure of higher-order plasmons in graphene nanoribbons (Paper II) Introduction to Paper II followed by the paper. Some details of the paper along with further discussions and insights are presented afterwards.

Chapter 7 | Conclusion and Outlook Summarizes the content of the thesis and presents possible outlooks.
The world can be described at many different levels of detail and approximation. In a simplified picture, this is done through a hierarchy of models of reality, each one including more details than the previous. It is the task of the physicist to choose an appropriate model for a given problem. A classic example would be that Newton’s Classical mechanics, and Einstein’s theory of relativity (TOR). At the low speeds we encounter in everyday life, Newton’s theories work absolutely fine – even the Apollo missions where completed without including relativistic correction [72]. Getting the Global Positioning System (GPS) to work is on the other hand not possible without the use of relativistic corrections [73]. Using Einstein’s theory to describe for instance a swinging pendulum would not be wrong, but needlessly complicated as the result would be indistinguishable from the Newtonian result.

Another example, that is perhaps more closely related to the point to come, is the fact that you would never try to understand the ocean currents, or just the behavior of water in a bucket, by modelling every single water molecule and their interactions. In a similar fashion, it is possible to describe graphene in a complex way, taking many details into account and in simpler ways that are correct in certain regimes while failing entirely in other. In this chapter, I will introduce the various approaches used throughout my PhD, beginning from one of the most capable (and used) ways of calculating quantum mechanical quantities, Density Functional Theory (DFT) and ending in a very different place with plasmons in an infinite graphene sheets, calculated from a uniform conductivity in a continuum model.

2.1 The electron structure problem

Matter is build up by atoms and it’s properties are determined by the electronic structure. The general aim of all quantum mechanical endeavors for finding the eigenstates of a system, is to solve the Schrödinger equation, here presented in its
CHAPTER 2. THEORY

The Hamiltonian acting on an eigenstate is the energy of the system times the eigenstate.

\[ H |\psi\rangle = E |\psi\rangle \]

\[ \text{The Hamiltonian acting \ldots is the energy of the system times the eigenstate.} \]

The wave function will depend on the spatial position of all electrons and atomic cores in the system and the problem is as such extremely difficult to solve in most cases. Tackling this problem is akin to include all water molecules in the bucket-allegory above. Luckily, there are a range of approximation and schemes that can be applied in order to come around this issue.

The first step to take is applying the Born-Oppenheimer approximation in which we decouple the electrons from the nuclei. This is done by making the ansatz that

\[ \Psi(R, r) = \Theta(R) \psi(R, r) \]

\[ \text{...the total wave function can be written... as a product of a nucleus part and an electron part,} \]

where \( R = \{R_i\} \) and \( r = \{r_i\} \) are the sets of all atomic and electronic coordinates respectively. This approximation is reasonable due to the large mass difference between the nucleus and the electron\(^1\) ensuring that the electrons virtually instantly collapse to the ground state whenever there is a change in the atomic positions \( R \). Now, we can simply write

\[ H_e = -\frac{1}{2} \sum_i \nabla_i \psi - \sum_{i,a} \frac{Z_a}{|\mathbf{R}_a - \mathbf{r}_i|} + \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \]

\[ \text{...the electron Hamiltonian as... the non-interacting kinetic energy... the electron-nucleus interaction... and the electron-electron interaction,} \]

with the \( i \) and \( j \) indexing all electrons and \( a \) indexing the nuclei. \( Z_a \) is the charge of the ion. For a fixed position of the nuclei, they simply set up an effective potential for the electrons that we can call the external potential, \( u_{\text{ext}}(r) \). Although this form is immensely simpler than without the Born-Oppenheimer approximation, and all interactions are simply given by the Coulomb interaction between two charged particles it is exceedingly difficult to use computationally due to the huge number of free parameters, namely the three-dimensional (3D) position of every electron in the system. Clearly, further simplifications are needed, and luckily, in the 60’s, Hohenberg and Kohn \[74\] provided the necessary foundation for what is now known as Density Functional Theory.

2.1.1 Density Functional Theory

The great insight from Hohenberg and Kohn was that the energy of the a system can be written directly as a functional of the electron density \( \rho(r) \). That is, instead of 3N

\(^1\)The ratio of the proton mass to the electron mass is \( \frac{m_p}{m_e} \approx 1836 \).
coordinates – where \( N \) is the number of electrons – it in principle suffices to use only 3 coordinates. This is the essence of the first of their two theorems, the second stating that the exact ground state can be found by variational principle. That is, minimizing the total energy by varying the electron density leads to the ground state density and energy.

Although it seems promising to reduce the multi-body problem to a problem in only three coordinates, Hohenberg and Kohn did not provide a method for doing so. This was done just a year later by Kohn and Sham \[75\] in an ingenious way. They proposed to create an auxiliary system of single-particle equations where all interactions are reduced to the interaction between an electron and the total density of all the particles. The single-electron eigenequations will include the

\[
\left(-\frac{1}{2}\nabla_i + v_{\text{eff}}(\mathbf{r})\right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})
\]

that we will take a closer look at in the following. It is not difficult to imagine at least part of what goes into the effective potential, given our attempt to describe the system from the perspective of a single electron moving in an electron cloud of all the electrons. There should still be interaction with the nuclei, there should be Coulomb interaction with the electron cloud, and finally we can include a term that essentially takes into account what has been missed by the other terms. We write this as

\[
v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\partial E_{\text{xc}}[\rho]}{\partial \rho(\mathbf{r})}
\]

We shall not delve into too many details of the exchange-correlation functional that is the only unknown part of the equation. For now it suffices to say that improving the approximations to this term is an ongoing research area and many approximations already exist. The simplest is the local density approximation (LDA) in which the correction at a position \( \mathbf{r} \) is determined as if the system was an infinite, uniform electron gas with the density \( \rho(\mathbf{r}) \). The next level of precision comes from including the local gradient of the density as is the case in the class of functionals called the generalized gradient approximations (GGAs). The Perdew-Burke-Ernzerhof (PBE) functional \[76\], that belong to this class, has been used in the work presented in this thesis.

Because the effective potential depends on the electron density when solving quantum mechanical problems in DFT:

1 **Construct** \( v_{\text{eff}} \) from the total electron density. If you don’t have \( \rho \), make a starting guess.

2 **Solve the Kohn-Sham equations** using the potential to get a set of wave functions.
3 Update the total density by summation of the single-particle densities:

\[ \rho(r) = \sum_i |\psi_i(r)|^2. \]  

Repeat 1–3 until self-consistency is reached.

2.1.1.1 A small note on basis sets

When all this is to be done on a computer, the wave functions must be represented on some finite basis set. In solid state physics where periodic boundary conditions are ubiquitous, plane waves are a popular choice for the basis set. That is indeed also what has been used in this work. Another possibility, more closely related to the following section, is the linear combination of atomic orbitals (LCAO) where the basis consists of atomic shell-like functions located at each of the atoms in the structure. This approach has the advantage that it can give good results for rather small basis sets, but, in contrast to the plane waves, it lacks a consistent, logical way of increasing the size of the basis set.

2.1.2 Tight-Binding and graphene

The tight-binding (TB) method is an approximate method for calculating the band structure by simplifying the Hamiltonian significantly. It is a semi-empirical method and the free parameters are usually fitted to either experimental or \textit{ab initio} values.

By writing the wave functions as

\[ \psi_m(r) = \frac{1}{\sqrt{N}} \sum_n e^{i \mathbf{k} \cdot \mathbf{R}_n} \phi_m(r + \mathbf{R}_n) \]

\[ \ldots \text{Bloch functions...} \ldots \text{built from atom-like orbitals...} \]

with \( \mathbf{R}_n \) being the atomic positions, we can make a simple model for the bands under the assumption that the electrons are tightly bound to their original atoms and thus only couple to atoms nearby. In second quantization we can write this Hamiltonian as

\[ H = -t_{ij} \sum_{\langle i,j \rangle} \left( c_i^\dagger c_j + \text{h.c.} \right), \]

where h.c. is short for the Hermitian conjugate, \( \langle i,j \rangle \) indicates a sum over pairs of atoms, and

\[ t_{ij} = \langle \phi_i | H | \phi_j \rangle \]

is the coupling energy between two atomic orbitals. The operator \( c_i \) \( (c_i^\dagger) \) is the annihilation (creation) operator on atom \( i \).

In graphene, the carbon atoms are placed in a hexagonal lattice as depicted in Fig. 2.1. The underlying triangular Bravais lattice is spanned by the lattice vectors \( \mathbf{a}_1 = \sqrt{3} a_0 [1, 0]^T \) and \( \mathbf{a}_2 = \frac{1}{2} a_0 [\sqrt{3}, 3]^T \) where the carbon-carbon bond length is \( a_0 = 1.42 \text{Å} \) and the lattice vector length is \( \sqrt{3} a_0 \). The rhombic unit cell contains two atoms parted into the A and B sublattice. The lattice in momentum space, shown at the
2.1. THE ELECTRON STRUCTURE PROBLEM

Figure 2.1: The atomic structure of graphene and the corresponding reciprocal space with primitive vectors $a_{1/2}$ and $b_{1/2}$. The atomic lattice consists of two triangular Bravais lattices, sublattice A and B. The Dirac cones of the band structure appear at the $K^{(0)}$ points on the corners of the hexagonal BZ in momentum space.

right in Fig. 2.1, has reciprocal vectors $b_1 = \frac{2\pi}{3a_0}[\sqrt{3}, -1]^T$ and $b_2 = \frac{4\pi}{3a_0}[0, 1]^T$. The first Brillouin zone (FBZ) and the high-symmetry points are indicated as well with the two inequivalent Dirac points: $K = \frac{2\pi}{\sqrt{3}a_0}[1, \sqrt{3}]^T$ and $K' = \frac{2\pi}{\sqrt{3}a_0}[-1, \sqrt{3}]^T$. These points are the most interesting parts of the FBZ as it is here the Fermi surface is placed at the apex of a cone-shaped band structure as we will see when we apply the TB framework to the present system. For doping levels up to $\sim 1$eV the Fermi surface will be a circle centered around the Dirac points. The atoms are bonded through $sp^2$ hybridized orbitals. This will, for each atomic site, amount to three $\sigma$-like bonds and one $\pi$-like bond from the $p_z$ orbital. As the $\sigma$ bonds are strong they will hybridize a lot and be far away from the Fermi level $[77, 78]$ where they have little importance for the properties we are interested in. It therefore suffices to use only one orbital per atomic site in the TB model. Furthermore, shown by Reich et al. $[79]$ and elsewhere, good agreement with DFT results can be obtained when only including interactions between nearest-neighbor atoms and this is the approach we will be following. The tight-binding method for graphene was first used by Wallace $[80]$, long before the experimental realization of the material. In his paper, the hopping parameter was given as $t = \pi 0.9$eV $\approx 2.8$eV which shows good agreement with more recent ab initio calculations $[79]$. Tight-binding is a true workhorse in the graphene community, and the method is heavily used, from calculating optical properties $[56, 59, 64, 65, 81]$ to determining transport properties $[82-84]$, and topological effects $[85, 86]$. Using orbitals localized on the two atoms in the unit cell, we can write the eigenstates in a way that fulfills Bloch’s theorem $[87]$: 

$$
\psi^k (r) = \sum_j e^{ikR_j} \left( c_A^j \varphi (r - R_j) + c_B^j \varphi (r - R_j - d) \right) \\
= \sum_j e^{ikR_j} \left( c_A^j |\varphi^A_j\rangle + c_B^j |\varphi^B_j\rangle \right)
$$
with
\[ \varphi^{A/B}(\mathbf{r} - \mathbf{R}_j - d\delta_{(A/B)B}) = \varphi_j^{A/B}(\mathbf{r}). \]
The vector \( \mathbf{d} \) points from the A atom to the B atom in the unit cell while \( \mathbf{R}_j \) runs over all cells. Now, calculating the overlap

\[
\langle \varphi_j^A | H | \psi^k \rangle = \left( -t \sum_{(i,j)} \left( \langle \varphi_j^A | \varphi_i^B \rangle + h.c. \right) \sum_m e^{ik_\mathbf{R}_m} \left( c_m^A \varphi_m^A + c_m^B \varphi_m^B \right) \right) = -tc_B^k \sum_{m'} e^{ik_\mathbf{R}_{m'}}^c \left( e^{i k_{\mathbf{R}_j} + e^{i k_{(\mathbf{R}_j + a_1)}} + e^{i k_{(\mathbf{R}_j + a_2)}}} \right),
\]

where the \( m' \)-sum is over the neighbors of the \( \varphi_j^A \)-atom. Since \( |\psi^k\rangle \) is taken to be an eigenstate of the Hamiltonian, Eq. (2.10) is also equal to

\[
\langle \varphi_j^A | H | \psi^k \rangle = \langle \varphi_j^A | \epsilon_k | \psi^k \rangle = \epsilon_k c_A^k e^{i k_{\mathbf{R}_j}}.
\]

Combining the two expressions leads to

\[
\epsilon_k c_A^k = -tc_B^k \left( 1 + e^{i k_{a_1}} + e^{i k_{a_2}} \right)
\]

and a similar expression for \( c_B^k \). This allows us to write the

\[
H_k = -t \begin{bmatrix} 0 & f_k \\ f_k^* & 0 \end{bmatrix}
\]

\[
\begin{array}{c}
\text{... k-dependent} \\
\text{Hamiltonian. . .}
\end{array}
\]

\[
\begin{array}{c}
\text{... as a two-by-two} \\
\text{matrix. . .}
\end{array}
\]

with \( f_k = 1 + e^{i k_{a_1}} + e^{i k_{a_2}} \).

From here, it is straightforward to find the eigenenergies and they are given by

\[
\epsilon_s(k) = s|f_k| = s \sqrt{1 + 4 \cos^2(\bar{k}_x) + 4 \cos(\bar{k}_x) \cos(\sqrt{3} \bar{k}_y)},
\]

where \( s = 1 \) (\( s = -1 \)) indicates the conduction (valence) band, and \( \bar{k}_x = \frac{\sqrt{3} a_1}{2} k_x \) and \( \bar{k}_y = \frac{\sqrt{3} a_2}{2} k_y \). Figure 2.2a and b show the resulting band structure with the remarkable Dirac points where the density of states (DOS) disappears exactly at the Fermi energy (panel c). This linear dispersion is striking and very different from the otherwise ubiquitous parabolic behavior.

\subsection*{2.1.3 The Dirac approximation}

Although the TB model can be solved analytically for infinite graphene, it is still possible to get additional insight by taking another step on our ladder of approximations. When going from DFT to our TB model we turned our attention exclusively to the bands close to the Fermi energy. In the Dirac approach, we take this almost to the
2.1. THE ELECTRON STRUCTURE PROBLEM

Figure 2.2: Graphene band structure in the TB approximation. (a): The energy of the upper band at all points of the FBZ together with the path used in the band structure plot in (b). In (c) is shown the Density of states where the Van Hove singularities that appear at the M point are clearly seen as peaks at energy $\pm t$.

extreme, and expand the TB model with respect to $k$ around the $K$ valleys where the bands are well described by this approach\(^2\). In fact, the bands are almost linear across more than 1 eV in either direction. As was the case for the TB model, this step was done decades before graphene was actually realized [88, 89]. As thus, we throw away all information about the rest of the Brillouin zone but gain a continuum approach which we can apply to other geometries – as we will see in Chap. 3 – and use as an input for analytical endeavors for describing the optical response – as we will explore in the following Sec. 2.2.4.

Redefining our $k$ as $k^\parallel K (0)$ and expanding around $k = 0$ ultimately leads to [90]

\[
H = \hbar v_F (\tau_z \otimes \sigma_x k_x - \tau_0 \otimes \sigma_y k_y)
\]

\[
= \hbar v_F \begin{bmatrix}
0 & k_x - i k_y & 0 & 0 \\
0 & k_x + i k_y & 0 & 0 \\
0 & 0 & 0 & \tau_x
\end{bmatrix},
\]

(2.16)

with the Fermi velocity $v_F = 3a_0 t/2\hbar \approx 0.9 \times 10^6 \text{ m s}^{-1}$, i.e. around 3\% of the speed of light. $\tau$ and $\sigma$ are both Pauli matrices in, respectively, valley space and pseudo-spin space, making the four dimensions corresponds to the two different $K/K'$ valleys, and the two sublattices $A/B$. We have adopted the convention of Brey and Fertig [91] such that the eigenstates have the form \([\phi^A, \phi^B, -\phi^{A'}, -\phi^{B'}]^T\).

The Hamiltonian is block diagonal, so focusing on the upper left corner, that is, only the $K$ valley electrons, we can find the eigenvalues and eigenstates. Due to the symmetry, the $K'$ result follows from a simple rewriting. We rewrite $k_x = k \cos \theta_k$, similarly for

\(^2\)This is in general formally called the $k \cdot p$ method.
CHAPTER 2. THEORY

\[ k_y = k \sin \theta_k, \text{ and } k = |k|, \text{ leading to the Hamiltonian} \]

\[ H = \hbar v_F \begin{bmatrix} 0 & ke^{-i\theta_k} \\ ke^{i\theta_k} & 0 \end{bmatrix} \]  

(2.17)

\[ \psi_k = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{i\theta_k/2} \\ se^{-i\theta_k/2} \end{pmatrix}, \quad \epsilon_k = \hbar v_F k \]

(2.18)

showing the simple linear energy dispersion. From this dispersion, when remembering that the material is two dimensional, follows the simple linear relation for the density of states:

\[ \text{DOS}(\epsilon) = \frac{2|\epsilon|}{\pi \hbar^2 v_F^2}. \]  

(2.19)

2.1.4 Summary

In this section, we have taken a tour through the various approaches to calculating the electronic structure that one can use in general, and, more specifically how they turn out when looking at bulk graphene. In Fig. 2.3, a rough sketch is shown of the band structures found in each of the three approaches. The best we can do is the full DFT calculation, solving the Kohn-Sham system of non-interacting electrons to find the true ground state electron density and the band structure that relies on all this information. The precision is high, but so is the computational cost. The TB method on the other hand gives also very precise predictions in graphene, but at a much smaller cost. With this approach, large structures can be handled, and it is heavily used in graphene research. Finally, in the Dirac limit, we completely give up on the notion of atoms and move into continuum theory. The price is yet again the precision of the predictions, but since the model is scale invariant, structures of any size can be modeled, and many problems can be dealt with (semi-)analytically.

2.2 Optical response

When a material is being subjected to an external field there will be a response of the electronic system. If the perturbation is not too large, the response will be approximately proportional to the applied field, which is exactly the starting point of the linear response theory used in the present work.

2.2.1 Linear response and RPA

Assuming a linear response, we can write the

\[ \delta n(\mathbf{r}, t) = \int d\mathbf{r}' \int dt' \chi(\mathbf{r}, \mathbf{r}', t - t') v_{\text{ext}}(\mathbf{r}', t') \]

(2.20)

...induced density as... ...a convolution between the response function and the applied field.
In its most general form, the response in \( \mathbf{r} \) at time \( t \) depends on the applied potential at all earlier times in every position in space\(^3\). It is only the time difference that matters so we can Fourier transform the equation to frequency space. Furthermore, if the medium is homogeneous, it will only be the difference in positions that come into play and that allows us to also transform the spatial coordinates to momentum space. The convolution then turns into a product:

\[
\delta n(q, \omega) = \chi(q, \omega) v_{\text{ext}}(q, \omega).
\]

If the response depended only on the perturbation in the same position, i.e. \( \chi = \chi_{\text{local}}(\mathbf{r}-\mathbf{r}') \) the response would be local. This can generally be a good model for large systems, where for instance the conductivity can be described as a uniform, local function. In contrast, for small structures the response will generally be nonlocal when the system size becomes comparable to the range of nonlocality.

Now, imagine that we can write the immediate response to an applied field as some irreducible response function, \( \chi_{\text{irr}} \). We can think of this as the first response of the system, before it reacts to its own response.\(^4\) As the induced charges give rise to a field through the Coulomb interaction, \( V \), we can thus formulate the

\[
V \chi_{\text{irr}} v_{\text{ext}} = V_{\chi}^{\text{irr}} v_{\text{ext}} + V_{\chi}^{\text{irr}} V_{\chi}^{\text{irr}} v_{\text{ext}} + \ldots
\]

\[
\ldots \text{total induced field as...} \quad \ldots \text{the first response...} \quad \ldots \text{plus the response to the first response...}
\]

\[
+ V_{\chi}^{\text{irr}} V_{\chi}^{\text{irr}} V_{\chi}^{\text{irr}} v_{\text{ext}} + \ldots
\]

\[
\ldots \text{plus the response to the response to the response, and so forth.}
\]

\(^3\)At least mathematically. The speed of light sets some natural limits on this in a real system.
\(^4\)This is not strictly correct, but I find the picture helpful. For a more thorough introduction, see e.g. Bruus and Flensberg [92] and Sólyom [93].
Removing the Coulomb operator to the left and \( v_{\text{ext}} \) we can rewrite the above expression as a Dyson like equation:

\[
\chi = \chi^{\text{irr}} + \chi^{\text{irr}} V \chi^{\text{irr}} + \chi^{\text{irr}} V \chi^{\text{irr}} V \chi^{\text{irr}} + \ldots \\
= \chi^{\text{irr}} + \chi^{\text{irr}} V \chi^{\text{irr}} \\
= \chi^{\text{irr}} (1 - V \chi^{\text{irr}})^{-1}.
\]

(2.23)

The final step of what amounts to the random phase approximation, first introduced by Bohm and Pines in a series of papers \([14, 16, 94]\), comes from approximating \( \chi^{\text{irr}} \) with the density response function of non-interaction electrons, \( \chi^0 \):

\[
\chi^{\text{RPA}} = \chi^0 (1 - V \chi^0)^{-1}.
\]

(2.24)

Approximating the irreducible response function with the non-interacting one entails the assumption that the response of the total field can be expressed as \( \delta n = \chi^0 v_{\text{tot}} \). We will look more into \( \chi^0 \) in the following section.

### 2.2.2 The non-interacting density response function

For non-interacting electrons, the density response function is given by Pitarke et al. \([95]\)

\[
\chi^0(r, r', \omega) = \frac{1}{\Omega} \sum_{i,j} (f_i - f_j) \frac{\psi_i^*(r) \psi_j(r) \psi_i(r') \psi_j^*(r')}{(\omega + i\eta) - (\varepsilon_j - \varepsilon_i)}.
\]

(2.25)

where \( \varepsilon \) is the energy and \( \Omega \) takes care of the dimension dependent normalization. \( \eta \) is a positive infinitesimal. The Fermi filling factors, \( f_{ij} = \{1 + \exp [(\varepsilon_{ij} - \varepsilon_F)/k_B T]\}^{-1} \), of the two states involved in a particular part of the sum show that this is a sum over excitations from an occupied to an unoccupied state. The expression for \( \chi^0 \) follows from the Kubo formalism, \textit{i.e.} calculating the density-density correlation function in the linear response regime, \( \chi = C_{\rho\rho}^{\text{R}}(t, t') = -i\theta(t - t') \langle [\rho(t), \rho(t')] \rangle \) for the non-interacting case. For an homogeneous electron gas the states would just be plane waves and the polarizability bubble will acquire the form known as

\[
\chi^0(q, \omega) = \frac{1}{\Omega} \sum_k \frac{\tilde{f}_{k+q} - \tilde{f}_k}{\omega + \varepsilon_{k+q} - \varepsilon_k + i\eta} \\
\ldots \text{the Lindhard function.}
\]

(2.26)

Inserting the graphene eigenstates, from the Dirac approximation, in the original expression (Eq. (2.25)) and writing the sum over \( \mathbf{k} \) and \( \mathbf{q} \) instead yields

\[
\chi^0(r, r', \omega) = \frac{1}{L^2} \sum_{\mathbf{k}, \mathbf{q}, s, s'} \frac{\tilde{f}_{\mathbf{k}+\mathbf{q}} - \tilde{f}_{\mathbf{k}}}{\omega + \varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}} + i\eta} ES
\]

(2.27)

with

\[
E = e^{-i\mathbf{k}\cdot\mathbf{r}} e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}} e^{-i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}'} \\
= e^{i\mathbf{q}(\mathbf{r}'-\mathbf{r})}
\]

\[
S = \frac{1}{4} \left[ \left( \begin{array}{c} e^{-i\delta k} \\ s \end{array} \right), \left[ \left( \begin{array}{c} e^{i\delta k} \\ s' \end{array} \right), \left( \begin{array}{c} e^{-i\delta k} \\ s' \end{array} \right) \right] \right] \\
= \frac{1}{4} \left( e^{-i\theta} + ss' \right) \left( e^{i\theta} + ss' \right) \\
= \frac{1}{2} (1 + ss' \cos \theta)
\]
2.2. OPTICAL RESPONSE

where $\theta = \theta_k - \theta_{k+q}$ is the angle between the $k$-vectors. $S$ is the difference from the pure homogeneous electron gas resulting in a suppression of backscattering in the intraband case. It should be noted that the states from Eq. (2.18) have been multiplied with a phase factor before insertion.

Finally, by taking the inverse of the discrete Fourier transform that appear on the RHS, we arrive at the expression

$$\chi^0(q, \omega) = \frac{1}{2L^2} \sum_{k,s,s'} \frac{(f_{k+q} - f_k)(1 + ss' \cos \theta)}{\omega + \epsilon_{k+q} - \epsilon_k + i\eta}.$$  

(2.28)

An alternative derivation of the resulting equation can be found in App. A. This entire expression can be evaluated analytically, as done by Wunsch et al. [96] and Hwang and Das Sarma [97]. The static case has previously been examined by Ando [98]. For future reference the polarizability is given as

$$\chi^0(x, \nu) = \text{DOS}(\nu_F) \left[ -1 + \frac{1}{8} F(x, \nu) \left\{ G(\Omega_+) - \theta(\Omega_+ - 1) \right. \right.$$  

$$\left. \times \left[ G(\Omega_-) - i\pi \right] - \theta(1 - \Omega_-)G(-\Omega_-) - i\pi \right\} \right]$$  

(2.29)

where $\Omega_{\pm} = \frac{2\pm i\nu}{x}$ and

$$F(x, \nu) = \frac{x^2}{\sqrt{\nu^2 - x^2}}, \quad x = \frac{\nu}{\nu_F}, \quad \nu = \frac{\nu}{\nu_F}$$

$$G(x) = x \sqrt{x^2 - 1} - \ln \left( x + \sqrt{x^2 - 1} \right).$$

The last $i\pi$ in (2.29) is the term corresponding to the undoped case labeled $P_0$ in Ref. [96] and $\Pi^-$ in Ref. [97]. For large energies, it is necessary to take the triangular warping of the Dirac cone into account. This is for instance done in the TB calculations in Ref. [99]. The density response function is related to the dielectric function described in the following section. We will use the nonlocal $\chi^0$ for graphene to calculate the plasmon dispersion in Sec. 2.2.4.

2.2.3 The dielectric function

The dielectric function, $\epsilon$, is the central ingredient in the description of the optical properties of a system. It relates the total potential to an external potential and is as such easily formulated in terms of the density response function as will be apparent in a moment. As for $\chi$, $\epsilon$ is generally nonlocal in space and time and we can write

$$v_{\text{ext}}(r, \omega) = \int \text{d} r' \epsilon(r, r', \omega) v_{\text{tot}}(r', \omega),$$  

(2.30)

assuming that the external potential is oscillating as $v_{\text{ext}}(r, r', t) = v_{\text{ext}}(r, r') e^{i\omega t}$. Writing this as a matrix equation instead – which eventually will be how it is represented
in the numerical implementation – shows that
\[
\frac{v_{\text{tot}}}{v_{\text{ext}}} \leq (1 + V_{\text{ext}})v_{\text{ext}}
\]
\[
\ldots \text{the inverse of } \varepsilon \ldots \text{ is given by the Coulomb interaction and the density response,}
\]
which by insertion of Eq. (2.24) yields the simple relation
\[
e^{RPA} = 1 - V_\chi^0.
\]

What we are particularly interested in regarding the dielectric function is the zero points. At these energies we find the plasmons – self-sustained modes that allow a finite total field even when no external potential is applied [100].

