

Chapter 2

Background Theory

The aim of this chapter is to describe the underlying physics of carbon based structures and percolation conduction in composite materials. This will be done through first presenting carbon and its fascinating allotropic family. The tight binding model will be used to consider the origins of graphite's electronic properties arising from its stacked structure. This will then be put into context and explained in relation to the properties of graphene and bilayer graphene.

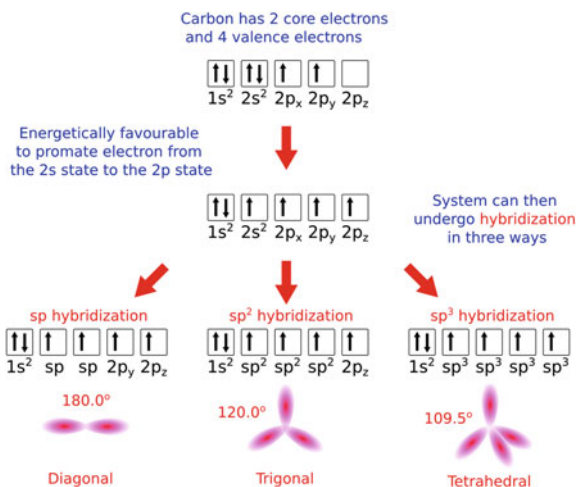
The second part of this chapter will be focused on conduction in composites. We will discuss how the incorporation of conductive particles into an insulating matrix enables conduction above the percolation threshold. We consider the significance of tunneling between particles in conduction lines and go on to derive the tunneling current through a single barrier system.

2.1 Carbon

2.1.1 Hybridization of *s* and *p* Orbitals

Carbon is the sixth element in the periodic table, the fourth most abundant element in the universe and the basic building block for all life. The majority of objects we encounter in our daily lives contain carbon; the air we breathe; the food we eat; the fuel in our cars; the plastic in our pens; and the paper we write on, all contain carbon compounds and molecules. The reason why carbon is found in such a diverse number of forms is because it can form many different types of bonds due to its unique electronic structure. Its six electrons are arranged around the nucleus with two electrons in the innermost tightly bound shell and four electrons in the outer valence shell. Carbon's minimum energy ground state has two valence electrons in the 2s subshell and two in the 2p subshell. What makes carbon special is that through just a small excitation an electron in the 2s subshell can be promoted into the 2p subshell. This is energetically favourable as all four orbitals become exactly half full

Fig. 2.1 Carbon can undergo three types of hybridization allowing it to form a vast array of different types of molecules and compounds



and can be used to form strong covalent bonds, which therefore reduces the overall energy.

The valence orbitals are able to hybridize in three different ways either by, sp hybridization, sp³ hybridization, or sp² hybridization, as shown in Fig. 2.1. Firstly, in sp hybridization a 2s orbital and one of the 2p orbitals hybridize to form two sp orbitals. The carbon forms two covalent sigma, σ , bonds which gives a bond angle of 180° with diagonal symmetry. The two remaining electrons in the 2p_y and 2p_z orbital form pi, π , orbitals perpendicular to the σ bonds. When two sp hybridized carbons are brought together the π orbitals surround the σ bond and form a triple bond. This occurs in the alkyne family of hydrocarbons.

Next, in sp³ hybridization all four orbitals can hybridize to form four new orbitals which are all equivalent. This occurs in diamond where each carbon forms four identical covalent bonds to neighbouring carbons. As each bond is equivalent a tetrahedral structure is formed with a bond angle of 109.5°. The four covalent σ bonds give rise to diamonds strong and rigid structure. As each valence electron is in a σ orbital it is tightly bound within the bond, forcing all the electrons to be localized to an atom, and thus making diamond electrically insulating. The antibonding state σ^* is at such a high energy above σ that electrons are not readily excited into it and so it is not possible for photons to be absorbed and is why diamond is transparent. Any colouring that does occur in diamond is due to presence of impurities absorbed as the diamond was formed.

Lastly, in sp² hybridization the 2s and two 2p orbitals hybridize to form three sp² orbitals. This enables the carbon to form three covalent σ bonds, separated by a bond angle of 120° with a trigonal symmetry. The fourth electron in the p_z orbital does not take part in the sp² hybridization. Instead it forms a delocalized π bond that has a figure of eight-like orbital in the plane perpendicular to that of the three σ bonds. Graphene, graphite and carbon nanotubes are all sp² hybridized.

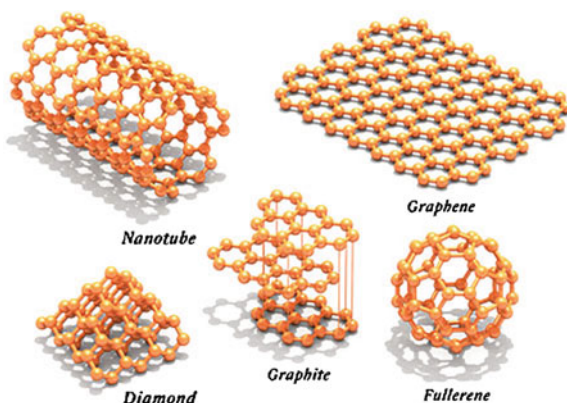
The delocalized π electron is responsible for giving these materials many of their interesting characteristics. The ability for the π electron to move freely between carbon atoms gives rise to a high electrical conductivity. The antibonding π^* state is at an energy very close to that of the π state which means the π electrons can readily absorb photons, making graphite black. The exact nature of the π bands formed in graphite will be covered in detail in the next section.

2.1.2 Allotropes of Carbon

Carbon is unique in its ability to form a complete range of dimensionally different allotropes. Due to carbon's ability to hybridize it is possible to form nano-sized balls (0D), long thin tubes (1D), single layers (2D) and crystals (3D), all of which are stable structures, Fig. 2.2. A short description of each of these is now given:

0D Buckyballs Buckminster fullerenes are spherical particles formed of 60 carbon atoms, C₆₀, arranged in a truncated icosahedral structure, like a football, of twenty hexagons and twelve pentagons with a diameter of 0.7 nm [2]. They were discovered in 1985 by Robert Curl, Harold Kroto and Richard Smalley who were awarded the Nobel Prize in Chemistry in 1996. The Buckyball is sp^2 hybridized however due to the curvature of the surface the bond angles are not exactly 120° and it is actually $sp^{2.3}$ hybridized [3]. Buckyballs caused much initial excitement and interest immediately after their discovery with many ideas for potential applications in electronics, chemistry and medicine. The development for applications has been held back by the cost of production. However the recent reduction of this cost, to around £150/g, has led to the use of fullerenes gaining momentum in the medical industry as a drug delivery system [4].

Fig. 2.2 Five of carbon's allotropes. The 0D fullerene, 1D nanotube, 2D graphene and 3D graphite are all sp^2 hybridized while diamond is sp^3 hybridized. Figure reproduced from [1]



1D Nanotubes Carbon Nanotubes can be thought of as a tightly rolled up graphene sheet that forms a hollow tube. Typically a nanotube will have a diameter of around 1 nm, and can have lengths of up to 18 cm [5] (although more common lengths are of the order 100 μ m). The chirality of the nanotube, conceptually the angle at which a graphene sheet has been rolled, determines the nanotubes electronic properties such as whether it is semiconducting or metallic. Nanotubes can be either just one carbon layer thick, single wall nanotubes (SWNTs), or have multiple concentric layers, multi-wall nanotubes (MWNTs). Undoubtedly nanotubes have made a huge impact to the nanoscience world with demonstrated applications in transistors [6], oscillators [7] and super tough fibres [8] to name but a few. It is interesting that no Nobel prize has yet been awarded for the discovery of nanotubes but this could be due to the contention over who actually discovered them. However, Sumio Iijima is generally given the credit for bringing nanotubes to the scientific communities attention with his paper in 1991 [9], in which he observed and imaged MWNTs and then two years later he also synthesized SWNTs [10]. Nanotubes cost vary from just £60/g for an assortment of nanotubes¹ to £410,000/g for purely semiconducting or metallic SWNTs.²