From the dielectric function, the energy-loss function can also be calculated. This is what would be measured in an electron energy loss spectroscopy (EELS) experiment. The expression for the loss spectrum is given by Grosso and Pastori Parravicini [101]
\[
\text{EELS}(\omega) = - \text{Im}\{\varepsilon^{-1}(\omega)\},
\]
which can be inferred from the fact that the power dissipated in the system, \(P\), is related to the imaginary part of the dielectric function \(\varepsilon\) and the amplitude of the total field \(U_0\) as \(P \propto \varepsilon_2|U_0|^2\). From the definition of the dielectric function, which couples the external field and the total field, we can rewrite this as \(P \propto \varepsilon_2|\varepsilon^{-1}U_{\text{ext}}|^2 = \text{EELS}(\omega)|U_{\text{ext}}|^2\), which reduces to Eq. (2.33).

### 2.2.3.1 A note on dimensionality

The density response function of a free-electron gas can be expanded for small values of \(q\). This corresponds to going towards the local limit in the same way as \(\omega \to 0\) is towards the static limit. The result including only the largest term in \(q\) is [100]
\[
\chi^0(\omega \to 0, 0) \propto \frac{n_0 q^2}{m \omega^2},
\]
with electron density \(n_0\) and effective mass \(m\), no matter the dimensionality. The Coulomb interaction, however, has different forms in \(q\) space dependent on the dimension. In fact [100]
\[
V = \begin{cases} 2K_0(aq) & \text{in 1D,} \\ \frac{2\pi}{q} & \text{in 2D, and} \\ \frac{4\pi}{q^2} & \text{in 3D,} \end{cases}
\]

which in combination with Eq. (2.32) gives the plasmon dispersions
\[
\omega \propto \begin{cases} q\sqrt{K_0(aq)} & \text{in 1D,} \\ \sqrt{q} & \text{in 2D, and} \\ \text{const.} & \text{in 3D.} \end{cases}
\]
2.2. OPTICAL RESPONSE

Figure 2.4: The Coulomb interaction and the dispersion of plasmons in one, two and three dimension. In dashed is indicated the low $q$ limit of the one-dimensional Coulomb interaction.

This is all shown in Fig. 2.4. The $a$ that appears in the Bessel function describing the 1D interaction is a small, but finite, width or radius of the otherwise one-dimensional system. It is necessary to include to ensure convergence of the Fourier transform \([100]\). For $q \to 0$, $K_0(aq) \approx -\ln(aq)$ which is shown as the dashed lines in Fig. 2.4.

2.2.4 Plasmons in bulk graphene

Armed with the understanding of the dielectric function, the Coulomb interaction in different dimensions as well as the density response function of graphene, we can take a more careful look at the plasmons in this material.

Although $\chi^0$ can be calculated including nonlocality, as it was given in Eq. (2.29), it can be more instructive to take a look at the local limit. As can be seen in Eq. (2.28), we can split the response in an intraband ($ss' = 1$) and an interband ($ss' = -1$) term. Evaluating these two terms for $q$ going to zero in the zero-temperature limit\(^5\), we can write the respective contributions to the conductivity as it is related to the density response through $\sigma(q, \omega) = \frac{i e^2}{q} \chi(q, \omega) [92]$. The resulting conductivities are

\[
\begin{align*}
\sigma_{\text{intra}}(\omega) &= \frac{i e^2 \epsilon_F}{\pi \hbar^2 (\omega + i\eta)} \\
\sigma_{\text{inter}}(\omega) &= \frac{e^2}{4\hbar} \left[ i \ln \frac{2\epsilon_F - \hbar \omega}{2\epsilon_F + \hbar \omega} + \Theta(\hbar \omega - 2\epsilon_F) \right].
\end{align*}
\]

Ignoring, for a moment, the interband part and taking the phenomenological loss parameter $\eta = 0$ gives rise to (in atomic units)

\[
\epsilon = \begin{cases} 
0 = 1 - \frac{2\pi q}{i\omega} \sigma(\omega) & \text{\ldots the plasmon condition}\ldots 
\end{cases}
\]

\(^5\)Details are shown in Appendix B

17
leading to

\begin{equation}
\omega(q) = \sqrt{2\epsilon_F q}
\end{equation}

\ldots a square root plasmon dispersion \ldots

as was the case for the 2D electron gas [102]. Including interband transitions screens the plasmon energy and redshifts it as seen in Fig. 2.5 where the full nonlocal dispersion relation, as determined from Eq. (2.29), is also shown. For large values of $q$, corresponding to short wavelengths, including nonlocality blueshifts the plasmon energy compared to the local model (when including interband transitions). This effect will be present in small structures where the plasmons are geometrically constrained to short wavelengths. The colormap in Fig. 2.5 shows the imaginary part of \( \chi^{\text{RPA}} \) that indicates the occurrence of electron-hole pair excitations and thus Landau loss of the plasmon. The region A in the figure is loss free while intraband loss occurs in region B and interband loss in region C.
In this chapter we will use the methods outlined in Chap. 2 to look closer at the graphene ribbon geometry. The outline is the following: We will first review the Dirac equation with the boundary conditions applicable for ribbons and compare the band structure and wave functions with the results from tight-binding and DFT. This part will also include some details on the implementation of the TB code. Some of the presented results are taken from Paper II in order to collect the electronic properties in one chapter. The practical details of calculating the plasmons of graphene ribbons within the TB approach are presented in the end.

3.1 Short introduction to the ribbon band structure

When looking at ribbons, the rhombic unit cell of the lattice (shown in Fig. 2.1 p. 9) is not the most convenient choice. In Fig. 3.1a is shown the smallest unit cell that can be repeated to construct both types of ribbons. The periodic directions of the armchair and zigzag ribbons are indicated by \( a \) and \( z \). This real space unit cell leads to a corresponding folding of the Brillouin zone [103] illustrated in Fig. 3.1b with the lattice vectors \( a' \) and \( z' \). A heuristic guess on the ribbon band structure can be made by projecting the infinite-graphene band onto the appropriate periodic axis. In AC ribbons, this results in a collapse of the two Dirac points into the \( \Gamma \) point – in ZZ ribbons, the band structure keeps \( K \) and \( K' \) separate. The projection process and the resulting band structures are illustrated in panel b and c, respectively. It can be inferred from this approach that whether AC ribbons are semi-metallic or semiconducting depends on the specific discretization of the Brillouin zone with every third repetition of the unit cell leading to allowed \( k \) points at exactly the Dirac valley (and consequently no band gap). We will return to these two types of AC ribbons in the section below. Figure 3.1c shows the actual projected band structure (blue) overlaid with the TB band structure of a 3 nm wide ribbon. The agreement is outstanding except for the
two bands in the ZZ case that appears next to the \( K \) points at zero energy. As we will see in the following (and the rest of the thesis), these are localized edge states that contribute with additional effect uninferrable from the bulk properties.

3.2 Dirac theory for graphene ribbons

The Dirac model allows for analytical insight into the band structure, also of finite graphene structures, e.g. graphene ribbons. For ribbons, this was first done in the seminal paper by Brey and Fertig [91] and the method is also outlined in the review by Castro Neto et al. [104]. The Dirac model has also been applied to triangles and hexagons [105], and disks [106, 107].

Looking solely at the \( K \)-valley part of the Hamiltonian,

\[
H^K = \hbar v_F \begin{pmatrix} 0 & k_x - i k_y \\ k_z + i k_y & 0 \end{pmatrix},
\]
from Eq. (2.17), we apply this twice to a state, $[\phi^A, \phi^B]^T$, and find the relations

\begin{align}
(3.2a) & \quad \left( k_x^2 + \frac{1}{k_y^2} \right) \phi^A = \tilde{\epsilon}^2 \phi^A, \\
(3.2b) & \quad \left( k_x^2 + \frac{1}{k_y^2} \right) \phi^B = \tilde{\epsilon}^2 \phi^B,
\end{align}

with $\tilde{\epsilon} = \epsilon/\hbar v_F$. As we are interested in the ribbon geometry shown in Fig. 3.2, where the ribbons have width $W$ and periodic boundary conditions in the $y$ direction, we replace $k_x$ with $-i\partial_x$ to obtain a differential equation with the general solutions

\begin{equation}
\phi^X(x) = Ae^{\beta x} + Be^{-\beta x},
\end{equation}

with $\beta = \sqrt{k_x^2 - \tilde{\epsilon}^2}$, and consequently $\epsilon = \hbar v_F \sqrt{k_x^2 - \beta^2}$ where $s = \pm 1$. The eigenmodes of the Hamiltonian can be found analytically for both ribbon geometries depicted in Fig. 3.2 by imposing proper corresponding boundary conditions for their wave functions. These boundary conditions are different for zigzag (ZZ) and for armchair (AC) edge terminations.

### 3.2.1 Zigzag edge termination

One edge of the ZZ ribbons consists exclusively of $A$-sublattice atoms, while the opposite edge belongs to the $B$ sublattice, as can be seen in Fig. 3.2. The boundary conditions are then straightforward, the wave function must go to zero at the edge, and thus

\begin{equation}
\phi^A(x = 0) = \phi^B(x = W) = 0.
\end{equation}
Chapter 3. Applications to the Ribbon Geometry – Electronic Structure and Methods

Inserting the boundary conditions for the $B$-lattice gives

$$\phi^B(x = W) = \frac{1}{\epsilon} (i \partial_x - ik_y) \phi^A(x = W)$$

$$0 = (i \partial_x - ik_y) \left[ Ae^{\beta x} + Be^{-\beta x} \right]_{x=W}$$

$$= A(k_y - \beta)e^{\beta W} + B(k_y + \beta)e^{-\beta W},$$

which combined with the other boundary ($\phi^A(0) = A + B = 0$) yields the dispersion relation $-e^{-2\beta W} + \frac{k_y - \beta}{k_y + \beta} = 0$ which can be written much more conveniently as

$$k_y = \frac{\beta}{\tanh(\beta W)}.$$ 

Equation (3.5) has at most one solution for real values of $\beta = \kappa \in \mathbb{R}$ which corresponds to an edge mode that falls off exponentially from the edge. From $\lim_{\kappa \to 0} \kappa / \tanh(\kappa W) = 1/W$, it follows that these modes only exist when $k_y \geq 1/W$. For imaginary values of $\beta = ik_n$, on the other hand, there are infinitely many solutions to the equation $k_y = k_n \tan(k_n W)^{-1}$ that are approximately $\pi/W$ apart. These are the bulk modes of the ribbon. The corresponding wave functions are

$$(3.6a) \quad \text{Edge:} \quad \phi_{s,k_y,z}(r) = Ce^{ik_y,2} \begin{pmatrix} \sinh(x\kappa) \\ \sinh[(W-x)\kappa] \end{pmatrix},$$

$$(3.6b) \quad \text{Bulk:} \quad \psi_{n,s,k_y}(r) = C_b e^{ik_y,2} \begin{pmatrix} \sin(xk_n) \\ \sin[(W-x)k_n] \end{pmatrix},$$

where $C_e$ and $C_b$ are the appropriate normalization factors given in Sec. C.1. We will take a closer look at the shape of the wave functions in Sec. 3.3 where we compare with the TB results.

### 3.2.2 Armchair edge termination

Looking at the armchair ribbon in Fig. 3.2, it is clear that both sublattices terminate at both edges. In contrast to the ZZ ribbon where the two Dirac valleys did not mix, this is not the case for AC ribbons, where the boundary conditions have the form [104]

$$0 = \phi^{A/B}(x = 0) + \phi^{A/B'}(x = 0),$$

$$0 = e^{iKW} \phi^{A/B}(x = W) + e^{-iKW} \phi^{A/B'}(x = W),$$

where $K = 4\pi/3\sqrt{3}a_0$ and $-K$ are the positions of the $K$-valleys in momentum space. This intervalley coupling introduced by the boundary conditions is also confirmed by Raman spectroscopy [108, 109] that can be used to distinguish between ZZ and AC termination. Together with the general form of the solution (Eq. (3.3)), the boundary conditions result in the four-vector eigenstates [53]

$$\psi_{n,s}(r) = C e^{i(k_y,2) \begin{pmatrix} e^{-i\theta} e^{ik_n x} \\ se^{i(k_n x)} \\ -e^{-i\theta} se^{-ik_n x} \end{pmatrix}},$$

(3.8)
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where $C$ is the normalization factor, $\theta$ is the argument of the $[k_n, k_y]^T$ vector, and

$$k_n = \frac{n\pi}{W} - \frac{4\pi}{3\sqrt{3}a_0} \frac{2\pi[3n - 2(N + 1)]}{3\sqrt{3}a_0(N + 1)} = \frac{\pi[3n - 2(N + 1)]}{3W}$$

(3.9)

gives the allowed (and $k_y$ independent) values of $k_n$. Here $n \in \mathbb{Z}$, and the corresponding eigenenergies are $\tilde{\varepsilon}_n = s\sqrt{k_y^2 + k_n^2}$. As can be deduced, we have expressed the width of the ribbon as

$$W = (N + 1)a_0\sqrt{3}/2,$$

(3.10)

where $N$ is the number of atomic rows. From this form it follows that every third ribbon, where $3n - 2(N + 1) = 0$ can be fulfilled, will be semi-metallic since there is a $n$ such that $\varepsilon_n(k_y = 0) = 0$. The remaining two thirds of the ribbons will have a band gap.

The way of defining the width in Eq. (3.10) gives the correct order of semi-metallic and semiconducting ribbons when compared with tight-binding calculations. For example, the narrow ribbon with $N = 2$, is just a one-dimensional chain with corresponding cosine band structure and no band gap. So $N = 2$ is a semi-metal and there should exist a solution of the above condition for a semi-metal, $3n - 2(2 + 1) = 0$, which is the indeed case for $n = 2$.

3.2.3 Scale invariance

As discussed later in Paper I, the entire Dirac equation is in fact scale invariant and we can rewrite all solutions in dimensionless quantities. The relevant sizes appearing in the ribbon system is the electron Fermi wavelength $\lambda_F = 2\pi k_F^{-1}$ and the ribbon width $W$. We therefore define the dimensionless ratio $\Lambda = k_FW$ and scale all momenta with $k_F$, distances with $W$, and energies with $\varepsilon_F$ to find the following results for ZZ ribbons (corresponding to Eqs. (3.5) and (3.6a)):

Bulk:

$$K_y = \frac{K_n}{\tan(K_n\Lambda)},$$

(3.11a)

$$E_n = \sqrt{K_y^2 + K_n^2},$$

(3.11b)

$$\psi(\tilde{x}) = C_0 e^{iK_y\Lambda \tilde{x}} \left( \frac{i s \sin(\tilde{x} \Lambda K_n)}{\sin((1 - \tilde{x}) \Lambda K_n)} \right),$$

(3.11c)

Edge:

$$K_y = \frac{K}{\tanh(K\Lambda)},$$

$$E_e = \sqrt{K_y^2 - K^2},$$

$$\phi(\tilde{x}) = C_0 e^{iK_y\Lambda \tilde{x}} \left( \frac{i s \sinh(\tilde{x} \Lambda K)}{\sinh((1 - \tilde{x}) \Lambda K)} \right),$$

(3.11d)

where $k_y \rightarrow K_y$, $k_n \rightarrow K_n$, $\kappa \rightarrow K$, $\epsilon \rightarrow E$, and $\tilde{x} = x/W$ is the dimensionless lateral position in the ribbon. For the AC ribbons we find that

$$K_n = \frac{\pi[3n - 2(N + 1)]}{3\Lambda}.$$

(3.12)

Utilizing the dimensionless form and scaling all quantities with the relative system size $\Lambda$, we can plot the band structures in a general form as depicted in Fig. 3.3. This is essentially the only three band structures that exist within the Dirac model on the ribbon geometry. In the first panel, the edge states of the zigzag ribbon are shown in red and we can see the transition from a bulk-like mode to the edge-like mode.
Figure 3.3: The band structures of ZZ and the two different types of AC ribbons in dimensionless quantities. The edge states that occur in ZZ ribbons are indicated with red. The positions of the lowest lying parabolic bands are shown with the dashed line. Figure taken from Paper I.

The center panel shows the semi-metallic AC band structure where the bands are degenerate. For the semiconducting ribbons (right panel), the degeneracy is lifted and a gap forms. It follows directly from the figure that

\[ \epsilon_g = \frac{2\pi \hbar v_F}{3W} \]

\( \ldots \) the gap size \( \ldots \) scales inversely with the ribbon size.

One noticeable thing in Fig. 3.3, is that the bottom of the lowest parabolic band is placed at three different levels. This is further investigated in the following, and the consequences are discussed in Paper I.

3.2.4 Parabolic approximation

It is an easy task to identify the band bottoms of the AC ribbons. Since \( K_n \) and \( K_y \) are independent, it is merely a matter of choosing \( K_y = 0 \) and the resulting band edge positions shown in Fig. 3.3 follow directly from \( E = \pm |K_n| \), and \( K_n \) is given in Eq. (3.12).

For the ZZ ribbon, we can approximate the bands with parabolas at the bottoms and, after some algebra, we find that the minimum occurs at \( K_y = \Lambda^{-1} \). Expanding for small \( K_y \) around that point gives

\[ E_n \approx \sqrt{\xi_n^2 + 1} \Lambda + \Lambda (K_y - \frac{1}{\Lambda})^2 \sqrt{\xi_n^2 + 1} \frac{1}{2\xi_n^2}, \]

where \( \xi_n = K_n \Lambda \) and fulfills \( \xi_n = \tan(\xi_n) \). One relevant conclusion of this is that the Fermi energy exactly touches the bottom of the lowest parabolic band (corresponding to \( E_1 = 1 \)) when

\[ \Lambda = \sqrt{\xi_1^2 + 1} \approx 4.6033, \]

as shown in Fig. 3.3. The values of \( x_n \) are approximately \( (n + \frac{1}{2})\pi \) for large values of \( n \).
3.3 Comparing the Dirac model with numerical methods

In this section, we will briefly compare the band structures and the eigenstates from the Dirac model with the more precise – but also more computationally demanding – results from TB as well as a few results from DFT. We will see that even where the Dirac model seems to fall short in describing the atomic details, a lot of insight is still to be found in this method.

3.3.1 Tight-binding for ribbons

The tight-binding wave functions and energies are found by directly diagonalizing a $N \times N$ matrix using the Scipy library for Python, where $N$ in the number of atoms in the supercell. As the Hamiltonian is $k$ dependent, the diagonalization is done on an evenly spaced $k$-point grid consisting of 5000 points in the one-dimensional BZ.

The TB band structures around the Dirac point for two 6 nm ribbons, ZZ and AC respectively, are shown in comparison with the Dirac model in Fig. 3.4. The first thing to notice is the striking similarity between the two. The red lines are the edge states in the Dirac model, and the dots from the TB calculations are colored according to the degree of localization on the outermost quarters of the ribbon. That is, we have defined an edginess factor as

$$
\lambda_n(k) = \frac{\sum_{l \in \Omega} |\psi_{nl}(k)|^2 - \sum_{l \in \Omega} |\psi_{nl}(k)|^2}{\sum_l |\psi_{nl}(k)|^2},
$$

(3.16)

where $l$ refers to the atomic sites. We have defined $\Omega$ as the two quarters of atoms closest to the edges and the expression thus yields unity if the electron is entirely...
in this region, zero if it is evenly distributed between the center and the edges, and negative one if it is only found in the ribbon’s middle half. For the ZZ ribbon, we see that this way of determining whether a state is an edge states agrees extremely well with the division between the two types of states in the Dirac approximation. For the AC ribbon, the eigenstates seem to be completely delocalized, which is also consistent with the fact that Dirac theory predicts plane wave states. Except at the Dirac point, the AC bands are slightly split in TB compared to Dirac where they are degenerate. This is explained when looking at the wave functions in the following Sec. 3.3.2, but the increased splitting at higher energies is a consequence of shorter-wavelength eigenstates that more closely probes the atomic structure.

One thing to remark is that more precise DFT calculations show that none of the AC ribbons are in fact semi-metallic \[110\]. They still fall into three categories where two of them have large gaps that are comparable with the ones found in TB and Dirac, while the last one has a much smaller, but finite gap. As the graphene plasmons are our ultimate objects of interest, we generally look at doped ribbons where this tiny gap is without importance.

### 3.3.2 Wave functions

In this section the analytically determined wave functions of the Dirac model will be compared to the numerical results of the TB calculations. As will become clear, when delving into the details, the Dirac model contains even more information than is superficially evident.

Figure 3.5 shows the sublattice wave function density for eight different states close
3.3. COMPARING THE DIRAC MODEL WITH NUMERICAL METHODS

Figure 3.6: Unweaving the numerical results of semiconducting AC ribbon wave functions. In DFT, the charges are projected onto individual atoms using a Bader analysis. For both DFT and TB, every third atom is connected revealing a smooth behavior across the ribbon. The resulting curves are then “unfolded” to uncover the underlying long-range oscillation that matches the Dirac model prediction.

to the Dirac point in a ZZ ribbon. The dots are the TB results for a 6 nm ribbon while the full lines are the Dirac results from Eq. (3.6a). The agreement is remarkable. Moving from left to right we see how $k_n$ gets smaller and the wavelength longer. This is especially clear in the bottom row, where, in the bottom right corner, we see the edge states that are clearly localized.

Looking at the AC wave functions in Eq. (3.8), comparison with TB could be expected to be a rather dull affair as the plane waves all just predict a uniform electron density. The reality is much more interesting, though.

Due to the intervalley coupling, we can predict interference between the $K$- and the $K'$-valley states resulting in short-range oscillations with a wavelength corresponding to the distance between the valleys [90]: $2\pi/|K - K'| = 3a_0\sqrt{3}/2$, which happens to be exactly the distance between every third atom along the ZZ direction in the lattice. This was predicted and confirmed through TB calculations by Brey and Fertig [90, 91]. In Figs. 3.6 and 3.7 the TB wave function densities of the lowest-lying bands at the Dirac point of the semiconducting AC ribbon are shown. By coloring and connecting the atoms depending on which group of thirds they belong to, it becomes clear that these oscillations obfuscate a much simpler underlying structure as seen in Fig. 3.6.

Starting from the first, second and third atom, every third atom is connected and colored in respectively blue, orange, and green. Each of these curves change smoothly across the ribbon. Furthermore, and this is the new insight presented in Paper II, “unfolding” the wave function reveals a smooth long-wavelength wave. The unfolding process is also illustrated in Fig. 3.6. Recalling from Eq. (3.9), the Dirac model predicts semiconducting ribbons to have wave functions with wavelengths

$$\lambda_{sc} = \frac{2\pi}{|k_n|}$$

$$= 6Wm, \quad \text{with } m \in \{1, 2, 4, 5, 7, 8, \ldots\}.$$ 

Taking the absolute square of such a wave yields half the wavelength and we find precisely 1, 2, 4, and 5 oscillations on the $3W$ distance in Fig. 3.6 and the two bottom rows of Fig. 3.7.
Figure 3.7: Higher order wave functions at the Dirac point of a semiconducting AC ribbon following the same approach as Fig. 3.6. The gray area shows the DFT electron density projected onto one dimension across the ribbon.

To really test the validity of this result, I have also performed a DFT calculation for the ribbon. As the calculation was done with a plane wave basis set, rather than localized atomic orbitals, there is no direct measure of the weight on each atomic site. With the resulting electron density, represented on a real-space grid, we can instead project the charges onto the nearby atoms using a Bader charge analysis and use that for a direct comparison with the TB results. It can be seen in the Figs. 3.6 and 3.7, that this changes the results very little and that the insight from the Dirac model is still valid. One small caveat when performing the DFT calculation is that one has to remember to terminate the edges with hydrogen to avoid loose bonds from the outermost carbon atoms. In real ribbons, there will also be some termination, but in TB we can safely ignore this as the influence on the properties is minute. In line with that statement, the Bader analysis finds almost exactly zero electrons on the hydrogen atoms and in the plots, we have shown only the carbon atoms to better compare with TB. Finally, we can generally write the density from state \( n \) at site atomic site \( i \) as

\[
\rho_n(x_i) = \mathcal{N} \sin^2 \left( \frac{\pi}{3} \left( x_i - [(i + N) \mod 3] k_n \right) \right),
\]

where the site index starts with 1 as in Fig. 3.6, \( x_i \) is the x-coordinate of the site, and \( \mathcal{N} \) is a normalization factor.

The semi-metallic AC ribbons behave slightly different as the wave functions do not unfold in the same manner. If we group the atoms by the same every-third method as before, we do however still observe the same kind of long range oscillation that matches the Dirac model predictions where

\[
\lambda_{sm} = \left| \frac{2\pi}{k_n} \right| = 2Wm, \quad \text{with } m \in \mathbb{N} \cup \{0\}.
\]

1Using the GPAW code with a cut-off energy of 500 eV and 15 \( k \)-points in the periodic direction of the supercell.
3.4. CALCULATING RESPONSE IN TB

As before, the density varies twice as fast and, as seen in Fig. 3.8, we find waves with wavelengths that are a whole number times \( W \). The middle third of the atoms (green) has the wave placed symmetrically around the center while it is shifted with one third of the wavelength in either direction for the two remaining thirds. A close look at the figure also reveals the origin of the broken degeneracy in TB: Focusing on the second band, the two states differs in which atom is the outermost. In the top subplot the outermost atom on the left side (blue) follows the likewise colored curve siphoned from the Dirac description. On the bottom plot, the outermost atom has switched to the other curve indicated by the mismatching colors. The effect gets stronger for fewer atoms, and for higher order bands as could be seen in Fig. 3.4.

To summarize, the electronic properties of the Dirac model provides excellent agreement with tight-binding calculations on a band structure, as well as on a wave function level. Although the precise atomic details are lost when linearizing the TB model, we can still extract some of these details by comparing the analytical results with the numerical ones. For the semiconducting AC ribbons where we also compared with DFT, we could see that the Dirac predictions are still accurate in comparison with a state-of-the-art quantum calculation.

3.4 Calculating response in TB

In the main part of the work done during the project I have used the electronic states to predict the optical response of the graphene ribbons. In this section, I will briefly present some of the implementation details of the TB calculations.

3.4.1 Density response function

We have been following the technique first realized by Thongrattanasiri et al. [56] and subsequently applied in a wide range of works [63–65, 114, 115]. The method works by
evaluating Eq. (2.25), but using the discrete basis of the tight-binding orbitals. This is done by transforming \( \sqrt{n}(r) \rightarrow a_{in} \) where \( i \) is an index of the atoms – or more generally the orbitals, but since we just have one \( p_z \) orbital per atom, it is the same in this case. As the ribbons are infinite in one direction we can turn that coordinate into an integral over the (1D) Brillouin zone which for \( q = 0 \) results in

\[
\chi_{ij}^0(\omega) = \frac{2e^2}{\hbar} \frac{b}{2\pi} \int_{\text{BZ}} \frac{dk}{\epsilon_{nm} + \hbar(\omega + i\eta)} a_{in}^* a_{jm}.
\]

Here the \( i, j \) run over atomic sites in the supercell, while \( n, m \) label the eigenmodes at wave vector \( k \). Similarly, all other quantities get transformed to the discretized basis such that the Coulomb interaction \( V(r, r') \rightarrow V_{ij} \), the induced density \( \rho(r) \rightarrow \rho_i \).

Although there exists different schemes to speed up the calculation, such as using Fast Fourier Transforms or Green’s function methods, that both result in a scaling of \( N^3 \) with \( N \) being the number of atoms, I have simply done a direct evaluation of Eq. (3.18) by inserting all the states from the TB calculation. Since this involves looping over pairs of sites and pairs of eigenstates (the \( i, j \) and the \( n, m \)), this approach scales as \( N^4 \). The code is written entirely in Python which is a very high level language, and is as such easy for development. It is however not optimized for speed, but fortunately a plethora of methods and models exist to circumvent this. I have used the Numba module that compiles the important part of the code to machine language and thus provides a significant speedup.

### 3.4.2 Coulomb interaction

The Coulomb interaction in particular needs some care to handle properly. In fact it has a divergence issue for \( i = j \) \( (r = r') \) as well as a convergence problem for large distances as the scaling is \( 1/r \). Beginning with the latter challenge:

Because of the periodicity, where the supercell has width \( b \), we write

\[
V_{ij} = \sum_n V_{i0,jn} e^{iqbn}
\]

\( \ldots \) the Coulomb matrix as \( \ldots \) site \( i \) in supercell 0 interacting with site \( j \) in cell \( n \).

This does not converge with respect to \( n \) as, assuming \( q = 0 \), the terms go as \( |nb|^{-1} \) for large \( n \). However, we are not really interested in the Coulomb interaction itself. What we seek is the dielectric function which depends on the product of \( V \) and \( \chi^0 \) (recall Eq. (2.32)) – and this product can indeed be converged. For practical reasons it is easier to calculate a modified Coulomb interaction that gives the correct product which is possible using a property of \( \chi^0 \). In real-space the relation between the induced charge and the total field is given by

\[
\delta n(r) = \int dr' \chi^0(r, r')V_{\text{tot}}(r').
\]
Since we cannot create or remove charges we must have that

\[ Z_d \delta n(r) = 0 \quad (r), \quad Z_d \delta n(r, r') = 0. \]  

(3.21)

In the discretized basis, this corresponds to

\[ \sum_j \chi_{ij}^0 = 0. \]  

(3.22)

When calculating the dielectric function in RPA, we need the product \( V \chi^0 \). Because of the charge neutrality expressed in Eq. (3.22), we can add or subtract a term to \( V \) as long as it is independent of \( j \). This allows us to calculate a modified Coulomb interaction term \( \tilde{V} \) that converges, by subtracting \( |n b|^{-1} \) from all the terms:

\[
\sum_k V_{ik} \chi_{kj}^0 = \sum_k \sum_n \sum_{i0,kn} e^{i q b n} \chi_{kj}^0 \\
= \sum_n \sum_k \left( \sum_{i0,kn} e^{i q b n} - \frac{(1 - \delta_{0n})}{|n b|} \right) \chi_{kj}^0 \\
= \sum_k \tilde{V}_{ik} \chi_{kj}^0,
\]

It is important to stress that this is not a screened Coulomb interaction in any physical sense. Since it by construction satisfies \( V \chi^0 = \tilde{V} \chi^0 \), it is merely a mathematical trick to handle the long-range convergence issue.

The first issue mentioned regarding the self-interaction, i.e. the divergence at zero distance, was handled by Thongrattanasiri et al. [56] by rigorously calculating the density weighted Hartree interaction taking the spatial extent of the \( p_z \) orbitals into account. At large distances, the interaction will simply be point-like and follow a \( 1/r \) behavior. But at short distances, and most importantly at the same site, there will be a difference. The most important change is that instead of diverging, the interaction saturates at a value corresponding the the distance \( 0.65a_0 \), where \( a_0 = 1.421 \) Å is the interatomic distance. As can be seen in Fig. 3.9 there is a slight correction at the nearest atom as well, while the interaction is virtually unchanged at large distances. We have acquired high precision fits of the correct interaction through private correspondence with the group of Thongrattanasiri.
Figure 3.10: Loss spectrum (top) and real part of the dielectric matrix eigenvalues (bottom) for a 6 nm wide zigzag graphene ribbon. The plasmons can be identified as either the peaks in the loss spectrum or as the zero points of the eigenvalues. $\varepsilon_F = 0.4\text{eV}$

### 3.4.3 Dielectric function

The proper interpretation of the dielectric function, now in its discretized form such that

$$
\varepsilon_{ij} = 1 - V_{ii} x_{ij}^0 ,
$$

has been thoroughly treated by Winther et al. [117]. As shown by Andersen et al. [118], we can use a spectral representation to write

$$
\varepsilon_{ij}(\omega) = \sum_n \varepsilon_n(\omega) \phi_{n,i}(\omega) \rho^*_{n,j}(\omega)
$$

...the dielectric matrix with... ...the eigenvalues, the induced field and induced charge,

where the two latter are, respectively, the right and left eigenvectors of the matrix. The occurrence of plasmons is thus connected to the zeros of the real part of the eigenvalues of $\varepsilon$ and we can use the eigenvectors to look at the spatial distribution. Additionally, we can still calculate the energy loss function by insertion of the eigenvalues into Eq. (2.33). As such, the plasmons can also be identified as the peaks in the loss spectra. As long as the imaginary part of $\varepsilon$ does not vary too much around a zero-point, the two methods will be equivalent [118, 119].

Figure 3.10 shows as an example, the resulting dielectric function of a 6 nm wide zigzag ribbon. In the bottom panel, the real parts of the eigenvalues are shown with the ones closest to zero indicated. We can see that we have multiple modes that are fairly evenly spaced. In the top of the figure is shown the largest component of the

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3Winther and Andersen are in fact the same person who changed name between the two papers.
loss spectra. The two first modes are clearly identifiable and match the energies from the $\text{Re}(c_n)$ analysis. The higher-order modes are broadened to an extent that make them almost impossible to determine from the loss function. In the bottom panel, in the middle between mode 2 and 3, there is also an eigenvalue close to zero. That is however not a plasmon, but corresponds to a single-particle transition as can be seen by fitting a single-pole Lorentz model of the dielectric function to the found curves [118, 119].

Armed with the certainty that the Dirac model is a good description of the electronic states in graphene ribbons, together with the necessary prerequisites to calculate the optical response in tight-binding, we move to the next chapters that focus on the density response and the plasmonic modes in the ribbons.
In this chapter, we will calculate the local conductivity within the Dirac approximation applied to zigzag ribbons. The work presented has not been published before. As we saw in Chap. 3, the zigzag termination leads to the appearance of localized edge states, that do not occur in the projected band structure of infinite graphene. They will contribute with new transitions affecting the plasmonic response, but their contribution becomes negligible when the ribbon width goes to infinity. A similar study of the edge contribution has previously been done by Christensen et al. [64], but in the following we also look at the corrections to the intra- and interband terms.

We will calculate \( \sigma(q \to 0, \omega) \) by inserting the bulk and edge states found in Sec. 3.2.1 into the quantum mechanical expression for the conductivity in the \( q \to 0 \) limit. Furthermore, we will assume that the field is perpendicular to the ribbons, which is the \( x \) direction for the chosen coordinate system. Using the expression for the dielectric function in reciprocal space from Grosso and Pastori Parravicini [101], we have

\[
\sigma(q, \omega) = \frac{i \omega}{\Omega q^2} \sum_k \sum_{n, n'} \frac{f_n k - f_{n'k+q}}{\omega + c_{nk} - c_{n'k+q} + i\eta} \left| \langle \psi_{nk} | e^{i q \cdot r} | \psi_{n'k+q} \rangle \right|^2 .
\]

We will begin by looking at the overlap integral. To broaden the perspective slightly, Eq. (4.1) can also be found by taking the head \( (i.e. \text{setting the reciprocal lattice vectors } G = G' = 0) \), which amounts to ignoring local field effects) of the more general expression for the polarizability of periodic materials as derived by Adler [120] and Wiser [121]. If we only consider interband transitions, the local limit follows from the expansion of the exponential function, \( e^{i q \cdot r} \approx 1 + q \cdot r \), where, since the eigenstates are orthonormal, only the second term survives in the overlap integral. This leads to the local interband expression (taking \( q \parallel \hat{z} \))

\[
\sigma_{\text{inter}}(\omega) = \frac{i \omega}{\Omega} \sum_k \sum_{n, n'} \left| f_n - f_{n'} \right| \left| \frac{\langle \psi_n | x | \psi_{n'} \rangle}{\omega + c_n - c_{n'} + i\eta} \right|^2 .
\]
Figure 4.1: In a doped graphene zigzag ribbon, three different transitions contribute to the conductivity as illustrated on these band structure sketches.

where the $k$ dependence is implicit. For intraband transitions, the highest-order term from the expansion of the matrix element will simply be unity \[122\]. Thus the local intraband conductivity has the form:

\[
\sigma_{\text{intra}}(\omega) = \lim_{q \to 0} \frac{i\omega}{\Omega q^2} \sum_{k} \sum_{n} \frac{f_{nk} - f_{nk+q}}{\omega + \epsilon_{nk} - \epsilon_{nk+q} + i\eta}.
\]

All that is left now is to insert the Dirac states into the above expressions. As we have two different kinds of states, bulk and edge, we will have three different contributions if the Fermi level is above the edge states: intraband within the bulk bands (\textit{intra}), interband between bulk bands (\textit{inter}), and finally the interband contribution for edge-to-bulk transitions (\textit{edge}). They are all illustrated in Fig. 4.1, and we will look at them one by one in the following.

One additional approximation that we will make is to take the temperature to zero. This turns the Fermi fillings into step functions and the energy-derivative of $f$ into a Dirac delta function.

\section{4.1 Intraband conductivity}

The derivation of the intraband conductivity of graphene ribbons is presented in the following. Further details are given in Sec. C.3.

For the intraband contribution we are expanding the Fermi filling difference and the energy difference in small $q$. We project $q$ into the $x$ and $y$ contributions such that

\[
q_x = q_y \frac{\partial k_n}{\partial k_y},
\]

and insert in the expression for the energies to find

\[
\epsilon_n(k_y) - \epsilon_n(k_y - q_y) \approx \hbar v_F q_y \frac{\epsilon_n(k_y W - 1)}{\epsilon_n^2 W - k_y}.
\]

Following the same approach for the Fermi distributions leads to

\[
f_n(k_y) - f_n(k_y - q_y) \approx \delta(k_f - \epsilon_n) q_y \frac{\epsilon_n(k_y W - 1)}{\epsilon_n^2 W - k_y},
\]
in the zero-temperature limit. The energies are a part of a denominator that we will also expand:

\[
\frac{1}{\epsilon_n(k_y) - \epsilon_n(k_y - q_y) - \hbar(\omega + i\eta)} \approx -\frac{1}{\hbar(\omega + i\eta)} + \frac{q_y \hbar \nu_F}{\hbar^2(\omega + i\eta)^2} \frac{\tilde{\epsilon}_n(k_y W - 1)}{\epsilon_n^2 W - k_y}.
\]

Combining all of these expressions, we arrive at the not very pleasing

\[
\sigma_{\text{intra}}(\omega) = \frac{2ie^2\omega}{\pi W q_y^2} \sum_{n} dk_y \left( -\frac{1}{\hbar(\omega + i\eta)} + \frac{q_y \hbar \nu_F}{\hbar^2(\omega + i\eta)^2} \frac{\tilde{\epsilon}_n(k_y W - 1)}{\epsilon_n^2 W - k_y} \right) \times \delta(k_f - \tilde{\epsilon}_n)q_y \frac{\tilde{\epsilon}_n(k_y W - 1)}{\epsilon_n^2 W - k_y},
\]

where we have turned the sum over \( k_y \) into an integral and introduced the constants that we had set to unity in the more general derivations presented earlier. The first term inside the integral is uneven in \( q \) and will disappear for symmetry reasons. Because of the delta function, the sum and integral can be turned into a sum over states at the Fermi level. Using the notation \( k_y^{(i)} \) to mean the \( k_y \) value of the \( i \)th crossing of the Fermi surface, we find

\[
\sigma_{\text{intra}}(\omega) = \frac{2ie^2\omega}{\pi W} \frac{\epsilon_F}{\hbar^2(\omega + i\eta)^2} \sum_{j} \left| \frac{k_y^{(i)}}{k_F} \right| \frac{W - 1}{\epsilon_F^2 W - k_y^{(i)}}.
\]

This expression can be evaluated numerically, but we can make further progress analytically by taking the asymptotic limit of \( W \to \infty \).

In this limit, the distances between the bands in \( k \) space become \( \pi/W \) and we find

\[
\sigma_{\text{intra}}(\omega) = \frac{2ie^2\omega}{\pi W} \frac{\hbar \nu_F}{\hbar^2(\omega + i\eta)^2} \sum_{n} \left| \frac{k_y^{(i)}}{k_F} \right| \frac{W}{\epsilon_F^2} \sqrt{1 - \left( \frac{n \pi}{k_F W} \right)^2} \approx \frac{ie^2\epsilon_F}{\pi \hbar(\omega + i\eta)} \left( 1 - \frac{2}{k_F W} \right),
\]

where the details of the evaluation of the sum is in Sec. D.1 and we have redefined \( \eta \) to its usual form [68, 101]. The width independent term can be recognized as the infinite graphene result (\( \sigma_{\text{intra}}^{\infty} \)), and the second term is thus the consequence of discretizing the bands crossing the Fermi level. The ratio between the calculated conductance and the bulk limit for both the analytical limit and the numerical evaluation of Eq. (4.7) is shown in Fig. 4.3 showing that the limit works very well already for \( \Lambda = k_F W \approx 10 \). The oscillations of the full expression stems from every time an additional band crosses the Fermi level. With the dotted line we have indicated the limit where it is only one band that is (partly) occupied (\( \Lambda = \Lambda_c \)). Below that point, the system behaves completely different as since it just one point that moves around on the Fermi circle (see Fig. 4.2). The allowed values and the points on the Fermi circle in \( k \) space are shown in Fig. 4.2 for different values of \( \Lambda \). The gray lines are placed with a spacing of \( \pi/\Lambda \).
CHAPTER 4. RESPONSE FUNCTION WITH DIRAC THEORY

Figure 4.2: Allowed modes in $k$ space (blue lines) and the intersections with the Fermi circle (black). The distance between the bands is approximately $\pi/\Lambda$ as indicated with gray lines.

Figure 4.3: The ratio intraband conductivities of the zigzag ribbon and bulk graphene with both the numerical evaluation and the analytic approximation for the ribbons. The vertical gray dotted line indicates the point where only one band crosses the Fermi level.

Inserting our new-found correction to the conductivity into the plasmon condition – here in dimension-independent form, with the Coulomb interaction $V_q$ – we find

\[
1 = V_q \frac{q^2}{i\omega} \sigma(\omega) \Leftrightarrow \\
\omega = \sqrt{1 - \frac{2}{k_F W}} \times \sqrt{V_q \frac{q^2 c_F}{\pi}}
\]

(4.9)

...a correction factor... ...to the normal plasmon dispersion.

We will return to this correction later in Chap. 5, but can already establish that it is small given the approximations made.

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4.2 Interband conductivity

Having established the size correction of the intraband conductivity, we continue looking for similar corrections in the other contributions to $\sigma$. For the bulk-bulk interband term we use Eq. (4.2) and calculate the matrix element by inserting pairs of states with the same band number but on each their side of the Dirac point, i.e. $s = -s'$ in the following. More details are shown in Sec. C.4. We calculate the matrix element:

\[
|M|^2 = |\langle n, k_y, s' | x | n, k_y, s \rangle|^2 = \frac{1}{4} \left( \frac{k_y W - 1}{\epsilon_n^2 W - k_y} \right)^2 .
\]

While inserting this in the expression for the conductivity, we can make some simplifications in the case we’re interested in. Since we are only allowing vertical transitions between bands with the same index and we assume zero temperature, the sum over pairs of states is going to be just a sum over unoccupied states – the corresponding filled ones will follow from the choice of the unoccupied state. Additionally, the $k_y$ direction is infinite and we can rewrite the sum as an integral, as we did for the intraband term. The final expression, where we have written the two terms $f_i - f_j$ and $f_j - f_i$ as one, is given by

\[
\sigma_{\text{inter}}(\omega) = \frac{ie^2 \omega}{2\pi W} \int \frac{dk_y}{\pi} \left( \frac{k_y W - 1}{\epsilon_n^2 W - k_y} \right)^2 \left[ \frac{1}{-2\epsilon_n - \hbar(\omega + i\eta)} - \frac{1}{2\epsilon_n - \hbar(\omega + i\eta)} \right],
\]

where the sum and the integral run over unoccupied states, i.e. where $\epsilon_n > \epsilon_F$. In the asymptotic limit of infinitely wide ribbons the matrix element can be expanded to

\[
|M|^2 \approx \frac{k_y^2}{\epsilon_n^2} + \frac{2(k_y^3 - k_y \epsilon_n^2)}{W \epsilon_n^6} + \frac{3k_y^4 - 4k_y^2 \epsilon_n^2 + \epsilon_n^4}{W^2 \epsilon_n^8}.
\]

Looking at the $1/W$ term, it can be seen that it will integrate to zero. This is clear when changing to polar coordinates where $k_y/\epsilon = \sin \theta$ and all the sines will be raised to an odd power. Inserting the width independent term of Eq. (4.12) allows us to rewrite expression (4.11) as\(^1\)

\[
\sigma_{\text{inter}}(\omega) = \frac{ie^2 \omega}{2\pi W} \int \frac{dk}{k_y} \sum_{n=1}^{k W/\pi} \left[ 1 - \left( \frac{n \pi}{kW} \right)^2 \right] \frac{2}{k^2} \left[ \frac{1}{-2\epsilon(k) - \hbar \omega^+} - \frac{1}{2\epsilon(k) - \hbar \omega^+} \right],
\]

where we recognize the same square root sum as we found in the intraband expression.

As the sum can be evaluated asymptotically in the limit of many bands as

\[
\frac{1}{W} \sum_{n=1}^{k W/\pi} \left[ 1 - \left( \frac{n \pi}{kW} \right)^2 \right] \approx \frac{k}{4} - \frac{1}{2W},
\]

we find a width independent integral and a $1/W$ correction.

\(^1\)See details in Sec. C.4
We will need the matrix elements where

\[ 4.3 \text{ Edge conductivity contribution} \]

The final contribution to the conductivity comes from the transitions between the localized edge states and the bulk states. This contribution will not be present in armchair ribbons, where there exist no edge states, and will also disappear in the bulk limit. Following the same lines as in the previous cases, it is straightforward to calculate.

We will need the matrix elements

\[ |M_n|^2 = |\langle n, k_y, s | x | k_y, s' \rangle|^2 \]

\[ = \frac{-\tilde{\epsilon}_s^2}{\tilde{\epsilon}_s^2 W - k_y} \frac{\tilde{\epsilon}_n^2}{\tilde{\epsilon}_n^2 W - k_y} \frac{(ss' - 1)\kappa k_n}{\tilde{\epsilon}_n \tilde{\epsilon}_s (\tilde{\epsilon}_n + \tilde{\epsilon}_s)^2}^2 \]

\[ = \begin{cases} \frac{4\kappa^2 k_n^2}{(\tilde{\epsilon}_s^2 W - k_y)(\tilde{\epsilon}_n^2 W - k_y)(\tilde{\epsilon}_n + \tilde{\epsilon}_s)^4} & \text{for } s = -s', \\ 0 & \text{for } s = s' \end{cases} \]

\[ \text{for } s = s' \]

The 1/W correction term follows from solving the integral (again, see App. D)

\[ \sigma_{\text{inter}}^{(1)}(\omega) = -\frac{i e^2 \omega}{2 \pi W} \int_0^\infty \frac{dk}{k} \frac{1}{k^2} \left( -2\epsilon(k) - \hbar \omega^+ - \frac{1}{2\epsilon(k) - \hbar \omega^+} \right) \]

\[ \text{(4.14)} \]

\[ \sigma_{\text{inter}}^{(1)}(\omega) = -\frac{e^2 v_F}{\hbar \omega W} \frac{i \ln \left( \frac{(2\epsilon_F)^2 - \hbar^2 \omega^2}{(2\epsilon_F)^2} + \Theta(\hbar \omega - 2\epsilon_F) \right)}{\pi} \text{.} \]

\[ \text{(4.15)} \]

The entire analytical approximation, i.e. \( \sigma_{\text{inter}}^{\infty} + \sigma_{\text{inter}}^{(1)} \), (orange) is plotted together with the numerical evaluation of the full expression (blue), as well as the bulk limit (black) in Fig. 4.4, using the dimensionless energy \( \nu = \hbar \omega / \epsilon_F \). The real part (full lines) shows the introduction of new states at exactly two times the Fermi energy. The discretization lowers this step with a 1/\( \Lambda \) correction as was the case for the intraband conductivity:

\[ \text{Re} \sigma_{\text{inter}}(\nu) = \sigma_0 \Theta(\nu - 2) \left( 1 - \frac{4}{\nu \Lambda} \right) \text{,} \]

\[ \text{(4.16)} \]

where \( \sigma_0 = e^2 / 4\hbar \) is the universal conductivity of graphene [123]. Since the number of bands at the Fermi level is linear in the energy, the effect falls off for higher \( \nu \). The effect in the imaginary part (dashed lines) then follows from the Kramers-Kronig relation. For all the shown values of \( \nu \) the approximation works extremely well below \( \nu = 2 \) while the large oscillations introduced whenever a new transition is possible (gray line) is not included in the analytical model. The tiny wiggles in the blue lines are numerical noise.

### 4.3 Edge conductivity contribution

The final contribution to the conductivity comes from the transitions between the localized edge states and the bulk states. This contribution will not be present in armchair ribbons, where there exist no edge states, and will also disappear in the bulk limit. Following the same lines as in the previous cases, it is straightforward to calculate.
4.3. EDGE CONDUCTIVITY CONTRIBUTION

Figure 4.4: The real and imaginary part of the interband conductivity in zigzag ribbons. The numerical evaluation (blue) has oscillations, at the positions of new possible transitions (gray), that are not captured in the asymptotic limit (orange) but the overall change is captured. For large values of $\Lambda$, the bulk limit (black) is reached.

showing that it is only the edge state from below the Dirac point that interacts with the bulk states above.

As we are summing over two different types of states – edge and bulk (where there is only one edge state for each $k_y$) – it is convenient to rewrite the sum from Eq. (4.2) as has been done below (see Sec. D.2).

$$\sigma_{\text{edge}}(\omega) = -\frac{2i\epsilon^2}{\pi W} \sum_n \int dk_y \frac{(\epsilon_n - \epsilon_s)}{(\epsilon_n - \epsilon_s)^2 - \hbar^2(\omega + i\eta)^2} \left( \epsilon_n^2 W - k_y \right) \delta_{n \Lambda} \left( \omega - \epsilon_n + \epsilon_s \right)^4.$$

The sum and integral are limited by the demand that the bulk states must be unoccupied and the edge states occupied.

In the limit of very wide ribbons, where $\kappa \rightarrow k_y, \epsilon_s \rightarrow 0$ exponentially fast, and $\epsilon_n^2 W \gg k_y$, we find that

$$\sigma_{\text{edge}}(\omega) = -\frac{8i\epsilon^2}{\pi W} \sum_n \int \frac{dk_y}{k_y} \frac{\hbar \nu_F}{\epsilon_n^2 - \hbar^2(\omega + i\eta)^2} \frac{k_y k_n^2}{W \epsilon_n^2}.$$

$$= -\frac{2i\epsilon^2}{\pi W} \int_{k_y}^{\infty} \frac{d\theta}{k_y} \sin \theta \cos^2 \theta \left[ \frac{1}{\epsilon_n - \hbar(\omega + i\eta)} + \frac{1}{\epsilon_n + \hbar(\omega + i\eta)} \right].$$

$$= \frac{4\epsilon^2 \nu_F}{3\pi \hbar \omega W} \left[ \frac{i}{\pi} \ln \left( \frac{\epsilon_n^2 - \hbar^2 \omega^2}{\epsilon_F^2} \right) + \Theta(\hbar \omega - \epsilon_F) \right].$$

Details of the integrals are given in App. D. We recognize a similar mathematical structure as for the bulk-bulk interband correction although the transitions begin at the Fermi energy in this case, compared to two times the Fermi energy in the
CHAPTER 4. RESPONSE FUNCTION WITH DIRAC THEORY

Figure 4.5: The edge contribution to the conductivity, scaled with $\Lambda$. In the large limit where many bands contribute, the numerical (blue) and the analytical (orange) results agree very well. At smaller values of $\Lambda$ large spikes show up at the transitions between the top of the edge band and the bottom of the bulk bands (gray lines). The dashed, gray lines show the position of the bottom of the bulk bands.

previous case (also see Fig. 4.1). The found result is exactly the same as has been found previously for graphene disks using the same approximations [64], although in the ribbon case, because of the simpler geometry, the factor $4/3\pi$ in front has been found completely analytical whereas it is necessary to make a fitting procedure in the disk case.

Figure 4.5 shows the analytical result in comparison with the direct evaluation of Eq. (4.17). Unlike the two bulk-bulk contributions, the analytical approximation does not seem to fit very well when $\Lambda$ gets much smaller than 10. In that region, the onset of the transitions moves away from $\nu = 1$. The bending of the edge band is partly responsible for this, and the effect is discussed further in Chap. 5. In graphene disks, the edge contribution was found to provide a redshift of the plasmon energies [64], matching well with TB results. In Paper I, we will see that this is not the case in graphene nanoribbons where the edge states add to the plasmon energy.

4.4 Summary

In this chapter, expressions for the local conductivity of zigzag graphene ribbons were developed. In case of the edge states contribution, a similar study for the disk geometry has been conducted previously by Christensen et al. [64], reaching the same exact expression as was found for the ribbons in the present work. For the intra- and interband terms, the calculated corrections both stem from the quantization of states, and a similar term could also be calculated for the edge contribution – it would just scale as $W^{-2}$ and has been neglected for that reason. The derived analytical
expressions match very well with the numerical evaluations at least down to $\Lambda = 10$. For the bulk terms, we are not aware of similar results elsewhere in the literature.
One interesting feature of the Dirac model is the scale invariance that was introduced in Sec. 3.2.3. In the paper enclosed below, we examine the validity of the scale invariance in narrow graphene ribbons using the tight-binding framework presented in the previous chapter. We find that the scale invariance emerges in wide ribbons where the calculated plasmon energies (scaled with respect to the Fermi energy) converge towards constant values. We also look at the region of the \((k_F, W)\) parameter space where the TB plasmon energies begin to deviate from a local model in which the ribbon is treated as having a uniform \(q\)-independent conductivity. It is shown that the place of departure from locality is different for zigzag and armchair ribbons and that the zigzag-specific edge states have a strong blueshifting effect in the nonlocal region. This blueshift is directly opposite of the redshift found for graphene disks [64]. Additionally, we see that the plasmons disappear when the Fermi level moves into the gap of semiconducting armchair ribbons. Lastly, we provide an overview of the possible plasmon energies for various ribbon widths and doping levels.

After the paper, additional information is presented. Some of it will consist of supplementary clarifications of the models and the results from the paper, while part of it will be new considerations and small results in itself.

As most of the theory used in the paper has already been introduced, the reader will find some overlap with previous chapters in the first three sections. In the paper’s Sec. IV, the local classical model is introduced and that, and the rest of the paper, includes new insights worth reading more carefully.
Emergent scale invariance of nonclassical plasmons in graphene nanoribbons

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Using a nearest-neighbor tight-binding model we investigate quantum effects of plasmons on few-nanometer wide graphene nanoribbons, both for zigzag and armchair edge terminations. With insight from the Dirac description we find an emerging scale-invariant behavior that deviates from the classical model both for zigzag and armchair structures. The onset of the deviation can be related to the position of the lowest parabolic band in the band structure. Dirac theory is only valid in the parameter subspace where the scale invariance holds that relates narrow ribbons with high doping to wide ribbons with low doping. We also find that the edge states present in zigzag ribbons give rise to a blue shift of the plasmon, in contrast to earlier findings for graphene nanodisks and nanotriangles.

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I. INTRODUCTION

Since its discovery [1], graphene has attracted much attention in the scientific community, initially mainly for its remarkable electronic properties as well as its unprecedented mechanical qualities [2]. However, the plasmonic capabilities of this conveniently tunable material have also received great interest in recent years [3–9] along with other two-dimensional (2D) materials [10]. As ever smaller and more precise devices [11–15] are produced, it is important to obtain corresponding theoretical understanding of plasmons in graphene nanostructures. For instance nanodisks and nanotriangles have both been investigated both theoretically [16–19] and in experiments [20], and more complex structures have also been studied [21–23].

The electronic properties of graphene nanostructure can be described on various levels of sophistication. Classically, it is a finite-size conductivity sheet. The simplest atomistic description is a tight-binding (TB) model for the electrons. The Dirac-equation continuum model for finite graphene structures is of intermediate complexity and describes low-energy electrons with linear dispersion being confined on finite graphene structures. Each of these three electronic models has its associated optical response, so that plasmonic excitations may also vary. While the tight-binding model is the most microscopic of them, it is important to know when the simpler Dirac or even the classical description suffices, and for which parameters the three models start to deviate from each other, and how important for optical properties are the different electronic edge terminations [24,25].