2D Graphene Graphene is single layer, one atom thick, two dimensional array of carbon hexagons. In 2004 Andre Geim and Konstantin Novoselov were able to successfully isolate single graphene flakes on an SiO₂ substrate using just a simple mechanical cleavage technique involving scotch tape [11]; remarkable considering graphene had been predicted to be thermodynamically unstable and therefore unattainable [12]. Their discovery led to a ‘graphene explosion’ as its unrivalled mechanical, electrical and thermal properties emerged, all of which originate from its sp² hybridization. They were awarded the Nobel Prize just six years later in 2010 for ‘groundbreaking experiments regarding the two-dimensional material graphene’. Graphene has been touted as the new silicon, however two key hurdles stand in the way namely, large scale production and the lack of a band-gap to allow the graphene to be turned off [13]. These are two very different problems; large scale production requires the ability to have a bottom up approach of growing defect free graphene which is technically extremely difficult, although some headway has been made with companies like IBM recently achieving wafer sized epitaxial graphene on SiC [14]. The other problem of switching graphene on and off, so as to make high gain transistors, is an intrinsic problem arising from the lack of a band-gap in graphene’s band structure. However this could be solved through bilayer graphene which

¹ Quote from www.nanoamor.com

² Quote from www.sigmaaldrich.com

is discussed in the following sections [15]. Currently purchasing a single gram of free standing graphene would cost in the region of £2.5 billion, although this would be enough to cover an area equivalent to ten tennis courts.

3D Diamond Diamond has been known to humans for thousands of years, as far back as Ancient India where it was used for religious icons and jewellery. Diamonds form at high temperature and pressures deep underground where the carbon is able to sp^3 hybridize. As already mentioned the sp^3 hybridization leads to exceptional hardness and thermal conductivity but low electrical conductivity [16]. A naturally occurring 5 carat (1g) diamond costs in the region of £100,000.

3D Graphite Graphite has also been known to humans for thousands of years with the Ancient Greeks having used it in pencils just like we do today. Graphite is built up from many stacked layers of graphene planes each slightly offset from the plane below. This is called a lamellar structure and the most simple stacking scheme is the Bernal AB stacking. The layers are loosely bound together through Van der Waals interactions from the p_z electron in the π orbital [17]. This is why layers of graphite can be easily sheared off. Graphite is also highly valued in industry applications as a dry lubricant for the same reasons [16]. Other uses of graphite include conductive fillers [18], battery electrodes [19] and in nuclear fission reactors [20]. The lamellar structure means that graphite is highly anisotropic with very different properties across its planes than perpendicular to them, for instance the electrical conductivity is 3,000 thousand times greater in the plane than across the plane [19]. The anisotropy will be a central feature to our explanation of the sharp NDR we observe in graphite-silicone composites. Solid blocks of HOPG graphite cost around £1,000/g.³

so why is it that the discovery of each new carbon allotrope, the buckyball, 1985, nanotubes, 1991 and graphene, 2004, has generated such huge excitement in the scientific community; opening up whole new areas and applications in physics?

The answer all lies with carbons ability to sp^2 hybridize forming a strongly bound lattice whilst leaving one free electron per carbon atom in the p_z orbital that can become delocalized. Collectively the delocalized electrons form the valence and conduction energy bands where they have high mobility and give rise to the unique and fascinating properties seen in these carbon structures.

³ Quote from www.2spi.com

2.2 Band Structure: Graphite to Graphene

A band structure arises when a large number of atoms, each with its own discrete energy levels, are brought close together. The outer electrons interfere with surrounding atoms which causes the discrete energy levels to broaden into a continuum, forming bands. Thus the band structure describes the range of energies that an electron may have and the forbidden energies, band-gaps, it cannot have.