In this paper we present quantum-mechanical calculations of graphene nanoribbons, with geometries as depicted in Fig. 1, in particular tight-binding calculations in the random-phase approximation (RPA). Important previous work on this topic includes theoretical contributions both for isolated nanoribbons and for arrays of them [26–33], as well as experimental studies [34–39] with ribbon widths down to 15 nm [40]. Furthermore, in a complementary analytical analysis we identify a scale invariance in the Dirac-equation model for graphene ribbons [41], a scale invariance that it shares with the classical model but not the tight-binding model. For the latter we identify the scale invariance as an emergent property. Thereby we obtain an illuminating overview for which parameters the Dirac-equation model can agree with the tight-binding models. Furthermore, we identify a scale invariant onset of quantum mechanical effects.

The paper is structured as follows. In Sec. II we briefly discuss the TB model and its numerical evaluation, and the corresponding optical response function in terms of the electronic states. In Sec. III we review the Dirac-equation model both for zigzag and armchair graphene ribbons, use the band structures to identify the onset of nonclassical effects, and we identify the dimensionless scaling behavior property. In Sec. V we compare our numerical TB calculations with our analytical predictions, and we conclude in Sec. VI. Detailed information can be found in two Appendixes.

II. NUMERICAL METHODS

A. Tight-binding model

We describe the graphene ribbon in a nearest-neighbor tight-binding model with the Hamiltonian

$$H = \sum_{(i,j)} -t(a_i^\dagger b_j + \text{H.c.}),$$  \hspace{1cm} (1)$$

where the sum is over pairs of neighboring sites. This model has proven useful for describing the band structure in a wide energy range around the Dirac point as the bands here are determined by interaction between the $p_z$ orbitals of the $sp^2$
hybridized carbon atoms. A hopping value of \( t = 2.8 \text{ eV} \) is used between all interacting atoms as it has generally been found to give good results [42].

We have used the smallest possible supercell, which includes one row of atoms for the zigzag (ZZ) ribbons and two rows for the armchair (AC) ribbons as illustrated in Fig. 1. The band structure and the states are found by direct diagonalization of the Hamiltonian with a \( k \)-point sampling of at least 5000 points in the Brillouin zone, which has been found to give converged results in the subsequent evaluation of the optical response.

In Fig. 2 we show the bands around the \( K \) point for two 6 nm-wide ribbons, one with ZZ and the other with AC edge terminations. The dots correspond to TB calculations, and the colors indicate the edginess (defined in Appendix A) of the corresponding states, with bright red corresponding to an edge state. The figure also shows the continuous bands calculated within Dirac theory, as discussed in Sec. III.

B. Response function and quantum plasmons

The optical response of a quantum mechanical system is described in full by the dielectric function, which relates to the noninteracting electron density-density response operator \( \chi^0 \) in the RPA as [43,44]

\[
\epsilon_{ij}(\omega) = \delta_{ij} - \sum_m V_{im} \chi_{mj}^0(\omega),
\]

where \( V_{ij} \) is the Coulomb interaction. Following the method of Ref. [26], \( \chi^0 \) is calculated from the TB eigenstates, in the case of only vertical excitations, i.e., neglecting intraband transitions, as

\[
\chi_{ij}^0(\omega) = \frac{2e^2}{\hbar} \frac{b}{2\pi} \int BZ dk \sum_{nm} f_{im} a^*_{in} a_{jm} \epsilon_{nm} \delta(\omega + \epsilon_{nm} - \epsilon_{in} - \epsilon_{jn}),
\]

Here the \( i, j \) run over atomic sites, while \( n, m \) label the eigenmodes at wave vector \( k \). Thus, \( a_{in} \) is the weight of the \( n \)th wave function on the \( i \)th site (implicitly at wave vector \( k \)). We have used the shorthand notation \( \epsilon_{nm} = \epsilon_n - \epsilon_m \) for the energy difference and similarly for the Fermi filling factors \( f \). Damping is included phenomenologically through the parameter \( \eta \), which we set to 1.6 meV throughout as in Ref. [26]. The parameter \( b \) is the width of the supercell in the periodic direction, see Fig. 1.

From the density-density response function we calculate the dielectric matrix \( \epsilon(\omega) = I - V\chi^0(\omega) \). This expression involves the Coulomb interaction \( V \) in real space, which is a subtle matter to handle [26], both due to its long-range behavior and because of the divergence at zero distance, but it can be done (details in Appendix B). As shown in Ref. [45], \( \epsilon(\omega) \) can be written in a spectral representation of its eigenvalues and left and right eigenvectors as

\[
\epsilon_{ij}(\omega) = \sum_n \epsilon_n(\omega) \phi^*_{n,i}(\omega) \rho_{n,j}(\omega),
\]

where the \( i, j \) are again site indices in the tight-binding basis and the \( \epsilon_n(\omega) \) the eigenvalues; the right eigenvector \( \phi_n \) is the induced field, and the left eigenvector \( \rho_n \) the induced charge of the plasmon. The zeros of the real parts of \( \epsilon_n(\omega) \) define the plasmonic modes. In this work, we concern ourselves with the dipole mode, i.e., the plasmon with the lowest-lying energy. There will be plasmons at higher energies as well, corresponding to higher-order modes in the ribbon. The zeros of \( \text{Re}(\epsilon_n) \) agree well with peaks in the energy-loss function \(-\text{Im}(\epsilon_n(\omega))\) as measured in electron energy-loss spectroscopy experiments, provided the frequency dispersion of the imaginary part of \( \epsilon_n(\omega) \) is small. The above method to calculate quantum plasmons based on a tight-binding formalism will be applied to graphene ribbons in Sec. II B.
III. ANALYTICAL MODEL

A. Dirac theory for graphene ribbons

Dirac theory is an approximate theory obtained by linearizing the TB model in the $K$ ($K'$) valleys where infinite graphene exhibits its Dirac cones. This allows one to get analytical insight into the band structure also of finite graphene structures. For graphene ribbons, this was first done in the seminal paper by Brey and Fertig [41] and the method is also outlined in Castro Neto et al. [42]. Here we first briefly review the Dirac theory, before presenting our new analytical insights and their comparison with full TB calculations.

In its essence, in the low-momentum limit the tight-binding Hamiltonian is approximated as

\[ H = \hbar v_F (t_0 \otimes \sigma_x k_x + t_\tau \otimes \sigma_y k_y) \]

\[ = \hbar v_F \begin{pmatrix} 0 & k_x - i k_y & 0 & 0 \\ k_x + i k_y & 0 & 0 & 0 \\ 0 & 0 & 0 & -k_x - i k_y \\ 0 & 0 & -k_x + i k_y & 0 \end{pmatrix}, \]

where $t_\tau$ and $\sigma_i$ are the Pauli spin matrices belonging to the valley space and sublattice space, respectively. For the eigenstates of the system we adopt the notation of Ref. [41]: $[\phi^A, \phi^B, -\phi^A, -\phi^B]^T$. The Hamiltonian in Eq. (5) is block diagonal, so we focus only on the upper left corner corresponding to the $K$ valley. By applying $H$ twice to a state $[\phi^A, \phi^B]^T$ we find the relations $(k_x^2 + k_y^2)\phi^{A/B} = \bar{\epsilon}^2 \phi^{A/B}$ with $\bar{\epsilon} = \epsilon/\hbar v_F$.

By replacing $k_x$ with $-i\partial_x$, a differential equation is obtained with the general solutions

\[ \phi^A(x) = Ae^{\beta x} + Be^{-\beta x}, \]

where $\beta = \sqrt{k_x^2 - \bar{\epsilon}^2}$, and consequently $\epsilon = s \hbar v_F \sqrt{k_x^2 - \beta^2}$ where $s = \pm 1$. The eigenmodes of the Hamiltonian can be found analytically for both ribbon geometries of Fig. 1 by imposing proper corresponding boundary conditions for their wave functions. These boundary conditions are different for zigzag and for armchair edge terminations.

1. Zigzag edge termination

In a ZZ ribbon the atomic structure terminates on an $A$ lattice site on one edge and on a $B$ site on the opposite edge, see Fig. 1. The proper boundary conditions, $\phi^A(x = 0) = \phi^B(x = W) = 0$, lead to the dispersion relation for the allowed states in a slightly different notation than in Ref. [41]:

\[ k_y = \frac{\beta}{\tanh(\beta W)}. \]

For fixed $k_x$, Eq. (7) has infinitely many solutions for imaginary $\beta = ik_0$ corresponding to the bulk modes, and at most one solution for $\beta = \kappa \in \mathbb{R}$ corresponding to an edge mode that falls off exponentially fast away from the edge. It follows from the limit $\lim_{\kappa \to 0} \kappa/\tanh(\kappa W) = 1/W$ that the edge states only exist for $k_y \geq 1/W$. This momentum cutoff has an associated energy cutoff $\epsilon_{\text{cut}} = \hbar v_F / W$.

The two types of solutions (bulk and edge modes) are shown in Fig. 2 as full lines in black and red, respectively. It is clear from the figure that the TB and Dirac methods to calculate the band structure give very similar energies in the vicinity of the $K$ point and that the analytically found edge states match almost perfectly with the edge ($\lambda \approx 1$) states in TB. From the analytical model we just determined the exact energy range where the edge states are found. Given the great agreement between the two approaches, in the following, where we want to distinguish between bulk and edge states, we use the energy cutoff $\epsilon_{\text{cut}}$ from Dirac theory to classify the TB states as either bulklike or edgelyke.

2. Armchair edge termination

As the termination of an armchair ribbon has a mix of $A$ and $B$ lattice sites, as depicted in Fig. 1, we demand that the sublattice wave function vanishes on both edges. This results in a mixing of $K$ and $K'$ states [41], which together with the general form of the solution (6) ultimately yield plane-wave states of the form $e^{ik_y x}$ with $k_y$ given by [41]

\[ k_y = \frac{n\pi}{W} - \frac{4\pi}{3\sqrt{3}a_0} = \frac{2\pi(3n - 2(N + 1))}{3\sqrt{3}a_0(N + 1)}, \]

with $n \in \mathbb{Z}$, and the corresponding eigenenergies $\tilde{\epsilon}_n = s \sqrt{k_x^2 + k_y^2}$. In the second equality we have expressed the width of the ribbon as $W = (N + 1)a_0\sqrt{3}/2$, where $N$ is the number of atomic rows. From this form it follows that every third ribbon, where $3n - 2(N + 1) = 0$ can be fulfilled, will be semimetallic while the rest will have a band gap.

B. Dimensionless scaling in Dirac theory

An important property of the Dirac theory is a scale invariance of the ribbons: If all equations are rewritten in dimensionless units where the energies are scaled in units of the Fermi energy $\epsilon_F$, momenta in units of the Fermi momentum $k_F$, and the distances with the ribbon width $W$, then one finds that the only system-dependent parameter is the dimensionless parameter $\Lambda = k_y W$. This insight is very useful, since it allows us to identify effects that should exist across all widths of ribbons, provided that their respective Fermi levels are scaled accordingly and of course that the Dirac model is valid.

In dimensionless form, the governing equations for the ZZ ribbons thus become

Bulk:

\[ K_y = \frac{K}{\tan(K \Lambda)}, \quad E_n = \sqrt{K_y^2 + K_0^2}, \]

Edge:

\[ \phi(\tilde{x}) = C_0 e^{i K \Lambda \tilde{x}} \left( i s \sin(\tilde{x} \Lambda K) \sin(1 - \tilde{x} \Lambda K) \right), \]

\[ \psi(\tilde{x}) = C_0 e^{i K \Lambda \tilde{x}} \left( i s \sin(\tilde{x} \Lambda K) \sin(1 - \tilde{x} \Lambda K) \right) \]
with dimensionless momentum $K_y \equiv k_y / k_F$. The corresponding dimensionless momenta and energies of the bulk modes $\psi(x)$ are denoted by $K_n$ and $E_n \equiv \varepsilon_n/k_F$, those for the edge modes $\phi(x)$ are called $K$ and $E$, and $x = x/W$ is the dimensionless lateral position in the ribbon. For the AC ribbons we find that

$$K_n = \frac{\pi [3n - 2(N + 1)]}{3\Lambda}. \quad (10)$$

Plots of the dimensionless band structures for the three different cases, zigzag, semimetallic, and semiconducting armchair ribbons are shown in Fig. 3. We emphasize the large differences between the band structures in the low-energy regime; especially the different placement of the bottom of the lowest parabolic band, to which we will return in the following.

One important consequence is that the scaling behavior of the electronic states will carry over to the plasmonic energies as well. As the band structure in the Dirac model is approximated with an infinite cone the (dimensionless) response will only depend on $\Lambda$, rather than on $\varepsilon_F$ and $W$ separately. This scale invariance holds, both when leaving out the edge states and when including them. The dimensionless form is used throughout the paper and thus we concern ourselves with the scaled plasmon energies given by $\hbar \omega_{\rho}/\varepsilon_F$.

Given the great agreement in the band structures of the numerical tight-binding and the analytical Dirac models, we expect that also for TB calculations there will be parameters for which the scaled plasmonic energies will be scale invariant for constant values of the parameter $\Lambda$, even though the scale invariance does not strictly hold in the TB model.

**C. Emergence of nonclassicality**

The quantum mechanical Dirac model for ribbons has a classical limit, and vice versa away from the classical limit we will identify the onset of nonclassical behavior. When there are many bands crossing the Fermi energy one would expect the system to behave classically. On the other hand, for combinations of widths and Fermi energies where the Fermi surface is only crossed by a few states we are starting to probe the quantumness of the system and expect deviations from the classical regime. As our heuristic measure, we take the bottom energy of the lowest parabolic band as the separation between the quantum and classical regimes. Interestingly, from Fig. 3 this value differs for ZZ and AC ribbons, and it differs also for the semimetallic and the semiconducting AC ribbons. These different critical values $\Lambda_c$ at which we predict the classical-to-quantum behavior to occur can be determined analytically (and further below we will test them against numerical TB calculations).

- **For zigzag.** By setting to zero the derivative of the energy with respect to the dimensionless momentum $K_y$, it is found that the sought bottom of the band occurs at $K_y = 1/\Lambda_c$, corresponding to $k_y = 1/W$. By inserting this into the scaled expression for the band energies, we find that

$$E_n = \sqrt{n^{-2} + K_n^2 (n^{-1})} = \sqrt{1 + \xi_n^2} \frac{\varepsilon_F}{\Lambda}, \quad (11)$$

where $\Lambda K_n = \xi_n = \tan(\xi_n)$. Looking for the solution where the Fermi energy crosses the bottom parabolic band, i.e., $\varepsilon_n/\varepsilon_F = E_n = 1$, it is found that the critical value is

$$\Lambda_c^{\text{ZZ}} = \sqrt{1 + \xi_n^2} \approx 4.6033. \quad (12)$$

This $\Lambda_c^{\text{ZZ}}$ is a dimensionless number, and with this single number we predict with Dirac theory the emergence of quantum effects both in narrow ribbons at high Fermi levels and in wide ribbons with low doping. As we will see below, this is indeed the value around which the dipole plasmon energies start to deviate from the classical results for zigzag ribbons.

- **For armchair.** For ribbons with armchair edge terminations, in the limit of many atoms, the band bottoms occur at $E_n = \pm n\pi/\Lambda$ for the semimetallic ribbons and at $E_n \in \{\pm (3n + 1)\pi/3\Lambda, \pm (3n + 2)\pi/3\Lambda\}$ for the semiconducting ribbons, with $n \in \mathbb{N}$. That is,

$$\Lambda_c^{\text{AC}} = \left\{\begin{array}{ll}
\frac{\pi}{\xi} & \text{for semimetallic AC ribbons} \\
\frac{\pi}{\xi} & \text{for semiconducting AC ribbons} 
\end{array}\right. \quad (13)$$

Unlike for the ZZ ribbons, the band structures for AC ribbons are symmetric around the Dirac points and in that sense they are thus more like the bulk graphene bands. Combined with the lower value of $\Lambda c^{\text{AC}}$, we expect classical behavior down to smaller values of $\Lambda$ for armchair ribbons.

**IV. CLASSICAL PLASMONS**

It is naturally also possible to calculate the plasmons classically. For the ribbon geometry this has already been done in different ways [7,26,46,47]. When combined with the continuity equation, the coupling between the potential $\phi(r)$ and the induced charge density $\rho(r)$ can be written as an integrodifferential eigensystem of equations as

$$\zeta_\omega \phi_\omega(r) = -\frac{1}{2\pi} \int d^2r' V' \cdot \left[f(r') V^2 \phi_\omega(r')\right] / |r - r'|, \quad (14a)$$

$$\zeta_\omega = \frac{2\varepsilon_F \omega W}{\sigma(\omega)}, \quad (14b)$$

where all coordinates and differential operators work in the 2D plane of the graphene. The graphene is treated as being embedded in an $\varepsilon = 1$ material. It has here been assumed that the conductivity is uniform inside the ribbon of width $W$, and
vanishes outside:

\[ \sigma(r, \omega) = \sigma(\omega) f(r), \quad \text{with} \]
\[ f(r) = \begin{cases} 
1 & \text{for} \ r \ \text{inside the ribbon}, \\
0 & \text{for} \ r \ \text{outside the ribbon}. 
\end{cases} \]

High-precision fits of the values of the eigenvalues \( \xi_n \) in Eq. (14) are given by Christensen (Ref. [46]) for the first seven modes. We have used these values in our classical calculations together with the low-temperature, local conductivity \( \sigma(\omega) \) for bulk graphene. This conductivity can be derived, among other ways, from the Dirac model in the limit of infinitely wide ribbons or from the general expression of the bulk polarizability of graphene as found by Hwang and Das Sarma, [48] and by Wunsch et al. [43]. Here we just present the resulting expressions for the intraband and the interband contributions that together make up \( \sigma(\omega) \):

\[ \sigma_{\text{intr}}(\omega) = \frac{e^2}{\pi \hbar^2 (\omega + i\eta)}, \]
\[ \sigma_{\text{inter}}(\omega) = \frac{e^2}{4\hbar} \left[ \int_\omega d\omega \ln \frac{2F_\omega - h_\omega + \Theta(h_\omega - 2\varepsilon_F)}{2F_\omega + h_\omega} \right], \]

where \( \Theta \) is the Heaviside step function. By combining Eqs. (14) and (15) we can find the plasma energies as a function of the ribbon width.

For our purposes it is essential to realize that Eq. (14b) can be rewritten in dimensionless variables as \( \sigma(\nu, \nu_n) = 2\varepsilon_F\hbar^2 \nu_n \nu, \) with the dimensionless plasmon energy \( \nu_n = h_\omega / \varepsilon_F \) and again \( \Lambda = \hbar F \). This insight turns out to be quite practical, because it is sufficient to calculate the connection between \( \nu_n \) and \( \Lambda \) only once to obtain the plasmon energies for all combinations of widths and Fermi momenta that satisfy \( \Lambda = \hbar F \). Moreover, in Sec. III B we saw that the Dirac model has the same scale invariance. So we find that the scaling property holds both inside and outside the classical regime, as long as Dirac theory is accurate. We will test the latter by comparing Dirac and classical theories with tight-binding calculations in the next section.

Let us summarize our models and explain our terminology. The classical model is a local continuum model that assumes that the conductivity of the nanoribbon is a uniform material parameter equal to the sheet conductivity of infinite graphene. For simplicity we call this model classical even though the value for the sheet conductivity by Eq. (15) depends on \( h \), which would be an argument for calling the model semiclassical instead. As a next level of modeling one could adopt a hydrodynamic continuum model (not done here) in which the response becomes nonlocal [17,46], and the conductivity would depend on two spatial coordinates. Hydrodynamic models are often classified as semiclassical [49]. Then comes the Dirac model, which is quantum mechanical in the sense that the bands are quantized and accounted for individually in the evaluation of the dielectric function. It incorporates some atomistic details via the boundary conditions and will thus provide different results for AC and ZZ edge terminations [17]. Finally, the TB calculations are fully quantum as all atoms and bands individually add to the evaluation of the plasmons.

V. NUMERICAL AND ANALYTICAL RESULTS COMPARED

We present two comparisons: quantum versus classical plasmons in Sec. VA, and properties of atomistic (TB) quantum plasmons versus those of continuum (Dirac) quantum plasmons in Sec. VB.

A. Quantum versus classical plasmons

Here we systematically investigate the range of validity of the classical description for graphene ribbons, by comparing with TB quantum calculations. In particular, we will test the heuristic value of the various \( \Lambda_c \) that we identified in Sec. III C for characterizing the emergence of nonclassical behavior in a scale invariant way. In Sec. II B we outlined how one can identify quantum plasmons of nanostructures within a tight-binding formalism, and here we apply this approach to graphene ribbons. The calculation of the corresponding classical plasmons was described in Sec. IV.

Guided by the scaling properties of the Dirac and classical models, in Fig. 4 we present the plasmonic energies as a function of the dimensionless variable \( \Lambda \). The figure shows a comparison of the scaled plasmonic energy as calculated with the TB model of Sec. II A and in the classical model for both ZZ and AC ribbons, and when considering only the intraband contribution (top panels of Fig. 4) or all transitions (bottom panels). By “intraband” we mean that we only include eigenstates with energies above the cutoff energy \( \epsilon_c = h F / W \) for the edge states for zigzag ribbons and above zero energy for armchair ribbons, which corresponds to only considering intraband transitions in a classical, wide-ribbon limit. For ribbons of finite widths, the transitions are intraband transitions in the sense that the bands in the upper cone are size-constriction foldings of the infinite graphene conduction band, although the actual transitions do occur between bands of the ribbon.

We see that for large values of \( \Lambda \), the classical and all TB calculations agree across all four panels. There is no visible effect of either edge terminations or other quantum effects there. Furthermore, the TB calculations for different Fermi levels agree very well as predicted from the scaling of the Dirac model. For smaller values of \( \Lambda \) the plasmon energies as calculated by the TB model start to depart from the classical values.

For zigzag ribbons, Fig. 4(a) constitutes a confirmation of our prediction in Eq. (12) that this onset of quantum behavior occurs at \( \Lambda_c \approx 4.6 \), the point at which the lowest of the parabolic bands of the zigzag ribbons crosses the Fermi level. This same onset is seen both in the “Drude-like” case [Fig. 4(a), top panel] and with all transition included [Fig. 4(a), bottom panel].

Another important feature of Fig. 4(a) is that the tight-binding plasmon energies for \( \varepsilon_F = 0.4 \) eV and 0.8 eV are indeed quite close to each other in the chosen dimensionless units, and closer to each other than to the classical plasmon curves. Dirac theory predicts that the two quantum plasmon calculations would coincide exactly, and the tight-binding calculations confirm that the scale invariance of Dirac theory indeed holds approximately. A better overview and insight when
FIG. 4. Scaled plasmon energy as a function of scaled ribbon width $\Lambda$. The value $\Lambda = 5$ corresponds for example to a width of $16.4$ nm for $\varepsilon_F = 0.2$ eV. (a) $\Lambda$ is varied by changing $W$ while keeping the Fermi energy fixed at either $0.4$ eV (triangles) or $0.8$ eV (dots). The vertical dashed line corresponds to $\Lambda_{zz}^c \approx 4.6$. The open symbols in the bottom panel correspond to calculations of plasmon energies where edge states were removed from the calculation. (b) Top: The intraband plasmons of AC ribbons, both the classical prediction and the quantum plasmon predictions for semiconducting and for semimetal ribbons. Blue and red dashed vertical lines correspond to $\Lambda_{ac}^c = \pi/3$ and $\pi$, respectively. (b) Bottom: As in the top panel, but now including all transitions. The small symbols are used for the peaks in the loss spectrum that are not associated with an actual plasmon defined as $\text{Re}\left(\varepsilon_n\right) = 0$.

scale invariance holds in TB calculations will be presented in Sec. V B below. The dotted line in the bottom panel shows the interpolated data from calculations of a $9$ nm wide ribbon at varying Fermi energy and provides the best guess, given the calculations that have been done, of the behavior of arbitrarily wide ribbons where the plasmon energies have converged with respect to the number of bands. This will be explored further in the following section. Comparing the results for the $\varepsilon_F = 0.4$ eV and $\varepsilon_F = 0.8$ eV ribbons we see that lowering the Fermi energy, which for constant $\Lambda$ corresponds to widening the ribbons, moves the points closer to the dotted line, as expected.

By excluding the zigzag edge states in the evaluation of $\chi$ open symbols in the bottom panel of Fig. 4(a), we find a significant plasmon red shift in the quantum regime. In other words, edge states of zigzag nanoribbons contribute with a significant blue shift of the plasmon energies in the quantum regime, while they have hardly any impact on the energy in the classical regime above $\Lambda_{zz}^c$. This effect of edge states becomes even more evident by directly plotting the energy shift as in Fig. 5. Clearly, for zigzag ribbons the edge states do not affect the plasmon energies for $\Lambda > \Lambda_{zz}^c$ and give rise to a blue shift for $\Lambda < \Lambda_{zz}^c$. The found blue shift is in stark contrast to the results for graphene disks [17] and triangles [18] in which the zigzag edge states are found to give rise to a net red shift of the plasmon energies. Back to our ribbons, for $\Lambda < 1$ the Fermi level crosses the edge state and the evaluation of the edge-state contribution in the manner described above becomes meaningless.

Having discussed quantum-classical transitions for zigzag ribbons, we now turn to Fig. 4 and study armchair ribbons in Fig. 4(b). The picture is slightly different for armchair ribbons as they exist as either semiconducting (sc.) or semimetallic (sm.). When including only intraband transitions, the scaled plasmon energies follow the classical behavior rather closely.

FIG. 5. Scaled plasmon energies in the presence of edge states minus scaled plasmon energies when neglecting the edge states, as a function of the scaled ribbon width $\Lambda$, for two fixed values of the Fermi energy.
across the entire range, except for a single outlier. As discussed above, because of the symmetry around the $K$ point of the armchair band structure, we do not expect the same kind of quantum-classical transition as for zigzag ribbons. In the bottom panel of Fig. 4(b) we have split the ribbons into the two types. The vertical, dashed lines indicate the position of the band bottom in the appropriate color. As expected, the deviation from classical results starts at lower $\Lambda$ than previously for the zigzag ribbons. The small symbols in the bottom panel of Fig. 4(b) denote peaks in the loss spectrum that are not associated with real plasmons as there is no simultaneous crossing of the real part of the dielectric eigenvalues with zero. For the semiconducting ribbons the plasmons cease to exist when the Fermi energy crosses the lowest parabolic band at $\Lambda = \pi/3$. For the semimetallic ribbons the plasmons cease to exist earlier, namely already below $\Lambda = \pi$. There seems to be an exception with the red square just above $\Lambda = 2$ (which lies beneath a small, red triangle), but as the TB calculations are done for room temperature $k_B T \approx 25$ meV, there will still be a finite population of electrons in the bottom parabolic band for this point. For the smallest values of $\Lambda$ for which plasmons still exist, the positions of the main dipole plasmon peaks become increasingly hard to locate, resulting in an increased scatter of the data points, as also reported elsewhere [17,26].

**B. Emergent scale invariance for plasmons**

In general, the tight-binding model for graphene ribbons does not have the same scale invariance that we found both for Dirac theory and for classical plasmonics, as the TB band structure does not consist of an infinite Dirac cone. This follows from the fact that, due to the infinite cone shape, the band structures for two different ribbon widths in the Dirac description are related by a simple scaling transformation while this is not the case for the more complex TB band structure. But since the low-energy bands calculated with TB and with Dirac theory agree so well, at least for the parameters of Fig. 2, the scale invariance will be an emergent property of the TB model, valid only in part of the parameter space spanned by $\{\epsilon_F, W\}$. Only in that subspace can classical and/or Dirac theory be expected to agree with TB calculations.

As a test of the proposed scale invariance we conduct a range of calculations where $\Lambda$ is held constant while the widths of the ribbons are varied, so doubling the size of the ribbon goes hand in hand with halving the Fermi energy. As previously stated, we expect the scaled plasmon energy to tend towards a constant when the ribbons get wider and the Dirac model becomes a better description. It is less clear how fast the limit will be reached. When the Fermi energy is above $2.0\text{eV}$ we are well out of the linear regime of the bands and do not expect the Dirac scaling to work anymore. For the armchair ribbons we distinguish between semiconducting and semimetallic ones, as this should have an impact for small values of $\Lambda$ where the Fermi energy is close to the difference in the band structures.

As one of our main results we present in Fig. 6 how the TB plasmon energies converge as ribbon widths are increased. For $\Lambda \gg 1$ the plasmon energies quickly converge for larger widths to a value that differs little from the classical plasmon energy. But it is important to notice that the wide-ribbon limits in this figure do not automatically coincide with the classical limit, as one might expect: for $\Lambda$ not much larger than unity, there is a clear discrepancy between the converged energies of the TB plasmons and the classical plasmons. Wherever the TB curves in Fig. 6 have become (almost) horizontal, the scale invariance that holds exactly for Dirac and classical plasmons has also emerged for TB quantum plasmons.

The bending of the curves for smaller widths illustrates the shortcomings of the scalability of the Dirac model: For it to hold exactly, we would need infinitely many bands in the band structure, but as the number of atoms in the full-width supercell decreases as $W$ is reduced (recall Fig. 1), we will get fewer bands instead and thus a deviation from the converged constant plasmon energy as obtained for wide ribbons. In
with (absolute) plasmon energy. The gray area corresponds to structures \( \Lambda_1 \)

**Fig. 6.** We would like to thank Thomas Christensen, Johan R. Maack, and P. André D. Gonçalves for stimulating discussions. This work was supported by the Danish Council for Independent Research–Natural Sciences (Project No. 1323-00087). The Center for Nanostructured Graphene is sponsored by the Danish National Research Foundation (Project No. DNRF103). N.A.M. is supported by VILLUM FONDEN (Grant No. 16498). K.S.T. acknowledges funding from the European Research Council (ERC) under the European Union’s Horizon 2020 Research and Innovation Program (Grant Agreement No. 773122, LIMA).

**Fig. 7.** The scaled plasmon energy as a function of the width and \( \Lambda \) for zigzag ribbons. The white lines indicate paths with constant (absolute) plasmon energy. The gray area corresponds to structures with \( \varepsilon_F > 2 \, \text{eV} \) where we expect to be outside the linear regime of the bands. For larger widths the contours start to converge as expected from Dirac theory. The departure from horizontal lines is a signature of having only a finite number of electronic states. The right y axis shows the classical results for comparison.

We would like to thank Thomas Christensen, Johan R. Maack, and P. André D. Gonçalves for stimulating discussions. This work was supported by the Danish Council for Independent Research–Natural Sciences (Project No. 1323-00087). The Center for Nanostructured Graphene is sponsored by the Danish National Research Foundation (Project No. DNRF103). N.A.M. is supported by VILLUM FONDEN (Grant No. 16498). K.S.T. acknowledges funding from the European Research Council (ERC) under the European Union’s Horizon 2020 Research and Innovation Program (Grant Agreement No. 773122, LIMA).
APPENDIX A: IDENTIFYING EDGE STATES IN TIGHT-BINDING

In the Dirac model the edge states of graphene zigzag ribbons are readily found as solutions that decay exponentially fast from the edge of the structure in contrast to the bulklike modes that behave more like standing waves. As the tight-binding model is solved numerically by diagonalizing the Hamiltonian we do not get this distinction for free, but need to analyze the resulting states subsequently in order to classify them properly. To give an overview of where in the band diagrams calculated in TB we find these edge states, we introduce an operational definition of edginess as

\[ \lambda_n(k) = \frac{\sum_{l \in \Omega} |\psi_{nl}(k)|^2 - \sum_{l \in \Omega} |\psi_{nl}(k)|^2}{\sum_i |\psi_{nl}(k)|^2}, \]

(A1)

where \( l \) refers to the atomic sites. In other words, the edginess \( \lambda_n \) of the \( n \)th state is found by the amount of the wave function localized on the edge of the ribbon, \( \Omega \), subtracted with the weight in the middle of the ribbon. In our case we define \( \Omega \) as the outermost quarters of the atoms on either side of the ribbon. Using this definition, an edge mode will have \( \lambda \approx 1 \) while eigenstates located entirely in the center of the ribbon will have \( \lambda = -1 \).

APPENDIX B: COULOMB INTERACTION IN REAL SPACE

At large distances, the Coulomb interaction between two sites will be predominantly pointlike and thus scale as their inverse distance. This long-range \( r^{-1} \) behavior makes it impossible to calculate the correct Coulomb interaction term in real space due to lack of convergence. Fortunately, this is not necessary either, as we ultimately are interested in the dielectric function. That is, we only need the correct \( V \chi^0 \) product, while not necessarily the correct form of the \( V \) matrix itself (which is ill defined). So, as we require charge neutrality, we utilize that \( \sum_j V_{ij}^0 = 0 \) to calculate a modified interaction \[ \tilde{V}_{ij} = \sum_{n,j} (V_{0,ijn} - |nb|^{-1}), \]

which fulfills \( V \chi^0 = \tilde{V} \chi^0 \) and falls off more quickly with distance than \( V \). We have used the notation \( V_{0,ijn} \) to mean the interaction between the \( i \)th site in the zeroth supercell and the \( j \)th site in supercell \( n \). It is important to stress that by this approach we do not screen the Coulomb interaction in a physical sense. Rather, it is a computational trick that allows us to evaluate the two well-defined matrices \( \tilde{V} \) and \( \chi^0 \) individually and to obtain the correct dielectric function from their product. Alternatively, one could have converged \( \sum_{n,j} V_{0,ijn} \chi_{ij}^0 \) directly with respect to \( n \).

In the short-distance limit, keeping the assumption of pointlike interactions would lead to a diverging Coulomb term for for the distance going to zero. Instead, for sites close to each other and, ultimately, for a site interacting with itself, the spatial extent of the \( p_z \) orbitals should be taken into account. This has been done by Ref. [26] and we adopt the same approach for all distances (with data acquired through private correspondence between our groups), whereby the Coulomb term no longer diverges for vanishing distances.


5.1 Additional information to Paper I

In this section, we will present some additional details and considerations in relation to Paper I. To begin with, we will take a closer look at the classical model for the plasmons and show that it can be interpreted as a bulk-like plasmon trapped between two edges that provide non-trivial reflection phases. Secondly, we look at the emerging behavior of the scale invariability and find good fits of the emergence, inspired by the quantization correction calculated in Chap. 4. Finally, we will spend a bit of time on the surprising blueshift that the edge states induce in zigzag ribbons.

5.1.1 Bulk-like plasmons and peak finding

Comparing Eq. (14b) in the paper with the plasmon condition displayed in Eq. (2.38) (page 17) we find that we can write a relation between

\[
\frac{2\pi}{q} = \frac{\pi W}{\zeta_n}
\]

\[
\ldots \text{the plasmon wavelength and} \ldots \quad \text{... the eigenvalues and}
\]

\[
\text{the ribbon width.}
\]

(5.1)

This means that the plasmons can simply be thought of as bulk-like modes travelling across the ribbon and reflecting on the edges to form standing waves [68]. If we choose a convention such that the dipole like mode has index \( n = 1 \) and a wavelength of \( 2W \) corresponds to a reflection phase of \( -\pi \) as is usually done in optics, we reach

\[
\varphi_n = (n - 1)\pi - \zeta_n
\]

\[
\ldots \text{an } n \text{ dependent reflection phase} \ldots
\]

(5.2)

which, as seen in Fig. 5.1, quickly converges, and for all values is rather close to \( \varphi \approx -0.75\pi \) [68, 69]. This is interestingly a result that is entirely independent of the actual conductivity, but follows from the geometry and the assumption that the conductivity is uniform within the ribbon and zero outside. We will say more about the standing wave model and explore it in detail with TB in Paper II.

The plasmon energies in TB were identified by fitting a Gaussian to the peaks of the loss function. The example of a 6 nm ribbon displayed in Fig. 3.10 (page 32) showed the pretty behavior for fairly wide ribbons where the peaks are not overlapping and are centered around the zeros of \( \text{Re}(\epsilon_p) \). In Fig. 5.2 a similar plot is shown for a 3 nm wide ribbon at \( \epsilon_F = 0.4 \text{eV} \). The main dipole plasmon peak is very broad and of almost the same height as the surrounding spectrum. We also see that the peak position is shifted from the zero point of the dielectric function. For even narrower ribbons, identifying a main peak becomes almost impossible as could also be seen from the scatter of the plasmon energies at low \( \Lambda \), especially in Fig. 4b in the paper.

5.1.2 Scaling behavior

In Paper I, it is shown that the scale invariance emerges as the ribbons get wider (Fig. 6 in the paper). As we have made some analytical considerations on the quantization
5.1. ADDITIONAL INFORMATION TO PAPER I

Figure 5.1: The classical calculation of the plasmon energies can be interpreted as a standing bulk wave with a mode-dependent phase shift plotted here. This result is independent of the Fermi energy and the ribbon width.

![Figure 5.1](image1.png)

Figure 5.2: Dielectric function and loss for a 3 nm wide zigzag ribbon.

![Figure 5.2](image2.png)

effects and corrections to ribbon conductivities in Chap. 4, it is worth considering if any of the findings are applicable to the TB results. In Eq. (4.9) we identified a discretization correction factor to the plasmon energies with the expression $\sqrt{1 - 2/\Lambda}$, when using the dimensionless quantity $\Lambda = k_F W$. However, the calculation leading to this factor was performed assuming zero temperature, in the local-response approximation, and under the assumption that the band structure is shaped as an infinite double cone. This is not the case for the TB calculations where the temperature is fixed at 300 K, $\chi^0$ is a function of $x$ and $x'$ (effectively of the basis functions that are located in real space), and there is a finite number of bands in the band structure.

In Fig. 5.3 where we have reproduced Fig. 6a from the paper, we have overlaid a
correction not unlike the one from the Dirac model, namely the orange curves following

$$\frac{\hbar \omega}{c_F} = \Omega_{\Lambda} \sqrt{1 - \frac{2 \text{ nm}}{\Lambda W}}.$$  

where $\Omega_{\Lambda}$ is adjusted for each of the $\Lambda$ values to match the energy for the widest ribbons. Although this relation is merely speculative, the great resemblance with the behavior found with TB persuade us to speculate about a reason.

A thing to note about the discretization correction from Eq. (4.9) is that the $1/\Lambda$ slightly covers up the fact that the correction is for the number of states that participate in the conductivity, $N$. Naturally, $N \propto \Lambda$ when $\Lambda$ is sufficiently large, but for a finite number of electrons, an additional effect kicks in. When the ribbon is made narrower, it is done by removing atoms in the TB calculation. The atom number, and in effect the number of bands, scales linearly with the width, which is not the case in the Dirac model. Another effect is that the relative number of edge states vary in the TB model. In Fig. 5.4, two band structures and the corresponding density of states are shown, one for a 2 nm wide ZZ ribbon, and one for an 8 nm ZZ ribbon. The wide ribbon has a smaller edge state contribution, as it should, but is not one fourth the size as the ratio between the widths would indicate. In fact, it is larger than that, meaning that for narrow ribbons, the edge effects get too small. Plotting, in Fig. 5.5, the same band structure for the 2 nm ribbon (black), but scaling the bands of the wide ribbon (red) with a factor of $8 \text{ nm}/2 \text{ nm} = 4$ gives further insight. The latter bands have been shifted to match the position of the first Dirac cone. The scale-invariance argument assumes that these two band structures are identical around the $K$ point. A striking difference is seen in the density of states, where the wide ribbon has a much larger peak from the edge states. The inset shows that the rest of the DOS is fairly similar. As we saw

Figure 5.3: Analytical approximations according to Eq. (5.3) (orange) of the emerging scale invariance of the plasmons in zigzag ribbons. See details in main text.
5.1. ADDITIONAL INFORMATION TO PAPER I

Figure 5.4: Band structures and DOS for a 2 nm (black) and a 8 nm (red) zigzag ribbon. Notice the relative low DOS peak from the edge states in the wide ribbon. The DOS is calculated as $\text{DOS}(\epsilon) = \sum_i \text{Im} [(\epsilon - \epsilon_i - i\eta)^{-1}]$ with $\eta = 0.01 \text{Ha}$.

Figure 5.5: Band structures and DOS for a 2 nm (black) and a 8 nm (red) zigzag ribbon where the latter has been scaled with a factor of 4, and translated to match the $K$-valley position. The densities of states are very similar except for the big difference in the edge-state peaks.

in the paper, for small $\Lambda$ the edge states blueshifts the plasmon energy. If the edge states get disproportionally fewer with the ribbon size it would result in a redshift which was what was observed in Fig. 5.3. This interpretation would also explain why we do not see the same breakdown of the scale invariance in AC ribbons.

One minor correction to the scaling argument in Eq. (5.3) is that the band-number proportionality with $\Lambda$ is only valid when many bands cross the Fermi level. This effect is smoothed by the finite temperature, but it should still not be valid for the lowest values of $\Lambda$. Consequently, we have used $\Lambda = 2$ in Eq. (5.3) for the curve with $\Lambda = 1.5$. 

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since the match was significantly better. We justify this with the fact that there is only one band crossing the Fermi level for both \( \Lambda \in (1.5, 2) \) and the other bands are fairly far away limiting the smoothing effect of the temperature.

The speculations presented above are by no means decisive and further analysis should be made before any conclusions are drawn. No matter what, we have discussed a couple of the shortcomings of the scale invariance, and the presented correction relation does seem to match very well. We have also identified two types of effects – one related to the relative ribbon size through the \( \Lambda \) parameter, and another size-dependent effect that depends on the absolute ribbon width.

From the quantization correction calculated in Eq. (4.9), we would expect to see a deviation from the local, classical model at much larger \( \Lambda \) than is the case in the papers Fig. 4. Inserting \( \Lambda = 10 \), when including only the intraband term, suggest that the plasma frequency should be only 90% of the non-discretized limit. This is certainly not the case in the TB calculations that match the classical description for all \( \Lambda \geq 5 \), and I do not know why.

5.1.3 Edge transitions and blueshift

The final thing I would like to touch upon in regard to Paper I, is the blueshift caused by the edge states. In Ref. [64] where the edge conductivity is calculated for graphene disks in a similar manner as in Chap. 4, it is shown that the edge states result in a redshift of the plasmon energies. In that case, however, almost all plasmons calculated with local response have energies below the Fermi energy, which is the energy onset of the edge contribution. The simple argument (supported by TB calculations) is that the new transitions screen the plasmonic energies and push them downwards. By contrast, in the calculations in Paper I, the plasmon energies are almost universally above Fermi energy (see Fig. 4 in the paper), and the added states are therefore below the plasmon and the opposite argument may be applied: The edge states give rise to a blueshift when the plasmon energy is above the Fermi energy, as observed in the paper.

This is a persuasive argument, but it cannot be the whole truth. When looking at the edge-bulk transition in detail (see Fig. 5.6), it becomes clear that it does not happen exactly at the Fermi energy when \( \Lambda \) is very low. This is illustrated in Fig. 5.6 where the gray area indicates what is below the edge transition energy. The three band diagrams illustrate how the energy begins at the Fermi energy, goes below due to the bending of the edge band and finally rises when the last parabolic band is empty. This was also the effect that caused the movement of the peak in Fig. 4.5 (p. 42). It is seen that, for \( \Lambda \lesssim 3 \), including edge states still produces an energy increase even though the edge transition lies above the plasmon when edge states are excluded. Alas, such a simple argument is not sufficient for understanding the effect of the edge states on the plasmons.

As we saw, for large \( \Lambda \) the edge transition does happen at the Fermi energy, so what about ribbons where the plasmon energy is below the onset of edge-bulk transitions? In that case, there seem to be no redshift either as can be seen in Ref. [56]. This contrasts the TB findings for triangles, hexagons and disks [68] that all display a clear redshift.
5.2 Summary

Numerous new insights have been presented in this section. The standing-wave picture of the plasmons, that derives from the classical model was introduced – and will be discussed much more in the next chapter. We discussed the breakdown of the scale invariance in more detail, presenting the large differences in the edge-state DOS between different ribbon sizes, and showed a model that, seems to describe the convergence behavior of the plasmon energies quite well, even though the model origin is not rigorously understood. Surprisingly, the discretization corrections calculated in Chap. 4, do not seem to match the TB calculations. Arguments for why the edge states not always give rise to redshifts, but also can give the blueshift we found in TB, were also presented, together with a more thorough analysis of the energy threshold for edge-bulk transitions within the Dirac model.
In Paper II the standing-wave model is examined in depth using the fully quantum mechanical tight-binding calculations. In this way, we go beyond the classical hard-boundary model and take into account that the plasmon may “spill out” of the ribbon or, alternatively, effectively be reflected before the edge. In fact, allowing for such differences is necessary in nanoribbons, since the width itself is not unambiguously defined at the atomic resolution. We could take the distance between the outermost atoms, which is the chosen approach, but it may not be the width that the plasmon feels. Besides the standing-wave model, Paper II also demonstrates the effect of the localized edge states on the plasmon broadening in zigzag ribbons by using the same technique as in Paper I, to exclude part of the states from the response calculations. Finally, we see that the atomic resolution oscillations of the electronic wave functions that were introduced in Chap. 3 also occur in the induced charges of the plasmonic modes.

As was the case for Paper I, the theory described in the following has already been presented earlier in the thesis, and the reader will experience a large overlap. In Sec. III, new information, in form of the standing-wave model used in the paper is introduced. Sec. VA of the paper reiterates a part of the results on the Dirac and TB wave functions presented in Sec. 3.3 (pp. 25–) although not to the same level of detail. The content of Sec. VB on the other hand, has not been presented previously, and demonstrates how the oscillations of the wave functions leave traces in the induced charges that build up the plasmons.
Edge-dependent reflection and inherited fine structure of higher-order plasmons in graphene nanoribbons

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We investigate higher-order plasmons in graphene nanoribbons, and present how electronic edge states and wavefunction fine structure influence the graphene plasmons. Based on nearest-neighbor tight-binding calculations, we find that a standing-wave model based on nonlocal bulk plasmon dispersion is surprisingly accurate for armchair ribbons of widths even down to a few nanometers, and we determine the corresponding phase shift upon edge reflection and an effective ribbon width. Wider zigzag ribbons exhibit a similar phase shift, whereas the standing-wave model describes few-nanometer zigzag ribbons less satisfactorily, to a large extent because of their edge states. We directly confirm that also the larger broadening of plasmons for zigzag ribbons is due to their edge states. Furthermore, we report a prominent fine structure in the induced charges of the ribbon plasmons, which for armchair ribbons follows the electronic wavefunction oscillations induced by inter-valley coupling. Interestingly, the wavefunction fine structure is also found in our analogous density-functional theory calculations, and both these and tight-binding numerical calculations are explained quite well with analytical Dirac theory for graphene ribbons.

I. INTRODUCTION

Numerous studies have over the recent years been conducted on graphene one-dimensional (1D) structures, emphasizing both single-particle excitations and collective plasmonic excitations.1–8 Ribbons are prime examples of such structures,9–11 while plasmons can also be localized and guided along other 1D structures.11–14 Principal motivations for studying plasmons in graphene ribbons are the strong confinement of the electromagnetic fields, long propagation lengths, as well as the convenient tunability through (electrostatic) doping.15 Creation of nanoribbons has come a long way.16–22 It is now possible to create ribbons with widths in the 10–20 nm range, both with top-down processes, allowing better scalability, and with bottom-up syntheses yielding high atomic precision.23 Together with methods for probing plasmons with high spatial resolution,4,7,24–26 this creates possibilities to measure novel quantum effects in graphene plasmonics.

We have previously elucidated the emergence of nonclassical behavior of the lowest-order plasmons in narrow graphene ribbons27 arising from the quantized nature of the bands. In this work, we analyze instead the higher-order modes, in order to study the impact of the precise atomic configuration on the plasmon reflection properties of the ribbon edges. The phase shift upon edge reflections of plasmons in graphene has previously only been treated in continuum theories, in Refs. 1, 28–30, where conductivity is handled as a local material parameter. Possible effects of the specific atomic configuration at the edge cannot be studied in such an analysis. In contrast, we here study edge reflections within tight-binding (TB) calculations for both armchair and zigzag ribbons (see Fig. 1). We also consider zigzag ribbons where the edge states have been excluded when calculating the optical response as detailed in our previous work.27 The latter allows us to study directly how graphene plasmons are affected by the localized electronic edge states of zigzag ribbons.

Furthermore, the atomistic nature of our calculations allows us to study the fine structure of the plasmons by

![Graphene nanoribbons](image)

FIG. 1. (Color online) A zigzag (left) and an armchair (right) ribbon with the axis used in the following being indicated. Sketch of the induced charges across the ribbon for dipolar and higher-order plasmons are illustrated in red (negative charges) and blue (positive). The fine structure presented in Sec. VB has been averaged out.
mapping the induced charges to individual atomic sites. The analysis reveals short-range oscillations inherited from the underlying wavefunctions, predicted by Dirac theory and confirmed both by TB and our \textit{ab initio} density-functional theory (DFT) calculations.

The structure of the paper is as follows: In Sec. III we present our analysis of a standing-wave model and the effect of the atomic edge termination on the edge reflection properties of graphene plasmons. Secondly, in Sec. IV, we briefly show our findings regarding the localized edge states. Finally, in Sec. V, we explore the fine-structure in Sec. V.

II. MODELS AND METHODS

A. Tight-binding model

The band structure of graphene is well described by a nearest-neighbor TB model with the Hamiltonian

$$\hat{H} = \sum_{\langle i,j \rangle} -t(a_i^\dagger b_j + h.c.),$$

where the sum is over pairs of neighboring sites and the $a$ and $b$ creation (annihilation) operators add (remove) an electron on the $A$ or $B$ sublattice, respectively. For the hopping parameter $t$ we use the value of 2.5 eV, first determined by Ref. 32.

The eigenstates are calculated on a dense $k$-point grid with 5000 points in the one dimensional Brillouin zone and used for calculating the optical response as outlined below. In ribbons with zigzag edges (left ribbon in Fig. 1) where localized edge states occur, we can classify the eigenstates as either bulk-like or edge-like using an energy cutoff derived from the Dirac model as presented in our recent work (Ref. 27). This will allow us to directly quantify the effect of the edge states on the energies and reflection properties of the graphene plasmons.

B. Response function

We calculate the optical response for $q = 0$ within the random-phase approximation (RPA) following the same methodology as Refs. 10 and 27, i.e. the non-interaction density-density response function is calculated in the site basis through direct insertion of the eigenstates in

$$\chi_{ij}^0(\omega) = \frac{2e^2}{\hbar} \sum_{nm} f_{nm} \frac{a_{in}^\dagger a_{jm}^\dagger a_{jn} a_{jm}}{\epsilon_{nm} - \hbar(\omega + i\eta)},$$

from which the dielectric function can be determined as

$$\epsilon_{ij} = \delta_{ij} - V_{ij}\chi_{ij}^0,$$

where $V$ is the Coulomb interaction. The $i, j$ are atomic site indices, while $n$ and $m$ label the eigenmodes at wave vector $k$. Thus, $a_{in}$ is the value of the $n^{th}$ wavefunction on the $i^{th}$ site (implicitly at wave vector $k$). As a shorthand notation, we have used $\epsilon_{nm} = \epsilon_n - \epsilon_m$ for the energy difference and likewise $f_{nm} = f_n - f_m$ for the difference in the Fermi filling factors. The phenomenological loss parameter $\eta$ is set to 1.6 meV as in Ref. 10. The width of the supercell in the periodic direction is labeled $b$. By excluding the edge states in the evaluation of the response function, their contribution can be assessed by comparing with the full expression.

The Coulomb interaction is included in real space using a fit of the distance dependent values for the correct Hartree interaction between two $p_z$ states. The spatial extend of the $p_z$ orbitals is taken from tabulated values. Charge neutrality ensures that the product $V\chi_{ij}^0$ can be properly converged, despite the long-range behavior of the Coulomb interaction.

C. Quantum plasmons

The dielectric function $\epsilon(\omega)$ can be written in a spectral representation of its eigenvalues and left and right eigenvectors as $\epsilon_{ij}(\omega) = \sum_n \epsilon_n(\omega) \phi_{n,i}(\omega) \phi^*_{n,j}(\omega)$, where the zeros of the real parts of $\epsilon_{ij}(\omega)$ indicates plasmonic modes, the right eigenvector $\phi_n$ is the induced field, and the left eigenvector $\phi_n^*$ is the induced charges of the plasmon.

In Fig. 2 the numerically calculated eigenvalues for a 6 nm wide ribbon with zigzag termination and a Fermi energy of 0.4 eV are shown below the panel showing the energy loss function, the latter defined as $-\text{Im}(\epsilon^{-1})$. The crossings of zero by the real part of the eigenvalues are indicated with red circles. The first two zeros of Re[$\epsilon_n$] clearly correspond to peaks in the loss spectra. Higher-order modes are more damped and hard to identify from the loss spectrum, but they can still be easily identified as the zeros of Re[$\epsilon_n(\omega)$].

![FIG. 2.](image-url) (Color online) From the dielectric matrix the plasmon modes can be found as peaks in the loss function (top panel) where the dipole plasmon stands out, or as the zeros of the real part of $\epsilon_n$ as shown in the lower panel. The data shown is for a 6 nm zigzag ribbon with $\epsilon_F = 0.4$ eV.
III. PLASMONS IN A STANDING-WAVE MODEL

It is well known that plasmons reflect with almost no loss on graphene edges.\textsuperscript{36,37} Thus, as a method of understanding the behavior of plasmons in graphene nanoribbons, we will adopt a Fabry–Pérot standing-wave model. As we only consider propagation in the $x$ direction, the picture is that the plasmon moves across the ribbon according to a certain dispersion relation, reaches an edge, and reflects back with an additional phase change from the reflection. The allowed modes are those where this process gives rise to constructive interference as illustrated in Fig. 1. The condition for this to occur becomes

$$2(n-1)\pi = 2qW_{\text{eff}} + 2\varphi \iff q = \frac{(n-1)\pi - \varphi}{W + \Delta W}.$$ \hspace{1cm} (4)

where $n$ is the integer mode index starting from $n = 1$ and $\varphi$ is the reflection phase change. Furthermore we introduced an effective width $W_{\text{eff}} \equiv W + \Delta W$ that takes into account that the plasmon may not reflect at exactly the positions of the outermost rows of atoms that define the geometric width $W$. The notion of effective sizes are also found in the area of optical antennas.\textsuperscript{38} A positive $\Delta W$ describes a plasmon that effectively spills out of the ribbon, while a negative value corresponds to a plasmon that is effectively more tightly confined than by the geometric width. As such, this is quite analogous to descriptions surface phenomena based on Feibelman parameters.\textsuperscript{39,40}

We have performed TB calculations for both armchair and zigzag ribbons and also considered zigzag ribbons where the edge states have been excluded when calculating the optical response, as detailed in our previous work.\textsuperscript{27} This allows us to understand the effects, if any, of the atomic edge termination and the localized edge states on the reflection properties of the graphene plasmons.

A. Linear mode dependence of higher-order modes

By finding the zeros of the real part of the eigenvalues of the dielectric matrix, as illustrated in the bottom panel of Fig. 2, we can find the plasmon energies as a function of mode index. We depict this data in the insets of Fig. 3. By inspection one can see that the plasmon energies depend more or less linearly on the mode number for the higher-order modes. Given this linear dependence, it seems that the higher-order plasmons on graphene ribbons behave analogously to light in a cavity between two mirrors. Assuming a linear dispersion as $\omega_n = v_p q_n$, where $v_p$ is a constant plasmon velocity, we therefore expect $\omega_n W_{\text{eff}}$ to be constant across different widths. To fit our non-dispersive model we do not use the lowest-order modes with $n \leq 3$, as indicated by the gray areas in Fig. 3. The reason is that the curves shown in the insets start deviating from the linear behavior for these lower mode numbers. The resulting fits are shown in Fig. 3 and the corresponding values are given in Tab. I. The linear fit is indeed quite good for the higher-order modes in all cases. Without edge-state contributions there is a slight upward bending of the lower-order modes that gets more prominent for the wider ribbons. When comparing ZZ with and without edges, we can tell that the edge states alter the behavior of the low-index modes, while the higher-order modes are still linear. The extracted plasmon velocities differ by $\sim 10\%$ and are all close to the Fermi velocity, $v_F = 0.91 \times 10^6$ m/s. As seen in Tab. I, in this model AC edges have a reflection phase of approximately $\pi$ and a small width correction $\Delta W \approx 0.4$ nm. The zigzag ribbons show a very different behavior with a larger $\Delta W$ of 1.44 nm and a considerable phase shift of $-2.67\pi$. Removing the edge states brings both $\varphi$ and $\Delta W$ closer to the results found for armchair ribbons.