The band structure tells us the relationship between the valence band, the highest filled energy band, and the conduction band, the lowest unfilled available energy band. When electrons move into the conduction band they are not bound to a specific atom and as a result are mobile and responsible for conduction. Therefore in metals, where the valence band overlaps the conduction band, electrons are readily able to conduct, which is why metals have high conductivities. Conversely, for an insulator there is a large band-gap leading to very low electrical conductivities.

Semiconductors have a small band-gap, typically $<4\text{ eV}$. Electrons can be excited through the band gap allowing the semiconductor to conduct under certain conditions. The Fermi energy, ε_f , gives the energy up to which the highest electron state is likely to be occupied. The Fermi energy can be shifted through applying electric potentials and when it is raised up into the conduction band, the semiconductor can readily conduct.

The next thing to consider is that for a crystalline solid the band structure will depend on the spatial distribution of the atoms in the crystalline lattice. To describe this dependence we use the Brillouin zone which is the primitive cell in reciprocal space. The Brillouin zone has points of high symmetry and it is around these points that all the interesting physics takes place [21].

Clearly the exact crystalline structure is very important in determining the band structure. One method that can be used to calculate the band structure in a crystal lattice is the tight binding model. It combines the solution for a single electron system and maps this onto a crystalline structure found from the unit cell and the corresponding lattice transformations from the translation symmetry. The solution for the total energy is a matrix of terms, the Hamiltonian, which can be used to find the band structure around the Brillouin zone. Using the tight binding model we will show that: graphite is a semi-metal with a 150 meV overlap between the conduction and valence bands [17]; graphene is a zero band-gap semiconductor and has charge carriers that mimic relativistic particles with zero rest mass [22]; and bilayer graphene can be influenced through a transverse electric field to have a finite band-gap [23].

2.2.1 3D Model of Graphite

The most widely used model for calculating the band structure of 3D graphite is the Slonczewski-Weiss-McClure (SWMC) model developed in 1957–1958 [24, 25]. It uses the tight-binding model from a 2D graphite approximation, developed by

Wallace [26] in 1947, and adds a perturbation calculation to take into account the interactions between layers. The solutions can then be found from a parametrized fourth order equation using various techniques or experimental values. This makes the model popular amongst experimentalists as the parameters have physical origins and can be validated experimentally. The model has been shown to work well in calculating the band structure around the edges of the Brillouin zone, H-K, close to the Fermi level, which is where the interesting physics occurs. The presence of many interacting layers alters the band structure so that the conduction and valence band overlap making graphite a semi-metal. Other methods can be used to describe the band structure right across the Brillouin zone however these tend not to be so accurate.

As discussed previously, graphite is built up from stacking layers of hexagonal graphene on top of each other in an AB stacking structure. This gives graphite a hexagonal unit cell that contains four atoms. We label these atoms A, A' and B, B' as they are inequivalent, labelled in Fig. 2.3. Atoms A and A' have neighbours directly above and below them, 3.35 Å away. Whereas B and B' lie directly above and below centers of the hexagons in neighbouring layers. The next atoms directly above or below B and B' are 6.71 Å, two layers, away. The non-equivalence of atoms A and B is important as it leads to some interesting features in the Fermi surface.

The difference between the carbon atoms A and B has a subtle effect on the band structure and properties of graphite. The coupling between these atoms lowers the symmetry of the system so that it has a three fold symmetry which leads to a trigonal warping of the Fermi surface.

Fig. 2.3 Graphite with an AB stacking structure has four atoms per unit cell. The atoms A and A' have neighbours directly above and below. Atoms B and B' are directly above and below the centers of a hexagon. The atoms that lie directly above or below are 6.71 Å, two layers, away. The parameters $\gamma_0, \gamma_1, \gamma_2, \gamma_3, \gamma_4, \gamma_5$ for the SWMC model are shown. Figure adapted from [27]

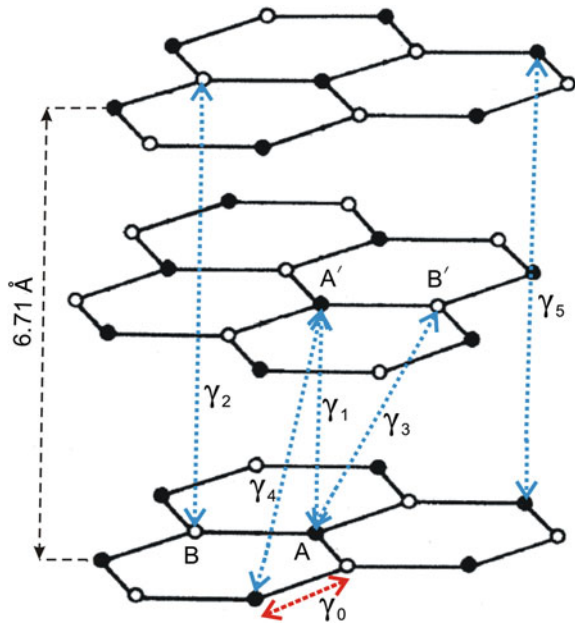
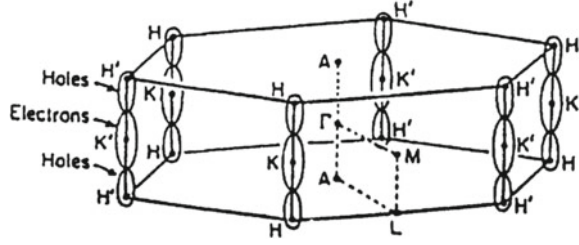


Fig. 2.4 The first Brillouin zone for graphite is a hexagonal prism with height $\frac{2\pi}{c}$. The points of high symmetry are the center Γ , corners H and H', centers of the top and bottom faces A, centers of the side faces M, centers of the of sides edges K and K' and the centers of edges of the top and bottom faces L. Figure reproduced from [28]



The first Brillouin zone of graphite is shown in Fig. 2.4. It is a hexagonal prism with height $\frac{2\pi}{c}$. This is not the true Brillouin zone, which should have a height of $\frac{4\pi}{c}$, however it is the one originally adopted by McClure and has become the conventional Brillouin zone to use. The points of high symmetry are the center Γ , corners H and H', centers of the top and bottom faces A, centers of the side faces M, centers of the of sides edges K and K' and the centers of edges of the top and bottom faces L [25].

Slonczewski, Weiss and McClure used perturbation theory to calculate the band structure of graphite taking into account the effects of interactions between the layers [24]. The SWMC model calculates the band structure and Fermi surface in the region of the H–K–H axis. The seven independent band parameters it uses are $\gamma_0, \gamma_1, \gamma_2, \gamma_3, \gamma_4, \gamma_5, \Delta$. The first six define the interaction energies, in eV, between the atoms in the unit cell, as shown in Fig. 2.3. While Δ gives the energy shift between atoms A and B arising from the offset stacking. If the exact values of these seven parameters are known, it is possible to calculate the energy bands near the H–K–H axis and completely determine the Fermi surface.

The calculation can be expressed in the form of the following Hamiltonian,⁴

$$\hat{H} = \begin{pmatrix} E_1 & 0 & H_{13} & H_{13}^* \\ 0 & E_2 & H_{23} & -H_{23}^* \\ H_{13}^* & H_{23}^* & E_3 & H_{33} \\ H_{13} & -H_{23} & H_{33}^* & E_3 \end{pmatrix}, \quad (2.1)$$

where,

$$\begin{aligned} E_1 &= \Delta + \gamma_1 \Gamma + \frac{1}{2} \gamma_5 \Gamma^2 & H_{13} &= \frac{-\gamma_0(1-v)\sigma e^{i\alpha}}{\sqrt{2}} \\ E_2 &= \Delta - \gamma_1 \Gamma + \frac{1}{2} \gamma_5 \Gamma^2 & H_{23} &= \frac{\gamma_0(1+v)\sigma e^{i\alpha}}{\sqrt{2}} \end{aligned} \quad (2.2)$$

⁴ For the complete derivation refer to Brandt et al. [29] or Charlier and Charlier [30].

$$E_3 = \frac{1}{2} \gamma_2 \Gamma^2$$

$$\Gamma = 2 \cos \pi \xi$$

$$H_{33} = \gamma_3 \Gamma \sigma e^{i\alpha}$$

$$\nu = \frac{\gamma_4 \Gamma}{\gamma_0}$$

The accepted values of the parameters have been found through a mixture of experiment and theory and have been revised many times over the years as experimental techniques have become more accurate with terms such as γ_2 even changing sign during the 1970s [29]. The most recent accepted values are shown in the bottom row of Table 2.1. The physical meaning of each SWMC parameter and what effect it has on determining the band structure is as follows.