<table>
<thead>
<tr>
<th>$\Delta W$ [nm]</th>
<th>0.38 $\pm$ 0.05</th>
<th>1.44 $\pm$ 0.04</th>
<th>0.72 $\pm$ 0.02</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varphi/\pi$</td>
<td>$-1.06 \pm 0.05$</td>
<td>$-2.67 \pm 0.05$</td>
<td>$-1.53 \pm 0.03$</td>
</tr>
<tr>
<td>$v_p$ [10$^6$ m/s]</td>
<td>1.02 $\pm$ 0.02</td>
<td>0.88 $\pm$ 0.00</td>
<td>0.90 $\pm$ 0.00</td>
</tr>
</tbody>
</table>

Although the linear fits are quite good, the model only works for the higher-order modes and the more-than-$2\pi$ phase shift for zigzag ribbons is hard to interpret. We therefore conclude that a better model is needed to obtain trustworthy quantitative values for the $\varphi$ and $\Delta W$. This model will be presented in the following.

B. Nonlocal dispersion and reflection phase shift

Building on the standing-wave model, we suggest that, while the plasmon is not at the edges, it disperses in the same manner as it would in an infinite sheet of graphene. Classically, that corresponds to a $\sqrt{q}$-dispersion, as is the case for the two-dimensional (2D) electron gas.\textsuperscript{41,42} However, we expect nonlocality to play an important role in these small structures and we thus use the dispersion relation found by using the nonlocal dielectric function for infinite graphene as calculated in Refs. 41 and 43. With this approach, an explicit $q$-dependence is included in the quantum mechanical conductivity altering the plasmon dispersion for larger values of $q$. As can be seen from Fig. 4, the included nonlocality makes the dispersion almost linear at larger $q$ and thus explains why the linear model worked for high mode indices.

We determine $\varphi$ and $\Delta W$ by fitting to the nonlocal dispersion curve getting the results shown in Fig. 4 with parameters shown in Tab. II. The model applies very well for the armchair ribbons, both for larger $q$ values where the
FIG. 3. (Color online) Using a linear dispersion relation and fitting the Fabry–Pérot model to the modes with \( n \geq 4 \) for AC, ZZ, and ZZ without edge states. The insets show the energy as a function of mode number for all the ribbons calculated. All calculations are for \( \epsilon_F = 0.4 \) eV.

FIG. 4. (Color online) The reflection phase and the width corrections are found by optimizing to the nonlocal plasmon dispersion of infinite graphene. The Fabry–Pérot model with this dispersion works very well for the armchair ribbons and for the zigzag ribbons when excluding the edge states.

The dispersion is linear, and for smaller \( q \) where the dispersion curve becomes flatter. The resulting plasmon reflection phase for AC ribbons is found to be close to \(-0.75\pi\).

The concomitant width correction \( \Delta W \approx -0.3 \) nm corresponds approximately to the width of two and a half atomic rows in the armchair configuration.

An alternative definition of the reflection phase (that differs by \( \pi \)) has been used in Refs. 1, 29, and 30. However, after converting to our definition these works report reflection phases that are all very close to \(-0.75\pi\). This is the same as was found in Ref. 28 that uses the same definition as we do. Because of this remarkable agreement in numerically determined reflection phases, it is worth mentioning at this stage that as far as we know there is no analytical theory that predicts an exact reflection phase of \(-3\pi/4\). However, in Ref. 28 the authors do present an analytical model that comes quite close and predicts \( \phi \approx -0.64\pi \).

The same nonlocal-dispersion model does not agree as accurately with the analogous tight-binding results for zigzag ribbons, as can be seen from the increased scatter of the points in the second panel of Fig. 4. Especially the behavior of the low-\( q \) plasmons in the TB calculations is not captured that well. As seen in the rightmost
panel, removing the edge states does improve the agreement, indicating that these states are responsible for a great part of the difference with armchair ribbons. We emphasize that the AC ribbons are well described by a \(-0.75\pi\) reflection phase in combination with the bulk plasmon dispersion down to very small sizes of only a few nanometers. However, because of the less convincing fit for the ZZ geometry, we will not take the resulting fitting parameters at face value, and perform instead an additional more thorough analysis.

TABLE II. Fitting parameters as determined from the nonlocal dispersion model used in Fig. 4.

<table>
<thead>
<tr>
<th></th>
<th>Armchair</th>
<th>Zigzag</th>
<th>Zigzag w/o edge states</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta W) [nm]</td>
<td>(-0.30 \pm 0.05)</td>
<td>(0.31 \pm 0.06)</td>
<td>(0.32 \pm 0.03)</td>
</tr>
<tr>
<td>(\varphi/\pi)</td>
<td>(-0.79 \pm 0.03)</td>
<td>(-1.33 \pm 0.05)</td>
<td>(-0.89 \pm 0.02)</td>
</tr>
</tbody>
</table>

C. Width-dependent phase shift

To get further insight into the plasmons in ZZ ribbons we optimize \(\varphi\) and \(\Delta W\) for each ribbon width individually. The results depicted in Fig. 5 show that there are only minor changes as a function of width for AC ribbons, which is to be expected since one set of (width-independent) parameters did very well previously. We distinguish between semi-metallic (triangles) and semiconducting (circles) AC ribbons and find that they behave slightly different for the small widths, as we have also examined in another context previously.\(^{27}\) The graphs for the two types of AC ribbons will merge for wider ribbons (not shown) as the band gap for the semiconducting ribbons closes. For ZZ ribbons, a standing-wave model with nonlocal bulk dispersion results in much greater variance in the reflection phase and the width correction between the different ribbon widths. In the zoomed view in the bottom middle panel of Fig. 5 we can see that only for the two widest \(\geq 13\) nm ribbons (yellow and light green dots) do the TB calculations follow the nonlocal dispersion model well. So it seems that our bulk-dispersion-in-between-reflections model does not apply to the narrower ZZ ribbons that we considered, while for AC ribbons it does for all sizes. Let us give an explanation why this would be the case. The electron density for an AC ribbon is virtually constant across the entire width of the ribbon, see Fig. 6. Hence, it is a fair assumption that the plasmon experiences a fairly constant bulk-like environment while propagating in between the ribbon edges. Turning our attention to the electron density in ZZ ribbons, the localized edge states give rise to increased electron density (see second panel of Fig. 6), and therefore an effectively different Fermi energy altering the dispersion of the plasmons in this region. The effective phase change will thus be the sum of the reflection at the edge and any phase picked up during propagation in the edge region. With wider ribbons, the relative size of the non-bulk-like region to the plasmon wavelength decreases and the phase shift converges close to \(-0.75\pi\) for ZZ ribbons as well. By comparing to the results from excluding edge states we see that both the phase and the \(\Delta W\) vary much less and that the fit hardly changes compared to the width-independent model. The latter was also the case for the AC ribbons.

The ZZ width correction finds its stable point close to \(-0.3\) nm exactly as the result found for AC ribbons. Only optimizing for the widest ribbon where the model is applicable yields \(\varphi = -0.77\pi\) and the fit shown in Fig. 7.

To conclude, a constant phase shift of the same size of \(-0.75\pi\) as the ones found in continuum theories works well for both AC and ZZ ribbons, although the picture starts to change for ZZ ribbons narrower than 15 nm. At these sizes an atomistic model is needed to properly account for the edge effects. We must stress that these findings depend on including the width correction, \(\Delta W\), not previously considered in earlier work. Leaving it out yields both different phases and in general worse fits. Naturally, since \(\Delta W\) is on the order of Angstr"omes, and the plasmon wavelength scales with the ribbon width, its importance will disappear for wide enough ribbons.

IV. EDGE-STATE INDUCED BROADENING

Besides the reflection properties dependence on the occurrence of localized edge states we also find that the plasmonic peaks are much wider in ZZ ribbons than in AC ribbons of comparable widths, see Fig. 8. A similar result has previously been reported in Ref. 10, and the hypothesis was put forward that the edge states give rise to the additional broadening. Here we will test the hypothesis: by excluding the edge states from the calculation of the optical response, we can directly determine the influence of said states on the broadening.

The result can be seen in Fig. 8, where the blue (orange) dots are the plasmon peak widths for ZZ (AC) ribbons with \(\epsilon_F = 0.8\) eV and the open symbols are ZZ without edge states. It confirms unequivocally and for the first time the hypothesis that the larger broadening for ZZ ribbons is indeed due to the presence of the edge states. It can be interpreted in this way that the edge states constitute an additional decay channel for the plasmons, leading to more broadening, in an electron energy range that would otherwise have a zero density of states. Indeed, this has been explored analytically for disk resonators\(^{44}\) and numerically for triangular flakes.\(^{45}\) As edge states are common to all graphene terminations, except the armchair edge,\(^{46–48}\) it is reasonable to expect that this edge-induced plasmon broadening will occur in most graphene nanostructures.
FIG. 5. (Color online) Optimizing $\varphi$ and $\Delta W$ for one width at a time showing that while the AC results are fairly constant, ZZ corrections seem to converge only for wider ribbons. The two types of points in the AC plots distinguish between semi-metallic (triangles) and semiconducting (circles) ribbons. The dashed line in the top plots indicates $-0.75$. Colors in bottom plots are the same as in Fig. 3.

FIG. 6. (Color online) The difference in the ground-state density for a 7 nm wide doped graphene ribbon, shown relative to the average density at the center half. While the density in AC ribbons is almost constant everywhere, the electronic edge states in ZZ ribbons alter the picture considerably. Results from TB with $\epsilon_F = 0.4$ eV.

V. INHERITED FINE STRUCTURE OF PLASMONIC MODES

In this section we will present our findings of the atomic-scale fine structure of the plasmonic modes of nanoribbons. As the induced charges are built from electron-hole pairs, some structural properties of the underlying wavefunctions will be inherited by the plasmons, as we show in the following.

A. Fine structure of wavefunctions

It is possible to get analytical insight into the shape of the wavefunctions from the Dirac model where the TB Hamiltonian is linearized around the $K$ and $K'$ valleys.
The resulting Hamiltonian has the form

\[ H = \hbar \nu \left( \tau_x \sigma_x k_x + \tau_0 \sigma_y k_y \right) \]

\[ = \hbar \nu \begin{pmatrix} 0 & k_x - ik_y & 0 & 0 \\ k_x + ik_y & 0 & 0 & 0 \\ 0 & 0 & -k_x + ik_y & 0 \\ 0 & 0 & 0 & -k_x - ik_y \end{pmatrix}, \]

where \( \tau_i \) and \( \sigma_i \) are all Pauli spin-matrices with the former belonging to valley space and the latter to the \( A/B \) sublattice space.

The armchair edge termination consists of alternating \( A \)- and \( B \)-lattice sites and the boundary conditions must thus mix the two valleys \( A \) and \( B \) at every third atom across the armchair ribbon. From this it follows that two neighboring atoms will usually have very different weights of the wavefunction. However, if we plot the same electron densities for every third site, such that the atoms 1, 4, 7, \ldots are connected, then we expect the change to be rather smooth. This “fine structure” oscillation is readily found in the TB results as shown in Fig. 9 and 10 for a 42-atom-wide armchair ribbon.

To emphasize the fundamental nature of this oscillation, we have also performed a DFT calculation of the same ribbon geometry, using a plane-wave basis set. Using a Bader charge analysis we have projected the electron densities corresponding to the lowest unoccupied wavefunctions (of undoped graphene) onto the individual carbon atoms such that we can compare with the TB results. The \textit{ab initio} calculations show very much the same fine-structure behavior as seen in the top rows of Fig. 9 and 10.

These rapid electronic variations are inherited by the spatial distributions of the plasmons of AC graphene ribbons, as we will see in the next section. Returning to the values of \( k_n \) we can also find the long-wavelength oscillation in both the DFT and TB results. As illustrated in Fig. 9, by “unfolding” the wavefunction such that it covers the full 3\( W \), we find that the behavior exactly matches a wave with the shape \( \cos(k_n x) \). It can be seen in Fig. 10 that this also works for the higher-lying wavefunctions. Generally, we find that for semiconducting AC ribbons the electron density from state \( n \) at site \( i \) can be written in as

\[ \rho_i = N \sin^2 \left( \frac{x_i - [i + N \mod 3] \cdot k_n}{W} \right), \]

where \( i \) is the site index as indicated in Fig. 9, \( x_i \) is the \( x \)-coordinate of the site, and \( N \) is a normalization factor.

## B. Fine structure of plasmons

As explained in the Methods section, the formalism for calculation of the plasmons in TB gives direct access to the induced electron density of the plasmonic modes as well as the induced field through the eigenmodes of the dielectric matrix. In Fig. 11 we show these densities for the four lowest-order modes in two zigzag and armchair ribbons, one 4 nm and one 8 nm of either kind. For the zigzag ribbon the density is shown on each of the \( A/B \) sublattices individually (gray lines) as well as the mean density found by averaging two interpolated splines fitted to the sublattice data (thick, black line). The mean induced density, which is also sketched in Fig. 1, shows the behavior that one would expect in a classical model, but there is a lot of fine-structure oscillations when looking at the atomic details. The charge fluctuates between the sublattices, although the variation becomes smaller in the higher-order modes and for the wider ribbons.

Charge densities in the armchair ribbons behave qualitatively different in that there is no \( A/B \) symmetry as for ZZ. As explained above, the valley-mixing imposed by the armchair boundary conditions leads to a periodic
FIG. 9. (Color online) Scheme for visualizing short- and long-range oscillations in the wavefunctions. Electron density (first column) is mapped to individual atoms and every third atom is connected in the plot (middle column). Finally, the map is “unfolded” to reveal the oscillation predicted from the Dirac model.

FIG. 10. (Color online) The electron densities of the three lowest unoccupied wavefunctions at the K-valley. The top row shows the DFT electron density (gray) and the result of a Bader charge analysis. The second row shows the TB results with every third atom connected. The short-wavelength oscillations of every third site are clearly visible in both TB and DFT. Unfolding the waves (as illustrated in Fig. 9) reveals the long-range oscillation in both TB and DFT in the bottom two rows. See details in main text.

behavior of the wavefunctions with a characteristic length scale corresponding to every third atom across the ribbon. We plot the induced charges projected on the three subsets formed by this rule (full, dashed, and dotted gray lines) and find a smooth behavior for all of them. The fine-structure is thus a fingerprint of the periodicity of the underlying wavefunctions that are involved in building up the plasmon. As before in Fig. 10, in Fig. 11 we show the average induced charges (black lines) and find that they also match very well with the classical picture despite the large local differences.

VI. DISCUSSION AND CONCLUSIONS

Using TB we identify numerous interesting effects in graphene nanoribbon plasmons. By looking at the dispersion of higher-order plasmons we find edge-dependent reflection properties of narrow ribbons. For armchair ribbons, the standing waves are well described with a constant phase shift of $-0.75 \pi$ and width correction $\Delta W = -0.3 \text{ nm}$ at least down to $\sim 2 \text{ nm}$ wide ribbons. The inclusion of $\Delta W$ is necessary to adequately describe the system within the Fabry–Pérot model, and leaving it out would render the $-0.75 \pi$ phase change inapplicable.
for the structures considered. In contrast to the result
found for AC ribbons, the $\varphi$ and $\Delta W$ do depend on the
width in zigzag ribbons as wide as $\sim 15$ nm. This behavior
is caused by the localized edge states that significantly
alter the electron density close to the ribbon borders. Sur-
prisingly, at the wider ribbon widths, both ribbon types
are characterized with the same width corrections and
reflection phases. These almost identical outcomes were
not put in by hand and are the result of independent
curve fitting. So we find that for wide enough ribbons
where $\Delta W$ is negligible, the reflection phase of $-0.75\pi$
found in previous numerical studies within continuum
models will also work for tight-binding models with either
different terminations, a phase which is not far from the value
of $-0.64\pi$ found analytically from a continuum model in
Ref. 28. This convergence of our results for the reflection
phases of the two ribbon types is consistent with Ref. 10,
where it is shown, using tight-binding calculations, that
in wide ribbons the energies of the lowest-order plasmon
of ZZ and AC ribbons coincide.

FIG. 11. (Color online) Induced charges for the first four plasmons for four different ribbons. The top view of the ribbons show
the charge on every atomic site. The gray graphs (full, dashed, and (for AC) dotted) show the charges split between the A and
B sublattices for the zigzag ribbon and spilt between every third atom in the armchair ribbon. The thick line is the average of
the thin lines and matches well with the classical expectation. There is a clear fine-structure in the distribution of the charges
that seem to disappear at higher-order modes. The bottom graph in each plot shows the induced field. There is evidently
considerable fine-structure in the induced charges on the atomic scale.
for the single-configuration electron density around the K-point in semiconducting ribbons.

Finally, we have studied edge-induced broadening, which for other geometries was discussed in Refs. 44 and 45. We confirmed the hypothesis put forward in Ref. 10 and directly showed the key role played by localized edge states in the broadening of the plasmonic peaks in ZZ ribbons, a broadening that we find is larger for narrower ribbons. As edge states occur in all but the armchair configuration, we predict that this broadening will be present in most graphene structures.

ACKNOWLEDGMENTS

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9 J. Christensen, A. Manjavacas, S. Thongrattanasiri, F. H. L. Koppens, and F. J. García de Abajo, ACS Nano 6, 4311 (2012).
10 S. Thongrattanasiri, A. Manjavacas, and F. J. García de Abajo, ACS Nano 6, 1766 (2012).
15 S. Huang, C. Song, G. Zhang, and H. Yan, Nanophotonics 6, 1191 (2016).

Same data as in Ref. 10 and acquired through private correspondence with the group.


We use the GPAW code with a cut-off energy of 500 eV and 15 $k$-points in the periodic direction of the supercell.

6.1 Additional information and further discussions on Paper II

In the following, I will present some more details on the two parameters of the standing-wave model used in the paper, followed by some additional analysis of the results from the paper. Subsequently, I will show the results of determining a \( q \)-dependent reflection phase, in a model where only one parameter is needed. Lastly, some additional data concerning the edge-broadening is shown, before a brief discussion on additional plasmonic modes that occur in a part of the ribbons.

6.1.1 Details of the standing-wave model

In the following, I will go more in detail with the standing-wave model, described by the equation

\[
q = \frac{(n - 1)\pi - \varphi}{W + \Delta W},
\]

as to uncover the differences between the width correction \( \Delta W \) and the reflection phase \( \varphi \), and to explain why both parameters are needed. But first a small note on conventions. We have chosen to label the lowest order standing wave, i.e. the dipole mode, with \( n = 1 \) and a phase that would be \(-\pi\) in a standard Fabry-Perot cavity with two mirrors. This is in line with the usual definitions in optics. In solid state physics it is more common to have zero phase shift, e.g. in the case of an electron in a quantum well. The latter approach, that just corresponds to redefining \( \varphi \) by adding \( \pi \), is what was used in [48, 69, 124].

Returning to the parameters of Eq. (6.1): they are related in the sense that they can both alter the wavelength of a standing wave, and for a fixed ribbon width and plasmon wavelength, we can choose either a \( \Delta W \) or a \( \varphi \), or some combination of the two, that in all cases would describe the system correctly. However, when varying the width or the mode number, the two parameters can no longer be exchanged. In Fig. 6.1 is shown the difference between a ribbon of width \( W \) with a reflection phase of \(-3\pi/4\) (red) and a ribbon with \( \varphi = -\pi \) but \( \Delta W = W/3 \) (blue). The parameters are chosen such that the first order mode in both cases has the same wavelength, \( \lambda_1 = \frac{3W}{\pi} \) as can be seen in Fig. 6.1c. As we look at higher-order modes, the difference between the two becomes clear as the plasmon wavelength scales differently between the two. This is illustrated in Fig. 6.1a. In Fig. 6.1b we have defined the effective width of the ribbon as \( \frac{nL}{2} \). For the trivial reflection phase \((-\pi\) this simply evaluates as \( W + \Delta W \) as can be seen from the straight blue line. For the system with an anomalous reflection phase (red), the effective width becomes mode dependent and trends towards \( W \). We can also deduce this from panel c where at the \( n = 8 \) drawing only a tiny bit of the red wave breaks out of the ribbon. If instead of fixing the width and varying the mode, we had done the opposite, we would find that the effective width was constant for the non-trivial phase shift, while changed for the ribbons with a width correction.

Although the two parameters evidently are different, they do however have the same qualitative effect. Increasing the phase and adding a \( \Delta W \) both increase the effective width of the ribbon. This manifests itself in an anticorrelation between the two when
Figure 6.1: Comparison of the effect of width correction of $\Delta W = W/3$ (blue) and a phase shift of $\varphi = -3\pi/4$ (red). The parameters are chosen to give the same lowest order mode. a) The wavelength as a function of mode index. b) The effective width is constant with the width correction and trends towards $W$ for the non-trivial phase change. c) The standing waves for three different indices highlighting the differences at higher mode numbers.

Figure 6.2: Root-mean-square error of the energies of the 14 nm wide zigzag ribbon compared to the bulk dispersion model for various values of $\varphi$ and $\Delta W$. The two parameters are anticorrelated as can be seen from the shape of the potential landscape. Performing the fitting procedure. In Fig. 6.2 are shown the root-mean-square errors for a range of $\varphi$’s and $\Delta W$’s when optimizing the plasmon modes to the bulk dispersion in the $\sim$14 nm wide zigzag ribbon. The white cross indicates the optimal value. It can clearly be seen from the elongated shape of the contours that an increase in one parameter can be compensated by a decrease in the other to yield an almost as good fit. This explains how the plasmons in AC ribbons could be described by just one parameter set in the paper – in Fig. 5 in the paper, as $\varphi$ increases, $\Delta W$ decreases proportionally. More on that in the following.
6.1. ADDITIONAL INFORMATION AND FURTHER DISCUSSIONS ON PAPER II

Figure 6.3: The optimal $\varphi$ and $\Delta W$ values for each ribbon with the ribbon width shown in color corresponding to the legend in Fig. 3 of Paper II. Width is increasing from darker to lighter colors.

As a different view of the data, Fig. 6.3 shows the optimal $(\Delta W, \varphi)$ set for each width of the three different systems. While, in the armchair case, the points roughly follow a line consistent with the anticorrelation of the two parameters, the corresponding curve in the zigzag case makes a distinct bend that goes orthogonal to that direction. We can interpret this in the following way: For AC, the different results (points in Fig. 6.3) can be translated along the diagonal line that they fall on, and still give almost as good fits. The $(\Delta W, \varphi)$ pair found for a single ribbon thus has a high degree of uncertainty, but optimizing for all ribbons at the same time shows that a single parameter set is enough. This was also the conclusion of the Paper I, that one model works across the entire range of widths. For ZZ, on the other hand, something different is going on. Part of the curve runs perpendicular to the anticorrelation direction, and as was found in the paper, there is no single parameter set that satisfactorily describes the system.

To further support the need for the width correction in the model, in Fig. 6.4 are shown an equivalent to Fig. 5 in the paper, but in a model where $\Delta W = 0$ by design. As is most clearly seen in the insets, this model performs worse in all cases. This is no surprise, and will always be the case when removing free parameters from a model, but, except for the very widest ZZ ribbon, the width-correction-free model is unable to describe the low-$q$ plasmons properly for any of the ribbons. For the zigzag ribbons, where the widest structures have been calculated, we still find that the phase shift approaches $-\frac{3\pi}{4}$. This is in agreement with the notion that $\Delta W$ becomes less and less important as the wavelengths of the plasmons increase together with the ribbon width.

6.1.2 A $q$-dependent reflection

Calculating corrections as a function of the width, or the mode number as in Fig. 5.1 (p. 57), is only meaningful in relation to the ribbon, but we can try to deduce something more general from the calculations and lift the perspective out of the ribbon geometry. Graphene plasmons are known to reflect on a boundary with almost unchanged intensity [125, 126] and it is indeed these reflected waves that are measured in scanning near-field optical microscopy (SNOM) measurements [23, 24, 70, 71]. What
we seek is a $q$-dependent reflection and we can think of the ribbon geometries as a way of computationally probing various momenta. Unlike the width-dependent phase reflection, the $q$-dependent one allows us a free choice of the width correction by redefining the $\varphi$.

From the standing wave model (Eq. (6.1)) we isolate the phase change to find

$$\varphi(\tilde{q}) = -\tilde{q}(\Lambda + \Delta \Lambda) + (n - 1)\pi,$$

where $q = \tilde{q}k_F$ and we are using the dimensionless units introduced earlier in Sec. 3.2.3. As mentioned, it is possible to

$$\tilde{\varphi} = \varphi + \tilde{q}\Delta \Lambda$$

that just provides a shift, linear in $q$, if it is held constant. In Fig. 6.5 we see all the plasmon modes as a function of $\Lambda$ with a standing-wave model of the bulk dispersion in gray. The data is for $c_F = 0.4\text{eV}$. In the plot we have used a phase shift of $-3\pi/4$ and $\Delta \Lambda = k_F\Delta W$ and

$$\Delta W = \begin{cases} 
-0.4\text{nm} & \text{for AC,} \\
-0.3\text{nm} & \text{for ZZ, and} \\
+0.3\text{nm} & \text{for ZZ w/o edges.}
\end{cases}$$

These are the width-correction values calculated in Paper II, except for the one for AC ribbons that we have adjusted slightly from the $-0.3\text{nm}$ found in the paper.
6.1. ADDITIONAL INFORMATION AND FURTHER DISCUSSIONS ON PAPER II

Figure 6.5: Plasmon energies for various ribbons in TB (colors) compared to a standing-wave model using the nonlocal dispersion (following from Eq. (2.29)) and a reflection phase of $-3\pi/4$. Small width corrections are also included; see main text and Eq. (6.4).

modification results in an almost constant reflection phase in the analysis presented below.

The phase shift can be determined for each plasmonic mode individually from Eq. (6.2) by simple insertion of the relevant quantities and using the bulk-graphene plasmon dispersion as the link between the energy and the momentum. The resulting phases are displayed in Fig. 6.6 in the following way: In the top row, there is a line for each ribbon, colored according to the width (following the same scheme as in the paper (Fig. 3) and the above figures 6.3 and 6.4). Going from left to right, each point on such a line corresponds to higher and higher order modes. The faint, gray lines indicate the phase under the circumstance that $\varepsilon W = 0$. The bottom row shows the same data as the top, but in gray. The blue line (area) indicates a running average (standard deviation) with a window size of 1.

There is some scatter in the data in Fig. 6.6, although the hope was that the calculated $q$-dependent reflection phase would be independent of the ribbon widths. For AC and ZZ w/o edges, the phase shift is almost constant (especially for AC) and this is achieved through the adjustment of the included $\Delta W$ as mentioned below Eq. (6.4). Of course, as we try to analyze the system as the reflection on just a single edge, it should not be interpreted as a width correction, but as twice the value of the shift of the effective reflection edge. As concluded in the Paper II, ZZ edges are not as simply described and the reflection phase varies strongly with $q$. We have also included the $\Delta W$ found in the paper for ZZ, but in this case, it does not provide a simpler model (compared to the gray data points in the upper row) as is the case for the AC and the ZZ w/o edges. For wider ribbons in both ZZ calculations (with and without edges), the reflection phase increases, as can be seen in Fig. 6.6. This could be an indication that the scatter is caused at least partly by the quantization effects studied in Paper I and discussed in Chap. 5.
CHAPTER 6. EDGE-DEPENDENT REFLECTION AND INHERITED FINE STRUCTURE OF HIGHER-ORDER PLASMONS IN GRAPHENE NANORIBBONS (PAPER II)

Figure 6.6: Top: Predicted phase change for each plasmon calculated in the ribbons. Modes occurring in the same ribbon are connected and colored according to the ribbon width. Gray points and lines indicate the results when no width correction is included. Bottom: Same data as above, but including a running mean filter as well as the running standard deviation (blue). The phase is almost constant when there are no edge states in the calculations, while the ZZ ribbon has a large $q$-dependence.