- γ_0 The interaction between nearest neighbours, atom A to atom B. This is the only band parameter that describes an interaction in the plane and also has the largest magnitude of 3.12 eV as the interactions are much greater in the plane. All the other parameters are out of the plane and of lesser energy.
- γ_1 Nearest neighbour interaction between atoms of type A. These are in neighbouring layers placed one under the other, i.e A to A'. This parameter determines the width of the π bands at the K points on the Brillouin zone, equal to $4\gamma_1$ [29].
- γ_2 Nearest neighbour interaction between atoms of type B, i.e B to B'. This is one of the most significant parameters as it determines the coupling between the π and σ bands and the magnitude of the overlap between π bands, which is equal to $2|\gamma_2|$ [29].
- γ_3 The interaction between A and B'. The presence of such coupling lowers the symmetry of the interaction Hamiltonian. This leads to trigonal warping in the Fermi surface around K.
- γ_4 The interaction between like atoms not directly above one another. This interaction gives rise to non-mirror like characteristics of the valence and conduction bands [31].
- γ_5 The interaction between two A atoms separated by a layer.
- Δ This is the energy shift due to the non equivalence of A and B. It is the direct measure of the potential energy difference between atom sites A and B [17].

There are four valence electrons in each carbon atom in graphite and four atoms per unit cell. Therefore the band structure will have 16 bands, with 12 σ bands and four π bands. Of the 12 σ bands six are bonding and the other six are antibonding with a higher energy. The separation between the bonding and antibonding groups is large, approximately 5 eV and therefore does not interest us here.

Table 2.1 Parameter values for the SWMC model

γ_0	γ_1	γ_2	γ_3	γ_4	γ_5	Δ	ε_F
3.16	0.39	-0.02	0.315	0.044	0.038	0.008	-0.024
3.12	0.377	-0.020	0.29	0.120	0.0125	0.004	-0.0206

Top row from Brandt et al. [29] and bottom row from a more recent review by Chung [17]

The π bands can be found between these two groups. Likewise there are two bonding π bands and two antibonding π^* bands which are strongly coupled. There are four electrons to fill the bands but not more than two electrons can sit in each band due to the Pauli exclusion principle. The Fermi level will thus lie in the middle of the four π bands.

The Hamiltonian in Eq. (2.1) can be solved to find the band structure close to the H–K–H axis of the Brillouin zone and can be seen in Fig. 2.5a. The two bonding π bands are labelled as E_2^- and E_3^- and the antibonding π^* bands as E_1^+ and E_3^+ . At the K points the E_3^- and E_3^+ bands overlap making a doubly degenerate band, E_3^0 which contains four states. The overlap is by 0.03 eV making graphite a semi-metal. The importance of the parameters Δ , γ_1 and γ_2 can be easily seen by examining the solution for the Hamiltonian only around K and around H using Eqs. 2.2:

<u>K</u>	<u>H</u>
$k_z = 0 \implies \xi = k_z c_0 / 2\pi = 0$	$k_z = \pi/c \implies \xi = k_z c_0 / 2\pi = 1/2$
$\Gamma = 2 \cos \pi \xi = 2$	$\Gamma = 2 \cos \pi \xi = 0$
$E_1 = \Delta + 2\gamma_1 + 2\gamma_5$	$E_1 = \Delta$
$E_2 = \Delta - 2\gamma_1 + 2\gamma_5$	$E_2 = \Delta$
$E_3 = 2\gamma_2$	$E_3 = 0$

It can be seen that the width of the π bands at K, between E_2^- and E_1^+ , is $4\gamma_1$. The Δ parameter at H stops all the bands becoming degenerate. The energy at the

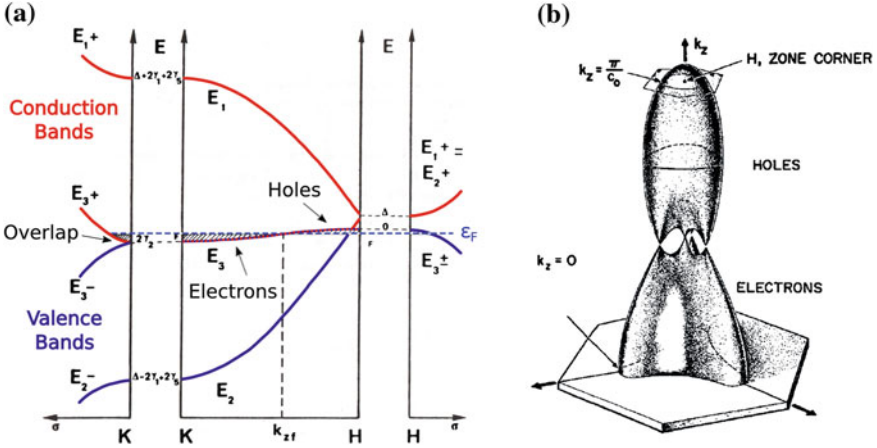


Fig. 2.5 **a** The band structure of graphite from K to H. The bands overlap around the Fermi level by 0.03 eV. Carrier pockets are created along the H–K–H axis where the doubly degenerate E_3 states lie close to ε_F , which creates a complex Fermi surface [30]. **b** The Fermi surface for graphite at the corners of the Brillouin zone centered around the H–K–H axis. All the free carriers are located along the zone edges, giving rise to slender Fermi surfaces. The γ_3 parameter leads to a trigonal anisotropy which is exaggerated here for clarity. Figures adapted from [30] and [17]

overlap of the doubly degenerate state E_3 is $2\gamma_2$. Referring back to Table 2.1 we can see that the $2\gamma_2 = -0.04$ eV while $\varepsilon_F = -0.0206$ eV so at K E_3 lies below the Fermi energy by 0.02 eV. At H we find $E_3 = 0$ which is 0.02 eV above ε_F .

Therefore the degenerate band, E_3^0 , moves from being below the Fermi energy at K to above the Fermi energy at H. The point where the change of sign occurs is labelled k_{zf} . Between K and k_{zf} all the E_3^0 states are filled with electrons while between k_{zf} and H the states are occupied by holes. This means that the charge carriers are localized in electron and hole pockets. However this is only a 2D cross section and if we then consider the third axis we can construct a Fermi surface as shown in Fig. 2.5b. The Fermi surface clearly shows the electron and hole pockets as we move from K to H, up the k_z axis. The Fermi surface is slender as it extends less than 1 % of the distance from K, the zone edge, to Γ , the zone centre [17].

In the construction of the Fermi surface there is a $\gamma_3 \cos \alpha$ term, where α describes an angle on the plane that is perpendicular to k_z [30]. This leads to an interesting feature on the Fermi surface around K whereby the electron pockets have a trigonal warping, unlike the holes which remain cylindrical near H. Furthermore the pockets are connected by four legs, three legs lie off the H–K–H axis and one leg which lies along the H–K–H axis [17]. The legs connect at k_{zf} and at the Fermi energy.

To summarize, graphite is a semi-metal due to the overlap of the conduction and valence bands, shown in Fig. 2.6a, of 0.03 eV. For reference the complete band structure is shown in Fig. 2.6b. The box indicates the K–H region, found using the SWMC model. The significance of the parameters in the model has been shown such as; the band overlap due to γ_2 ; the on-site energy term Δ which stops the valence and conduction bands becoming entirely degenerate at H; and γ_3 which leads to trigonal warping in the Fermi surface for the electron pockets. The importance of these parameters will become apparent when we next consider the band structure of graphene and bilayer graphene.