6.1.3 Edge induced broadening

In Paper II, the edge-broadening effect of the edge states was demonstrated using calculations with $e_F = 0.8\,\text{eV}$. In Fig. 6.7 are shown the widths of the dipole plasmon peaks for systems where the Fermi energies are $0.4\,\text{eV}$ (squares). The same effect as was presented in the paper (Fig. 8) is seen – namely that the edge states give rise to peak broadening. By comparing the two figures, at first, it looks as if the scale invariance presented in Paper I also applies to this case: The onset of the broadening is around $8\,\text{nm}$ for $e_F = 0.4\,\text{eV}$ while it was $4\,\text{nm}$ for twice the Fermi energy in the paper. However, the energies do not follow the same pattern. In fact, multiplying the widths of the $e_F = 0.8\,\text{eV}$ ribbons by two while keeping the energy axis unchanged yields the faint, round points in Fig. 6.7 that almost exactly follow the same curve as the untransformed $0.4\,\text{eV}$ results. It would require more examination of this to give a satisfactory explanation.
6.1. ADDITIONAL INFORMATION AND FURTHER DISCUSSIONS ON PAPER II

Figure 6.7: Width of the plasmon peaks for the ribbons with $\epsilon_F = 0.4\text{eV}$ (squares) showing that the edge states introduce additional broadening of the peaks. In faint circles are shown the similar results for $\epsilon_F = 0.8\text{eV}$, but with the widths multiplied by a factor of two.

6.1.4 Spatial distribution of the plasmons

In the paper, focus is entirely placed on the bulk-like plasmonic modes that occur in all the ribbons. For at some of the ribbons, however, there are more modes appearing in the spectrum, and these will be briefly presented in the following. The novel modes are found at very high energies for the $\epsilon_F = 0.4\text{eV}$ ribbons used as the dataset in Paper II. For $\epsilon_F = 0.8\text{eV}$, the novel modes been observed in ribbons that are 5 nm or wider. The loss function and the real part of the eigenvalues of the dielectric matrix of such a 6 nm ZZ ribbon are shown in the top two panels of Fig. 6.8. The large peak of the dipole plasmon is clearly visible above the leftmost zero-point of the dielectric function. In contrast to the spectra shown previously, two distinct types of zero-points are seen for the higher order modes. One where the branch of the dielectric function seem to continue with the same slope, and one where it bends right next the zero-point. These have been labeled with a and b respectively. The b branches are also observed in most of the $\epsilon_F = 0.4\text{eV}$ ribbons, but without them crossing zero – this can e.g. be seen in Fig. 2 in the paper. The induced densities of the three a/b pairs in Fig. 6.8 seem to follow the usual standing wave picture with an additional node occurring every time. Between the a and b modes there are some subtle differences that are clearly seen in the sublattice split densities (gray full and dashed lines). As most easily seen in 2 and 3 the b mode has an additional large split between the sublattices just inside the edge, and the energy is always larger for the b mode. We have not analyzed these modes enough to say anything conclusively, but they may be related to the subsurface plasmons predicted in thin sodium slabs [118].

6.1.5 Summary and perspective

In Paper II, three main results were presented. We showed that the standing-wave model with the infinite-graphene dispersion relation works very well for AC ribbons
Figure 6.8: Loss function and real part of the eigenvalues of the dielectric matrix for a 6 nm wide zigzag ribbon with a Fermi energy of 0.8 eV. In the bottom are shown the induced charges of the modes marked with red circles – the "b"-modes marked with a lighter shade of red. Two distinct types of modes appear.
down two only a few nanometers wide. This was further strengthened in the additional analysis of $q$-dependent reflection phases, that showed a constant $q$ at the armchair edge, provided that the edge position was corrected with -0.2 nm ($-0.4\text{nm}/2$). For zigzag ribbon, it was found that the reflection did depend on $q$ fits together with the need for a width-dependent analysis in the paper.

The edge states in zigzag ribbons were demonstrated to be responsible for the additional broadening of the plasmon peaks compared to AC ribbons. This finding is in agreement with previous work [56, 64]. A very recent experimental paper by Duan et al. [71] looks at the plasmon reflection at armchair and zigzag edges. They find that the plasmons reflected at the zigzag edge is less damped than the ones reflected at the armchair edge. How this fits together with the theoretically predicted additional plasmon broadening is uncertain at the moment.

The final part presented in this chapter, is the shape of the plasmons, i.e. the spatial distribution of the induced charges. Paper II revealed how the electron wave function oscillations discussed in Chap. 3 are transferred to the plasmons’ shapes. In zigzag ribbons, the induced charges vary smoothly across the ribbon on each sublattice individually, and in armchair ribbons the smooth behavior follows every third atom. The effect in AC ribbons comes from the intervalley scattering introduced by the AC boundary conditions. We also mentioned a new type of plasmons, that do not correspond to the classical bulk-like plasmons, in the very end.
Chapter 7

Conclusion and Outlook

The field of plasmonics is vast and interesting, and graphene has rightfully received a lot of attention in this area. Among the abundance of plasmonic materials and structures, in this thesis we have focused entirely on the graphene nanoribbons, using insight from the Dirac model, the tight-binding method, and Density Functional Theory. It has proven very useful to utilize the analytically solvable Dirac model as a tool for understanding and interpreting numerical results. One of the places this manifested itself was in the fine-structure oscillations of the induced charges of the plasmons. From the Dirac analysis of the wave functions, we could understand the every-third-atom oscillation in armchair ribbons as a consequence of the valley-mixing boundary conditions. We also demonstrated how the Dirac model contained even more information than what was superficially apparent on the wave-function level.

In wide graphene ribbons, great agreement with the quantum mechanical tight-binding calculations of the plasmons was found by simply applying a classical scheme with a local, uniform conductivity, and hard boundary conditions. As we have shown in Chap. 5, this agreement does not persist when either the ribbons get too narrow, or the Fermi energy gets too low, as expressed through the dimensionless variable $\frac{\omega}{\gamma}$. In this nonclassical regime, we have demonstrated a large difference between the zigzag ribbon and the armchair ribbon – a contrast attributed to the localized electronic edge states that occur at the zigzag boundary. Besides the roles of nonlocality and the band structure differences between armchair and zigzag ribbons, we also find a strictly size-dependent effect in zigzag ribbons, making the scale invariance from the Dirac model an emerging behavior of the narrow ribbons.

Within the Dirac model, we have calculated a uniform, local conductivity of zigzag ribbons in the wide-ribbon limit as presented in Chap. 4. The expressions correctly converge towards the bulk limit, and the contribution from the edge states matches work done previously on graphene disks [64]. The analytically derived ribbon-conductivity predicts corrections due to size-quantization – the effect of having only a finite number
of bands crossing the Fermi level. We did not observe the same effect in the TB calculations where plasmons in ribbons in the $5 < \Lambda < 10$ range occur at the same energies as predicted by the standing-wave model with a local conductivity – as long as the ribbons are wider than $\sim 5 \text{nm}$.

In Chap. 6, we showed that the microscopic tight-binding calculations of higher-order plasmons can be understood by analogy of standing waves in a Fabry-Pérot cavity, if we allow for both a reflection phase and an effective width of the ribbon that slightly differs from the geometrical width. Remarkably, we found that plasmons in armchair ribbons as small as 2 nm, can be well described by a single width correction on a couple of Ångströms and a constant, non-trivial phase shift at the edge. We presented the importance of the edge states in narrow ribbons leading to a breakdown of the simple standing-wave model, where the reflection phase for zigzag ribbons was found to be width dependent in very narrow ribbons. In an approach meant to generalize the results, the reflection phase of a plasmon scattering on an edge was found to be dependent on the plasmon wavelength for zigzag edges, but independent for armchair edges.

Although the plasmon dispersion has been central to this work, especially in the standing-wave model, we have not considered the dispersion along the ribbon, but only the bulk form. The ribbon dispersion has been studied in the Dirac approximation previously [53, 57, 58], but to our knowledge, there have not been any calculations taking the edge details into account. The dipole plasmon should be localized at the edge, so one interesting future project could be to calculate the dispersion for the two ribbon types, to find any differences in the dispersion. This would then possibly be an optical probe of the atomic details at the edge. While I have focused on graphene ribbons in this thesis, it could be interesting to also study other two-dimensional materials – such as the recently synthesized borophene that exhibits strong anisotropy [127–129] – among other things to see if the reflection phase results apply to the same degree.
Starting from the general, non-local expression for the imaginary part of the dielectric function in two dimensions (spin-degeneracy is included):

\[
e_2(\mathbf{q}, \omega) = \frac{4\pi^2e^2}{q\omega} \sum_{ij} \left| \langle \psi_i | e^{i\mathbf{q}\mathbf{r}} | \psi_j \rangle \right|^2 \delta(\epsilon_i - \epsilon_j - \hbar\omega)(\mathbf{f}_j - \mathbf{f}_i),
\]

we define the Fermi-Dirac-distribution operator \( \hat{f} \), such that

\[
\hat{f} | i \rangle = f_i | i \rangle.
\]

Furthermore, we rewrite the delta function in terms of a time integral,

\[
\delta(\epsilon_i - \epsilon_j - \hbar\omega) = \int_{-\infty}^{\infty} dt e^{i(\epsilon_i - \epsilon_j - \hbar\omega)t}
\]

and remember that \( e^{Ht} | i \rangle = e^{\epsilon_i t} | i \rangle \). These considerations allow us to write

\[
e_2(\mathbf{q}, \omega) = \frac{4\pi^2e^2}{q\omega} \sum_{ij} \int dt e^{iHt} e^{i\mathbf{q}\mathbf{r}} e^{-iHt} | j \rangle \langle j | \left[ \hat{f}, e^{-i\mathbf{q}\mathbf{r}} \right] | i \rangle e^{-\hbar\omega t},
\]

and by using completeness, \( \sum_j | j \rangle \langle j | = 1 \),

\[
e_2(\mathbf{q}, \omega) = \frac{4\pi^2e^2}{q\omega} \sum_{ij} \int dt e^{iHt} e^{i\mathbf{q}\mathbf{r}} e^{-iHt} \left[ \hat{f}, e^{-i\mathbf{q}\mathbf{r}} \right] | i \rangle e^{-\hbar\omega t}.
\]

To evaluate the above expression, we want to know how the operator \( e^{i\mathbf{q}\mathbf{r}} \) works on an eigenstate of the system:

\[
e^{i\mathbf{q}\mathbf{r}} | k, s \rangle = \frac{1}{\sqrt{2}} e^{i(k\cdot\mathbf{q})r} \left( e^{i\theta_s/2} \right) \left( e^{-i\theta_s/2} \right).
\]
where \( s = \pm 1 \) indicates the conduction and valence bands, respectively. Obviously, it must be possible to write the state as a linear combination of the eigenstates. In particular of the states with momentum \( \mathbf{k} + \mathbf{q} \) in this case.

\[
e^{i\mathbf{q} \cdot \mathbf{r}} |\mathbf{k}, s\rangle = \alpha_+ |\mathbf{k} + \mathbf{q}, +\rangle + \alpha_- |\mathbf{k} + \mathbf{q}, -\rangle
\]

(A.7)

\[
e^{i\mathbf{k} \cdot \mathbf{r}} = \frac{1}{\sqrt{2}} e^{i\mathbf{k} \cdot \mathbf{r}} \left[ \alpha_+ \left( e^{i\theta_{kk'}^q/2} + e^{-i\theta_{kk'}^q/2} \right) + \alpha_- \left( e^{i\theta_{kk'}^q/2} - e^{-i\theta_{kk'}^q/2} \right) \right]
\]

Equating Equations (A.6) and (A.7) yields the result

(A.8)

\[
e^{i\mathbf{q} \cdot \mathbf{r}} |\mathbf{k}, s\rangle = \cos \left( \frac{\theta_{kk'}^q}{2} \right) |\mathbf{k} + \mathbf{q}, s\rangle - i \sin \left( \frac{\theta_{kk'}^q}{2} \right) |\mathbf{k} + \mathbf{q}, -s\rangle
\]

with \( \mathbf{k}' = \mathbf{k} + \mathbf{q} \) and \( \theta_{kk'}^q = \theta_k - \theta_{k'} \), and bold vector notation is sometimes not used where it probably ought to.

Now the steps left is mainly a matter of bookkeeping and utilizing the orthonormality of the states.

Looking at the matrix element in (A.5) we can see that the first operator \( e^{iHt} \) can just be applied to the bra and put outside as a factor \( e^{i\mathbf{c} \cdot \mathbf{l}} \). We’re left with

(A.9)

\[
\langle k, s | e^{i\mathbf{q} \cdot \mathbf{r} e^{-iHt}} \hat{f} e^{-i\mathbf{q} \cdot \mathbf{r}} |k, s\rangle
\]

(A.10)

\[
= \left( \langle k', s | \alpha - i \langle k', -s | \beta \rangle \right) e^{-iHt} \left( \hat{f} e^{-i\mathbf{q} \cdot \mathbf{r}} \langle k, s | - \hat{f} \langle k, s | \right)
\]

(A.11)

\[
= \left( \langle k', s | \alpha - i \langle k', -s | \beta \rangle \right) e^{-iHt} \left( \hat{f} \left( \alpha |k', s\rangle + i \beta |k', -s\rangle \right) \right)
\]

(A.12)

\[
e^{-\imath \gamma k' \mathbf{c}^2 \mathbf{f}_{k', s} + \imath \gamma k' \mathbf{c}^2 \mathbf{f}_{k', -s} - \mathbf{f}_{k, s} \left( e^{-\imath \gamma k' \mathbf{c}^2 \mathbf{f}_{k', s}^2} + e^{\imath \gamma k' \mathbf{c}^2 \mathbf{f}_{k', s}^2} \right)}
\]

(A.13)

\[
e^{-\imath \gamma k' \mathbf{c}^2 \mathbf{f}_{k', s} + \imath \gamma k' \mathbf{c}^2 \mathbf{f}_{k', -s} - \mathbf{f}_{k, s} \left( e^{-\imath \gamma k' \mathbf{c}^2 \mathbf{f}_{k', s}^2} + e^{\imath \gamma k' \mathbf{c}^2 \mathbf{f}_{k', s}^2} \right)}
\]

where we have used that \( H |\mathbf{k}, s\rangle = s\gamma k |\mathbf{k}, s\rangle \).

Inserting the matrix element at performing the time integral yields

(A.14)

\[
\epsilon_2(\mathbf{q}, \omega) = \frac{4\pi^2 e^2}{q^2 \mathcal{D}} \sum_{\mathbf{k}, s} \left[ \cos \left( \frac{\theta_{kk'}^q}{2} \right) \left( f_{k', s} - f_{k, s} \right) \delta(s\gamma(k - k') - \hbar\omega) + \sin \left( \frac{\theta_{kk'}^q}{2} \right) \left( f_{k', s} + f_{k, s} \right) \delta(s\gamma(k + k') - \hbar\omega) \right]
\]

and using the Kramers-Kronig relation with the real part of the dielectric function,

(A.15)

\[
\epsilon(\mathbf{q}, \omega) = 1 + \frac{4\pi e^2}{q^2 \mathcal{D}} \sum_{\mathbf{k}, s} \left[ \cos^2(\theta_{kk'}^q/2) \left( f_{k', s} - f_{k, s} \right) \frac{\sin^2(\theta_{kk'}^q/2)}{s\gamma(k - k') - \hbar(\omega + i\eta)} + \frac{\sin^2(\theta_{kk'}^q/2)}{s\gamma(k + k') - \hbar(\omega + i\eta)} \right]
\]

where the \( \eta - 0^+ \) limit is implicit. In the RPA, we can write the dielectric function as \( \epsilon = 1 - V_g \Pi \). Remembering that the 2D Coulomb interaction is \( 2\pi e^2/q \); using the relations
\[ \sin^2(\phi/2) = (1 - \cos \phi)/2 \] and \[ \cos^2(\phi/2) = (1 + \cos \phi)/2; \] and knowing the relation between the polarizability and the conductivity, \( \sigma = i e^2 \omega / q^2 \Pi \), we can find the conductivity as

\begin{equation}
\sigma(q, \omega) = \frac{g i e^2 \omega}{q^2 \omega^4} \sum_{s,s'} \frac{(1 + ss' \cos \theta_{kk'}) (f_{k',s'} - f_{k,s})}{\gamma (s k - s' k') - \hbar(\omega + i \eta)},
\end{equation}

where spin and valley degeneracy is hidden within the \( g \). This expression is directly relatable to Eq. (3) in Wunsch et al. [96] and Eq. (3) in Hwang and Das Sarma [97] where, in both cases, the polarizability is expressed.
Appendix

Local Conductivity in Bulk Graphene

Calculation of the local conductivity in bulk graphene

B.0.0.1 Intraband

The final equation from App. A is solved in [96, 97] and also referenced in the main text. We are interested in the local limit where \( q \to 0 \). It is clear that the angle between the \( \mathbf{k} \) and the \( \mathbf{q} \) vectors will be of importance. We denote it \( \varphi \) in the following. Let’s begin with intraband part where \( s = s' \). We look at the individual terms one by one:

\[
\begin{align*}
1 + ss' \cos \theta_{kk'} & \approx 2 - \frac{q^2 \sin^2 \varphi}{2k^2} + \ldots \\
\end{align*}
\]

\[(B.1)\]

\[
\begin{align*}
f_{k',s'} - f_{kk,ss} & \approx q \cos \varphi f^I_{kk,ss} + q^2 \cos^2 \varphi f^I_{kk,ss} + \ldots \\
\end{align*}
\]

\[(B.2)\]

and

\[
\begin{align*}
\frac{1}{s \gamma q \cos \varphi - \hbar (\omega + i \eta)} & \approx \frac{-1}{\hbar (\omega + i \eta)} - \frac{s \gamma q \cos \varphi}{\hbar^2 (\omega + i \eta)^2} + \ldots. \\
\end{align*}
\]

\[(B.3)\]

We change the sum to an integral over \( k \)-space

\[
\begin{align*}
\frac{1}{\omega f} \sum_k \to \frac{1}{4\pi^2} \int_{-\infty}^{\infty} \int_{-\pi}^{\pi} dk \, d\varphi \, k,
\end{align*}
\]

\[(B.4)\]

and begin the sorting out of all these terms. Let’s begin with the the combinations involving the first term in (B.3). All terms with \( q^n \) where \( n > 2 \) will go quickly to zero. The \( q \cos \varphi f^I_{kk,ss} \) term gives zero when the cosine is integrated over a full period. What is left is then \( q^2 \cos^2 \varphi f''_{kk,ss} / 2 \). Since the second derivative of the Fermi distribution is an odd function around the Fermi energy the integral over \( k \) will be zero in the limit of zero temperature. We continue by looking at the second term in Eq. (B.3).
APPENDIX B. LOCAL CONDUCTIVITY IN BULK GRAPHENE

The only term left using the same considerations as above is the one containing $s \gamma q^2 \cos^2 \varphi f'_{k,s}$.

$$\sigma_{\text{intra}}(q \to 0, \omega) = \frac{g \epsilon^2}{4 \pi q^2} \int_0^\infty d k \int_{-\pi}^\pi d \varphi k \frac{s \gamma q^2 \cos^2 \varphi f'_{k,s}}{\hbar^2(\omega + i \eta)^2} \tag{B.5}$$

$$= \frac{g \epsilon^2}{4 \pi \hbar^2(\omega + i \eta)^2} \int_0^\infty d k \gamma k f'_{k,s} \tag{B.6}$$

$$\approx \frac{g \epsilon^2 |\epsilon_F|}{4 \pi \hbar^2} \tag{B.7}$$

$$= \frac{i \epsilon^2 |\epsilon_F|}{\pi \hbar^2(\omega + i \eta)} \tag{B.8}$$

where the penultimate equality is valid at zero temperature when the derivative of the Fermi distribution becomes a delta function at the Fermi energy; and $\eta$ has been rescaled with a factor of 2.

B.0.0.2 Interband

The interband term is easily calculated by first doing the sum over $s$ and then taking the second order expansion of the cosine term and zeroth order of the other terms. The step functions arise at the zero temperature limit.

$$\sigma_{\text{inter}}(q, \omega) = -\frac{g \epsilon^2}{q^2 \omega} \sum_k (1 - \cos \theta_{kk}) \left[ \frac{f_{k'\downarrow} - f_{k\uparrow}}{\gamma(k + k') - \hbar(\omega + i \eta)} + \frac{f_{k'\uparrow} - f_{k\downarrow}}{-\gamma(k + k') - \hbar(\omega + i \eta)} \right] \tag{B.9}$$

$$\approx -\frac{g \epsilon^2}{q^2 \omega} \sum_k \left(1 - \left(1 - \frac{q^2 \sin^2 \varphi}{2 k^2}\right)\right) \left[ \frac{\Theta(k - k_F)}{2 \gamma k - \hbar(\omega + i \eta)} + \frac{-\Theta(k - k_F)}{-2 \gamma k - \hbar(\omega + i \eta)} \right] \tag{B.10}$$

$$= -\frac{g \epsilon^2 \pi}{2(2\pi)^2} \int_{k_F}^\infty \frac{d k}{k} \left[ \frac{1}{2 \gamma k - \hbar(\omega + i \eta)} - \frac{1}{-2 \gamma k - \hbar(\omega + i \eta)} \right] \tag{B.11}.$$
C.1 Eigenstates for zigzag ribbons

We want to find a simple expression for the eigenstates in the zigzag case, given the boundary conditions. From the general expression (Eq. (3.3)) and the $A = -B$ demand from one of the BCs, we find that

$$\phi^A(x) = Ce^{ik_y \sinh(zx)},$$  \hspace{1cm} (C.1)

with $C$ as the proper normalization constant and the exponential factor as a consequence of Bloch’s Theorem. From the Hamiltonian in Eq. (2.17), we easily realize the relation

$$\phi^B(x) = \frac{1}{\epsilon} (i\partial_x - ik_y)\phi^A(x).$$  \hspace{1cm} (C.2)

Simply inserting in the expression yields

$$\phi^B(x) = \frac{ie^{ik_y \sinh(zx)}}{s\sqrt{k_y^2 - z^2}} (z \cosh(zx) - k_y \sinh(zx))$$  \hspace{1cm} (C.3)

$$= \frac{-isCe^{ik_y \sinh(zx)}}{2\sqrt{k_y^2 - z^2}} \left(ze^{2x} + ze^{-2x} - (k_y e^{2x} - k_y e^{-2x})\right)$$  \hspace{1cm} (C.4)

$$= \frac{-isCe^{ik_y \sinh(zx)}}{2(z - k_y)(k_y + z)} \left((z - k_y)e^{2x} + (z + k_y)e^{-2x}\right).$$  \hspace{1cm} (C.5)

Rewriting Eq. (3.5) in the form $(k_y - z) = (k_y + z)e^{-2Wz}$ we can rewrite the square-root part as

$$\frac{1}{\sqrt{(k_y - z)(k_y + z)}} = \frac{e^{Wz}}{k_y + z} = \frac{e^{-Wz}}{k_y - z}.$$  \hspace{1cm} (C.6)
Utilizing these two forms results in

\[
\phi^R(x) = \frac{-i\sigma C e^{ik_y y}}{2} \left( e^{(x-W)x} + e^{-(x-W)x} \right) \\
\psi_{n,s,k_y} = Ce^{ik_y y} \left( i\sigma \sinh(x z_n) \right) \left( \sinh((W-x)z_n) \right),
\]

where both solutions have been multiplied by the phase factor \(i\sigma\) to get to a form similar to Brey and Fertig [53] in the last step.

The normalization constants are derived in the following where \(z_n = k\) is a real number for the surface states, and \(z_n = -ik_n\) gives rise to the bulk states.

Surface state:

\[
\int_0^W dx \|\phi(x)\|^2 = \int_0^W dx C_s^2 \left( \sinh^2(x k) + \sinh^2((W-x)k) \right) \\
= -C_s^2 \left( W - \frac{\sin(2kW)}{2k} \right) = 1 \Rightarrow \\
C_s^2 = -\frac{2k}{2kW - \sin(2kW)} \\
= -\frac{2k}{2kW - \frac{2k}{e_s^2}} = -\frac{1}{W - \frac{k}{e_s^2}} \\
= \frac{\tilde{e}_s^2}{k_y - \tilde{e}_s^2 W} \\
\]

Bulk state:

\[
\int_0^W dx \|\psi(x)\|^2 = \int_0^W dx C_b^2 \left( \sin^2(x k_n) + \sin^2((W-x)k_n) \right) \\
= C_b^2 \left( W - \frac{\sin(2k_n W)}{2k_n} \right) = 1 \Rightarrow \\
C_b^2 = \frac{2k_n}{2k_n W - \sin(2k_n W)} \\
= \frac{2k_n}{2k_n W - \frac{2k_n}{e_n^2}} = \frac{1}{W - \frac{k}{e_n^2}} \\
= \frac{\tilde{e}_n^2}{W - k_y} \\
\]

### C.2 Conductivity contributions

The full expression for the conductivity in the x-polarized local-response approximation is (as given in Eq. (4.2))

\[
\sigma(\omega) = \frac{2\epsilon n^2 \omega}{\omega^2} \sum_{i,j} |f_i - f_j| \frac{|\langle \psi_i | x | \psi_j \rangle|^2}{\epsilon_i - \epsilon_j - \hbar(\omega + i\eta)}.
\]
As there are two different kinds of states, the bulk and the surface state, the conductivity can be split in three contributions. One involving only bulk states, $|\langle \psi_i | x | \psi_j \rangle|^2$, one with surface states only, $|\langle \phi_i | x | \phi_j \rangle|^2$, and one with the interaction between bulk and surface $|\langle \psi_i | x | \phi_j \rangle|^2 + |\langle \phi_j | x | \psi_i \rangle|^2$.

The terms including only bulk states will converge towards the infinite graphene sheet result, while the surface-surface terms will give zero contributions due to their identical fermi-distributions. Thus, we are interested in the cross terms, simplified below with $|i\rangle \langle j|$ representing bulk (surface) states.

\[
\sigma_{\text{B}}(\omega) \propto \sum_{i,j} \left( f_{i,j} \frac{|\langle i | x | j \rangle|^2}{\epsilon_{i,j} - \tilde{\omega}} + f_{j,i} \frac{|\langle j | x | i \rangle|^2}{\epsilon_{j,i} - \tilde{\omega}} \right)
\]

\[
\sigma_{\text{S}}(\omega) \propto \sum_{i,j} \left( f_{i,j} \frac{|\langle i | x | j \rangle|^2}{\epsilon_{i,j} - \tilde{\omega}} - f_{j,i} \frac{|\langle j | x | i \rangle|^2}{\epsilon_{j,i} - \tilde{\omega}} \right)
\]

\[
\sigma_{\text{IS}}(\omega) \propto \sum_{i,j} \left( f_{i,j} \frac{|\langle i | x | j \rangle|^2 (\epsilon_{i,j} - \tilde{\omega}) - (\epsilon_{j,i} - \tilde{\omega})}{\epsilon_{i,j} - \tilde{\omega} \epsilon_{j,i} - \tilde{\omega}} \right)
\]

Finally, we arrive at the simple expression for the edge contribution to the conductivity

\[
\sigma_{\text{E}}(\omega) = \frac{4ie^2}{\pi A} \sum_{i,j} f_{i,j} \frac{\epsilon_{i,j} |\langle \psi_i | x | \phi_j \rangle|^2}{\epsilon_{i,j}^2 - \hbar^2 \left( \omega + i\eta \right)^2}
\]

### C.3 Intraband

We need the derivative of the band with respect to $k_y$: Since the relation determining the allowed $k$-values is given by $k_y = k_n/\tan(k_n W)$, we find

\[
\frac{\partial k_n}{\partial k_y} = \left( \frac{\partial k_y}{\partial k_n} \right)^{-1} = \frac{-\sin(k_n W)}{k_n W - \cos(k_n W)}
\]

\[
\frac{\partial k_n}{\partial k_y} = \frac{-k_n}{\epsilon_n^2 W - k_y}
\]

In the expression for the conductivity, besides the matrix element just calculated, are also the difference between the two Fermi functions and between the energies. It is therefore necessary to calculate how these terms will behave in the small $q$ limit. Let
us begin with the energy:

\[ \epsilon_n - \epsilon_m = \hbar v_F \left[ \sqrt{k_n^2 + k_y^2} - \sqrt{\left(k_n + q_y \frac{k_n}{\epsilon_n^2 W - k_y}\right)^2 + (k_y - q_y)^2} \right] \]

\[ \approx \hbar v_F \left[ -q_y \frac{k_n}{\epsilon_n^2 W - k_y} - k_y \right] \]

\[ = \hbar v_F q_y \frac{\tilde{\epsilon}_n(k_y W - 1)}{\epsilon_n^2 W - k_y} \]

and following the same approach for the Fermi distributions leads to

\[ f_n - f_m = \delta(k_f - \tilde{\epsilon}_n) q_y \frac{\tilde{\epsilon}_n(k_y W - 1)}{\epsilon_n^2 W - k_y}. \]  

(C.29)

The energies are a part of a denominator that we will also expand:

\[ \frac{1}{\epsilon_n - \epsilon_m - \hbar(\omega + i\eta)} \approx \frac{1}{\hbar(\omega + i\eta)} + \frac{q_y \hbar v_F}{\hbar^2(\omega + i\eta)^2} \frac{\tilde{\epsilon}_n(k_y W - 1)}{\epsilon_n^2 W - k_y}. \]  

(C.30)

Combining all of these expressions, we arrive at the not very pleasing

\[ \sigma_{\text{intra}}(\omega) = \frac{i e^2 \omega}{\pi W q_y^2} \sum n \int dk_y \left( -\frac{1}{\hbar(\omega + i\eta)} + \frac{q_y \hbar v_F}{\hbar^2(\omega + i\eta)^2} \frac{\tilde{\epsilon}_n(k_y W - 1)}{\epsilon_n^2 W - k_y} \right) \delta(k_f - \tilde{\epsilon}_n) q_y \frac{\tilde{\epsilon}_n(k_y W - 1)}{\epsilon_n^2 W - k_y}. \]

As seen, the delta function is in \( \tilde{\epsilon}_n \) while the integral is over \( k_y \). This situation is handled by utilizing that

\[ \int_{-\infty}^{\infty} dk_y \delta(k_f - k) = \sum_j \left| \frac{\partial k}{\partial k_y} \right|_{k_y = k_j}^{-1}, \]

(C.32)

such that \( k(k_j) = k_F \). It is straightforward to find the derivative of \( k \):

\[ \frac{\partial k}{\partial k_y} = \frac{1}{2\tilde{\epsilon}_n} \left( \partial_{k_y} k_n^2 + 2k_y \right) \]

\[ = \frac{1}{2\tilde{\epsilon}_n} \left( \frac{-2k_n^2}{\epsilon_n^2 W - k_y} + 2k_y \right) \]

\[ = \tilde{\epsilon}_n \frac{(k_y W - 1)}{\epsilon_n^2 W - k_y}, \]  

(C.33)

(C.34)

(C.35)

which when inserted in the previous expression results in

\[ \sigma_{\text{intra}}(\omega) = \frac{i e^2 \omega}{\pi W q_y^2} \sum n \left( -\frac{\text{sign}(k_y^{(i)} - 1/W)}{\hbar(\omega + i\eta)} + \frac{q_y \hbar v_F}{\hbar^2(\omega + i\eta)^2} \frac{(\epsilon_n^{(i)} W - 1)}{k_F^2 W - k_y^{(i)}} \right) q_y, \]

(C.36)
where the sum is over allowed points on the Fermi surface. The first term in the sum will vanish due to symmetry with the other $K$-valley. Finally

\begin{equation}
\sigma_{\text{intra}}(\omega) = \frac{ie^2\omega}{\pi W} \frac{\epsilon_\text{F}}{\hbar^2(\omega + i\eta)^2} \sum_i \left| \frac{k_y^{(i)} W - 1}{\epsilon_\text{F}^2 W - k_y^{(i)}} \right|.
\end{equation}

Looking at the asymptotic limit we find

\begin{equation}
\sigma_{\text{intra}}(\omega) = \frac{ie^2\omega}{\pi W} \frac{\hbar \epsilon_\text{F}}{\hbar^2(\omega + i\eta)^2} \sum_i \frac{k_y^{(i)}}{k_y}.
\end{equation}

\begin{equation}
\approx \frac{2ie^2\omega \hbar \epsilon_\text{F}}{\pi \hbar^2(\omega + i\eta)^2} \left( k_y W / \pi - \frac{1}{2W} \right)
\end{equation}

\begin{equation}
\approx \frac{i e^2 \epsilon_\text{F}}{2 \pi \hbar^2(\omega + i\eta)} \left( 1 - \frac{2}{k_y} \right),
\end{equation}

where we have used the result from the similar sum in the interband section and redefined $\eta$ to its usual form. The width-independent term can be recognized as the infinite graphene result, save a factor of 2 since we haven’t included valley degeneracy.

### C.4 Interband

We employ the local-conductivity expression and calculate the matrix element:

\begin{equation}
|M_{nn}|^2 = \left| \langle n, k_y, s' | x | n, k_y, s \rangle \right|^2
= \left( \frac{e^2}{\hbar^2} \frac{k_y(W - \sin(2k_n W) + \cos(2k_n W) - 1)}{(\epsilon_\text{F}^2 W - k_y) 4k_n^2} \right)^2.
\end{equation}

Since

\[\sin(2k_n W) = 2 \sin(k_n W) \cos(k_n W) = 2k_n k_y / \epsilon_n^2 \quad \text{and} \]
\[\cos(2k_n W) - 1 = -2 \sin^2(k_n W) = -2k_n^2 / \epsilon_n^2\]

we can rewrite the expression to

\begin{equation}
|M_{nn}|^2 = \frac{1}{4} \left( \frac{k_y W - 1}{\epsilon_n^2 W - k_y} \right)^2.
\end{equation}

Looking at the general expression for the conductivity

\begin{equation}
\sigma(\omega) = \frac{2ie^2\omega}{\omega} \sum_{ij} \frac{f_{ij}}{\epsilon_{ij} - \hbar(\omega + i\eta)} |M|^2
\end{equation}

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we can make some simplifications in the case we’re interested in. Since we are only allowing vertical transitions between bands with the same index and we assume zero temperature the sum over pairs of states is going to be just a sum over unoccupied states and the corresponding filled ones. Additionally, the \( k_y \) direction is infinite and we can rewrite the sum to an integral. The final expression for the interband conductivity is given by

\[
\sigma_{\text{inter}}(\omega) = \frac{ie^2 \omega}{4\pi W} \sum_n \int dk_y \left( \frac{k_y W - 1}{\varepsilon_n^2 W - k_y} \right)^2 \left[ \frac{1}{-2\varepsilon_n - \hbar(\omega + i\eta)} - \frac{1}{2\varepsilon_n - \hbar(\omega + i\eta)} \right],
\]

where the sum and the integral is over unoccupied states, \( i.e. \) where \( \varepsilon_n > \varepsilon_F \).

In the asymptotic limit of infinitely wide ribbons the matrix element can be expanded to

\[
|M|^2 \approx \frac{k_y^2}{\varepsilon_n^4} + \frac{2(k^2 - k_y \varepsilon_n^2)}{W \varepsilon_n^6} + \frac{3k^4 - 4k_y^2 \varepsilon_n^2 + \varepsilon_n^4}{W^2 \varepsilon_n^6}.
\]

Keeping only the width-independent term, the expression reduces to

\[
\sigma_{\text{inter}}^{\infty}(\omega) = \frac{ie^2 \omega}{8\pi^2} \int_{k > k_F} d^2k \left( \frac{k_y^2}{\varepsilon_n^2} \right)^2 \left[ \frac{1}{-2\varepsilon_n - \hbar(\omega + i\eta)} - \frac{1}{2\varepsilon_n - \hbar(\omega + i\eta)} \right]
\]

\[
= \frac{ie^2 \omega}{8\pi} \int_{k_F}^{\infty} dk \int_0^{2\pi} d\theta \frac{\sin^2 \theta}{k^2} \left[ \frac{1}{-2\varepsilon_n - \hbar(\omega + i\eta)} - \frac{1}{2\varepsilon_n - \hbar(\omega + i\eta)} \right]
\]

\[
= \frac{ie^2 \omega}{8\pi} \int_{k_F}^{\infty} \frac{1}{k} \left[ -2\varepsilon_n - \hbar(\omega + i\eta) - 2\varepsilon_n - \hbar(\omega + i\eta) \right]
\]

\[
= \frac{e^2}{8\hbar} \left[ \frac{i}{\pi} \ln \left( \frac{2\varepsilon_F - \hbar \omega}{2\varepsilon_F + \hbar \omega} \right) + \Theta(\hbar \omega - 2\varepsilon_F) \right].
\]

Looking at the next order terms in the width, the \( 1/W \) part will integrate to zero. This is clear when changing to polar coordinates where \( k_y/k = \sin \theta \) and they all are raised to an odd power. The \( 1/W^2 \) should, however, contribute.

The result from the angle integration is

\[
\int_0^{2\pi} d\theta \left( 3\sin^4 \theta - 4\sin^2 \theta + 1 \right) = \frac{3\pi}{4} - 4\pi + 2\pi
\]

\[
= \frac{\pi}{4}.
\]

The remaining part of the integration is of the form

\[
\int_{k_F}^{\infty} \frac{1}{k^3} \left[ \frac{1}{k - a} - \frac{1}{k + a} \right].
\]

The final result is

\[
\sigma^{(2)}(\omega) = \frac{e^2 \omega}{64W^2k_F^2 \varepsilon_F} \left[ \frac{8ie_F^2}{\pi \hbar^2 \omega^2} \left( 1 - \frac{\varepsilon_F}{\hbar \omega} \ln \left( \frac{2\varepsilon_F - \hbar \omega}{2\varepsilon_F + \hbar \omega} \right) + \Theta(\hbar \omega - 2\varepsilon_F) \right) \right].
\]
Written in dimensionless units, we have

\[
\hat{\sigma}^{(0)}(v) = \frac{1}{2} \left[ i \frac{1}{n} \ln \left| \frac{2-v}{2+v} \right| + \Theta(v-2) \right]
\]

\[
\hat{\sigma}^{(2)}(v) = \frac{v}{16\Lambda^2} \left[ \frac{8i}{\pi v^2} \left( 1 - \frac{1}{v} \ln \left| \frac{2-v}{2+v} \right| \right) + \Theta(v-2) \right].
\]

However, there is another correction coming from the sum over states in the \(k_x\) direction. We will see this by more carefully converting the sum into an integral by using delta functions.

\[
\sigma_{\text{inter}}(\omega) = \frac{i e^2 \omega}{4\pi W} \sum_n \int \frac{dk_y}{2\pi} \left\{ \frac{k_y^2}{\epsilon_n^2} \right\} \int \frac{dk_x}{2\pi} \frac{\delta(k_x - k_n)}{2\pi} \left[ \frac{1}{-2\epsilon_n - \hbar\omega} - \frac{1}{2\epsilon_n - \hbar\omega^+} \right] - \frac{1}{2\epsilon_n - \hbar\omega^+}
\]

\[
= \frac{C}{W} \sum_n \int \frac{dk}{k_F} \delta(k x - k_n) \int \frac{d\theta}{2\pi} \sin \theta \left[ \frac{1}{-2\epsilon_n - \hbar\omega} - \frac{1}{2\epsilon_n - \hbar\omega^+} \right] \sin^2 \theta_i \frac{1}{2\epsilon_n - \hbar\omega^+}
\]

where \(k_n\) in the limit of wide ribbons becomes equidistant:

\[
= \frac{C}{W} \sum_n \int \frac{dk}{k_F} \frac{1}{k} \sum_i \frac{1}{k - \sin \theta_i} \sin^2 \theta_i \left[ \frac{1}{-2\epsilon_n - \hbar\omega} - \frac{1}{2\epsilon_n - \hbar\omega^+} \right] \frac{1}{2\epsilon_n - \hbar\omega^+}
\]

where \(\theta_i\) fulfills \(\cos \theta_i = n \pi / k W\), giving rise to

\[
= \frac{C}{W} \int \frac{dk}{k_F} \sum_{n=1}^{\infty} \frac{2}{k^2} \sqrt{1 - \left( \frac{n \pi}{k W} \right)^2} \left[ \frac{1}{-2\epsilon_n - \hbar\omega^+} - \frac{1}{2\epsilon_n - \hbar\omega^+} \right].
\]

In the infinite limit, the sum over \(n\) can be turned into an integral and we will recover the pristine graphene result from above.

Using the from Sec. D.1 expression for the conductivity leads to

\[
\frac{1}{W} \sum_{n=1}^{k W/\pi} \sqrt{1 - \left( \frac{n \pi}{k W} \right)^2} \approx \frac{k}{4} - \frac{1}{2W}
\]

for large values of \(k W/\pi\).

As we already have found the result using the first term, we focus our attention on the width-dependent correction term

\[
\sigma_{\text{inter}}^{(1)}(\omega) = -\frac{i e^2 \omega}{4\pi W} \int \frac{dk}{k_F} \frac{1}{k^2} \left[ \frac{1}{-2\epsilon_n - \hbar\omega^+} - \frac{1}{2\epsilon_n - \hbar\omega^+} \right] + \Theta(h\omega - 2\epsilon_F),
\]

resembling the expression from the edge-bulk interaction. The final expression is

\[
\sigma_{\text{inter}}^{(1)}(\omega) = -\frac{i e^2 v_F}{2\pi \hbar \omega W} \left[ \ln \left( \frac{(2 \epsilon_F)^2 - \hbar^2 \omega^2}{(2 \epsilon_F)^2} \right) - i \pi \Theta(h\omega - 2\epsilon_F) \right]
\]
APPENDIX C. DETAILS OF THE RIBBON CONDUCTIVITY DERIVATIONS

C.5 Edge-bulk

The edge-bulk interaction is interesting because it adds a new contribution that does not exist in the infinite case. Following the same lines as in the previous cases, it is pretty straightforward to calculate. The overlap integral, where we have already taken care of the delta function in the $k_y$ direction, is expressed by

$$|M_n|^2 = |\langle n, k_y, s' | x | k_y, s \rangle|^2$$

$$= \left| C_{n,k_y,s'}^* C_{k_y,s} \right|^2 \int_0^W \langle x | \hat{\psi}_{n,k_y,s'} \hat{\psi}_{k_y,s} \rangle^2 dx,$$

and we will begin by looking at the integral, $\mathcal{F}$.

The integrand of $\mathcal{F}$ when written out is

$$x(ss' \sinh(xx) \sin(xk_n)) + \sinh[(W-x)x] \sin((W-x)k_n),$$

and integrating this expression over $x$ from 0 to $W$ we find

$$\mathcal{F} = (\kappa^2 + k_n^2)^2 \left\{ 2 - 2ss' \right\} \kappa k_n$$

$$+ \kappa \cosh(kW) \left\{ (2ss' - 2)k_n \cos(k_nW) + ss'(\kappa^2 + k_n^2)W \sin(k_nW) \right\}$$

$$- \sinh(kW) \left\{ ss' k_n (\kappa^2 + k_n^2)W \cos(k_nW) + (ss' - 1)(\kappa^2 - k_n^2) \sin(k_nW) \right\},$$

which, by substitution of the trigonometric functions, can be rewritten as

$$\mathcal{F} = (\kappa^2 + k_n^2)^2 \left\{ 2 \kappa k_n (1 - ss') + \frac{\kappa k_n k_y}{\varepsilon_s} \left( 2 \frac{k_n k_y}{\varepsilon_s} (ss' - 1) + ss'(\kappa^2 + k_n^2)W \frac{k_n}{\varepsilon_n} \right) \right\}$$

$$- \frac{\kappa}{\varepsilon_s} \left\{ ss' \frac{k_n k_y}{\varepsilon_n} (\kappa^2 + k_n^2)W + \frac{k_n}{\varepsilon_n} (ss' - 1)(\kappa^2 - k_n^2) \right\} \right\}$$

$$= 2 \kappa k_n (1 - ss') + 2 \frac{\kappa k_n k_y}{\varepsilon_s} \left( ss' - 1 \right) + \frac{\kappa k_n}{\varepsilon_n} (ss' - 1)(\kappa^2 - k_n^2)$$

$$\frac{(\kappa^2 + k_n^2)^2}{\varepsilon_n \varepsilon_s (\kappa^2 + k_n^2)^2}$$

$$\frac{(ss' - 1)kk_n \left[ 2\kappa^2 - (\kappa^2 - k_n^2)^2 - 2\varepsilon_n \varepsilon_s \right]}{\varepsilon_n \varepsilon_s (\kappa^2 + k_n^2)^2}$$

$$\frac{(ss' - 1)k k_n \left[ \varepsilon_n^2 + \varepsilon_s^2 - \varepsilon_n \varepsilon_s \right]}{\varepsilon_n \varepsilon_s (\kappa^2 + k_n^2)^2}$$

$$\frac{(ss' - 1)k k_n \left( \varepsilon_n^2 - \varepsilon_s^2 \right)}{\varepsilon_n \varepsilon_s (\kappa^2 + k_n^2)^2}$$

$$\frac{(ss' - 1)k k_n \left( \varepsilon_n - \varepsilon_s \right)^2}{\varepsilon_n \varepsilon_s (\kappa^2 + k_n^2)^2}.$$
Inserting the normalization constants found in Appendix C.1 yields
\[ |M_n|^2 = |C_s C_b \mathcal{F}|^2 \]
\[ = \frac{-\tilde{\epsilon}_s^2}{\tilde{\epsilon}_s^2 W - k_x \tilde{\epsilon}_n^2 W - k_y} \left| -2\kappa k_n \right|^2 \]
\[ = \frac{-4\kappa^2 k_n^2}{(\tilde{\epsilon}_s^2 W - k_x)(\tilde{\epsilon}_n^2 W - k_y)(\tilde{\epsilon}_n + \tilde{\epsilon}_s)^4}, \]
which provides us with the expression for the edge contribution to the conductivity:
\[ \sigma_{\text{edge}}(\omega) = -\frac{2i e^2 \omega}{\pi W} \sum_n \int dk Y \frac{(\epsilon_n - \epsilon_s)}{(\epsilon_n - \epsilon_s)^2 - \hbar^2 (\omega + i\eta)^2 (\tilde{\epsilon}_s^2 W - k_y)(\tilde{\epsilon}_n^2 W - k_y)(\tilde{\epsilon}_n + \tilde{\epsilon}_s)^4}. \]

The sum and integral are limited by the demand that the bulk states must be unoccupied and the edge states occupied.

In the limit of very wide ribbons, where \( \kappa \to k_y \) and \( \epsilon_s \to 0 \) exponentially fast, and \( \tilde{\epsilon}_s^2 W \gg k_y \), we find that
\[ \sigma_{\text{edge}}(\omega) = -\frac{8i e^2 \omega}{\pi W k_F} \sum_n \int dk Y \frac{h v_F}{\epsilon_n^2 - \hbar^2 (\omega + i\eta)^2 \epsilon_n^2} \frac{k_y k_n^2}{\tilde{\epsilon}_n^2 W} \]
\[ \overset{C.65}{=} -\frac{2i e^2 \omega}{\pi^2 W k_F} \int_0^\infty dk Y \int_0^{\pi} d\theta \frac{\sin \theta \cos^2 \theta}{k^2} \left[ \frac{1}{\epsilon_n - \hbar (\omega + i\eta)} + \frac{1}{\epsilon_n + \hbar (\omega + i\eta)} \right] \]
\[ \overset{C.66}{=} \frac{4 e^2 v_F}{3\pi \hbar \omega W} \left[ \frac{i}{\pi} \ln \left| \frac{\epsilon_F^2 - \hbar^2 \omega^2}{\epsilon_F^2} \right| + \Theta(\hbar \omega - \epsilon_F) \right]. \]

The details of solving the integral is shown in App. D.3.
D.1 Summation of states at the Fermi circle

\[ \sum_{n=0}^{N} \sqrt{1 - \frac{n^2}{N^2}} \]

Looking in detail at the sum, we will compare it to the trapezoidal sum rule for the corresponding integral. We define the function \( f(x) = \sqrt{1 - \frac{x^2}{N^2}} \) and write

\[ \int_{0}^{N} dx f(x) \approx I_N \]
\[ = \frac{1}{N} \left[ \frac{1}{2} f_0 + f_1 + f_2 + \cdots + f_{N-1} + \frac{1}{2} f_N \right], \]

with \( f_n = f(n) \). The sum, on the other hand, can be written as

\[ \frac{1}{N} \sum_{n=1}^{N} f(n) = S_N \]
\[ = \frac{1}{N} [f_1 + f_2 + \cdots + f_{N-1} + f_N]. \]

Since \( f_N = 0 \) equating the two expression yields

\[ S_N = I_N - \frac{f_0}{2N} = \frac{\pi}{4} - \frac{1}{2N}, \]

where we have taken the \( N \to \infty \) limit of \( I_N \).

To be more thorough, there should also be an error term included in the expression for \( I_N \). However, as the asymptotic error estimate for a trapezoidal sum scales as \( N^{-2} f' \propto N^{-3/2} \) this correction will be of lower order than the one already found.
D.2 Rewriting the sum over states

The full expression for the conductivity in the x-polarized local-response approximation is

$$\sigma(\omega) = \frac{2ie^2\omega}{a^2} \sum_{i,j} \left\{ f_i - f_j \right\} \frac{|\langle \psi_i | x | \psi_j \rangle|^2}{\epsilon_i - \epsilon_j - \hbar(\omega + i\eta)}.$$  \hspace{1cm} (D.2)

As there are two different kinds of states, the bulk and the edge state, the conductivity can be split in three contributions. One involving only bulk states, $|\langle \psi_i | x | \psi_j \rangle|^2$, one with edge states only, $|\langle \phi_i | x | \phi_j \rangle|^2$, and one with the interaction between bulk and edge $|\langle \psi_i | x | \phi_j \rangle|^2 + |\langle \phi_j | x | \psi_i \rangle|^2$.

The terms including only bulk states will converge towards the infinite graphene sheet result, while the edge-edge terms will give zero contributions due to their identical Fermi distributions. Thus, we are interested in the cross terms, simplified below with $|i \rangle (|j\rangle)$ representing bulk (edge) states.

$$\sigma_E(\omega) \propto \sum_{i,j} \left\{ f_{i,j} \right\} \frac{|\langle i | x | j \rangle|^2}{\epsilon_{i,j} - \omega} + f_{j,i} \frac{|\langle j | x | i \rangle|^2}{\epsilon_{j,i} - \omega}$$  \hspace{1cm} (D.3)

$$\propto \sum_{i,j} f_{i,j} \left( \frac{|\langle i | x | j \rangle|^2}{\epsilon_{i,j} - \omega} - \frac{|\langle j | x | i \rangle|^2}{\epsilon_{j,i} - \omega} \right)$$  \hspace{1cm} (D.4)

$$\propto \sum_{i,j} f_{i,j} \frac{|\langle i | x | j \rangle|^2((-\epsilon_{i,j} - \omega) - (\epsilon_{i,j} - \omega))}{(\epsilon_{i,j} - \omega)(-\epsilon_{i,j} - \omega)}$$  \hspace{1cm} (D.5)

Finally, we arrive at a simple expression for the edge contribution to the conductivity

$$\sigma_E(\omega) = \frac{4ie^2\omega}{a^2} \sum_{i,j} f_{i,j} \frac{\epsilon_{i,j}}{\epsilon_{i,j} - h^2(\omega + i\eta)} |\langle \psi_i | x | \phi_j \rangle|^2.$$  \hspace{1cm} (D.7)

D.3 Integrals

D.3.1

Integral in the calculation of the interband conductivity for infinite graphene. Partial fractions are used. This is a bit sloppy: the Cauchy Principal Value should be taken properly to get the absolute value of the argument to the logarithm as written below.
This maneuver is done correctly in one of the later integrals in this appendix.

(D.8) \[ P \int_{k_F}^{\infty} \frac{1}{k} \left[ \frac{1}{k+a} + \frac{1}{k-a} \right] \, dk \]

(D.9) \[ = \frac{1}{a} \int_{k_F}^{\infty} \frac{1}{k-a} - \frac{1}{k+a} \, dk \]

(D.10) \[ = \frac{1}{a} [\ln(k-a) - \ln(k+a)]_{k_F}^{\infty} \]

(D.11) \[ = \frac{1}{a} \ln \left( \frac{k-a}{k+a} \right)_{k_F} \]

(D.12) \[ = \frac{1}{a} \ln \left( \frac{k_F-a}{k_F+a} \right) \]

### D.3.2

Angle integral occurring when changing from \( \int d\zeta \) to \( \int \zeta d\zeta \):

(D.13) \[ \int \cos^2(x) \sin(x) \, dx = -\cos^3(x) - \int (-2) \cos^2(x)(-\sin(x)) \, dx, \]

using integration by parts. This leads to

(D.14) \[ 3 \int \cos^2(x) \sin(x) \, dx = -\cos^3 x \Rightarrow \]

(D.15) \[ \int \cos^2(x) \sin(x) \, dx = -\frac{1}{3} \cos^3(x). \]

### D.3.3

\[ I = \int_{-\infty}^{\Delta} \frac{1}{x^2} \left[ \frac{1}{x+(a+\Delta i)} + \frac{1}{x-(a+\Delta i)} \right] \]

\[ \Rightarrow \int_{-\infty}^{\Delta} \frac{1}{x^2} \left[ P \frac{1}{x+a} - i\pi \delta(x+a) + P \frac{1}{x-a} + i\pi \delta(x-a) \right] \]

For the imaginary part, as \( x' > 0 \), we find

\[ \text{Im} I = \frac{\pi}{a^2} \Theta(a-x'). \]

Using partial fractions we try to rewrite the real integrand

(D.16) \[ \frac{1}{x^2(x \pm a)} = \frac{A}{x} + \frac{B}{x^2} + \frac{C}{x \pm a} \Rightarrow \]

(D.17) \[ 1 = Ax(x \pm a) + B(x \pm a) + Cx^2. \]

As this must hold for all values of \( x \) we choose the three cases \( x \in (-a, 0, a) \) leading to

(D.18) \[ x = 0 : \quad B = \pm \frac{1}{a} \]

(D.19) \[ x = \pm a : \quad C = \frac{1}{a^2} \]

(D.20) \[ x = \mp a : \quad A = -\frac{1}{a^2}. \]
i.e.

\[
\int \frac{1}{x^2} \left[ \frac{1}{x + a} + \frac{1}{x - a} \right] \, dx = \frac{2}{a^2 x} + \frac{1}{a^2(x + a)} + \frac{1}{a^2(x - a)}.
\]

Integrating this leads to

\[
\int_{x'}^{\infty} \left[ -\frac{2}{a^2 x} + \frac{1}{a^2(x + a)} + \frac{1}{a^2(x - a)} \right] \, dx =
\]

\[
\frac{1}{a^2} \left[ -2\ln x + \ln(x + a) + \ln(x - a) \right]_{x'}^{\infty} =
\]

\[
\frac{1}{a^2} \left[ \ln \left( \frac{x^2 - a^2}{x^2} \right) \right]_{x'}^{\infty} =
\]

\[
-\frac{1}{a^2} \ln \left( \frac{x^2 - a^2}{x^2} \right) ,
\]

for \( x' > a \) and

\[
\frac{1}{a^2} \lim_{\epsilon \to 0^+} \left[ \ln \left( \frac{x^2 - a^2}{x^2} \right) \right]_{x'}^{a - \epsilon} + \left[ \ln \left( \frac{x^2 - a^2}{x^2} \right) \right]_{a + \epsilon}^{\infty} =
\]

\[
\frac{1}{a^2} \lim_{\epsilon \to 0^+} \left( \ln \frac{(a - \epsilon)^2 - a^2}{(a - \epsilon)^2} - \ln \frac{x^2 - a^2}{x^2} \right) + 0 - \ln \frac{(a + \epsilon)^2 - a^2}{(a + \epsilon)^2} =
\]

\[
\frac{1}{a^2} \lim_{\epsilon \to 0^+} \ln \frac{(a + \epsilon)^2(x^2 - 2ac)}{(a - \epsilon)^2(x^2 + 2ac)} - \ln \frac{x^2 - a^2}{x^2} =
\]

\[
-\frac{1}{a^2} \ln \left( -\frac{x^2 - a^2}{x^2} \right)
\]

for \( 0 < x' < a \). I.e.

\[
I = \frac{1}{a^2} \left[ -\ln \left( \frac{x^2 - a^2}{x^2} \right) + i\pi \Theta(a - x') \right]
\]
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