2.2.2 Graphene's Band Structure

When Wallace in 1947 worked on calculating the band structure of graphite he started by first considering a single 2D graphite layer, graphene [26]. This was a sensible approach as graphite layers are only weakly bound together through Van der Waals interactions. Wallace was able to demonstrate, with the use of a nearest neighbour tight binding model, an analytical expression for the band structure of the π bands of graphene [26, 32].

Amazingly Wallace's analytical expression predicted that graphene would be a zero band-gap semiconductor with the valence and conduction bands exactly touching at the Fermi energy at the corners, K and K' of the hexagonal Brillouin zone. With most importantly, a linear dispersion between the energy and wave vector $\mathbf{k}$.

The significance of the linear dispersion with regard to massless Dirac fermions was only understood some 40 years later by Semenoff in 1984 [33]. Graphene became a toy model for theoreticians interested in $(2 + 1)$ dimensional quantum electronics

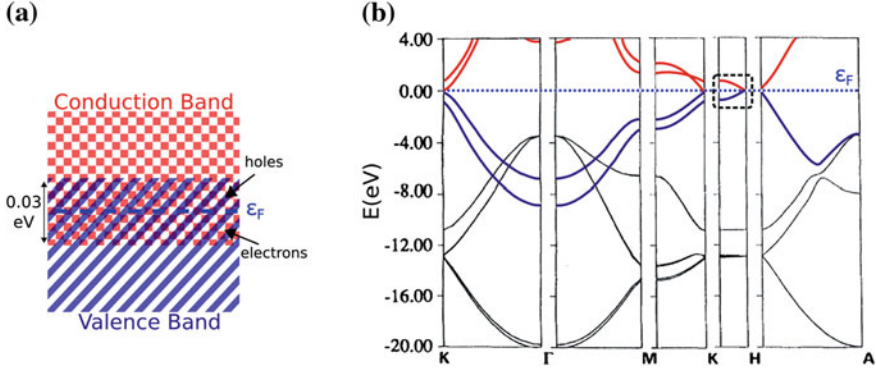


Fig. 2.6 **a** A schematic of the band structure of graphite to show that the valence and conduction band overlap by 0.03 eV around the Fermi level making graphite a semi-metal. **b** The complete band structure of graphite around the Brillouin zone. The red lines show the conduction bands and the blue lines are the valence bands. The black box indicates the section of the band structure found using the SWMC model. Figure adapted from [28]

to play with [13]. However theoreticians also predicted that 2D crystals were an impossibility as they would be thermodynamically unstable [12, 34]. Thus despite some attempts to isolate graphene through different physical and chemical methods, including intercalation, it was generally expected that graphene would just remain a theoreticians toy model [32, 35, 36].

Therefore in 2004 the discovery of single layer graphene flakes by Konstantin Novoselov and Andre Geim, in their own words, “flaunted common wisdom by experimental discovery”. They used scotch tape to mechanically exfoliate thin layers of graphite from a HOPG block and repeated the process on the exfoliated layers over and over until they were left with just single layer graphene flakes. The flakes were then transferred to a SiO_2 substrate. Part of the success of their discovery lies in their realization that single layers were visible under an optical microscope if the SiO_2 substrate had a thickness of 300 nm. Successive papers in 2004, 2005 and 2007 showed that graphene did indeed have the properties of a material with massless Dirac fermions arising from the linear E - $\mathbf{k}$ dispersion [11, 13, 22].

The complete band structure for graphene around the Brillouin zone can be seen in Fig. 2.7a. Methods for calculating this can be found in either the original Wallace and Slonczewski papers or Castro’s more recent review [24, 26, 37].

The valence and conduction band exactly touch at the Fermi level, the Dirac point. This makes graphene a zero band-gap semiconductor. If we now examine the band structure more closely around the Fermi energy, at low energies we see that there is a linear dispersion between E and $\mathbf{k}$, Fig. 2.7(b) center-inset, with:

$$E_k = v_F |\mathbf{k}|, \quad (2.3)$$

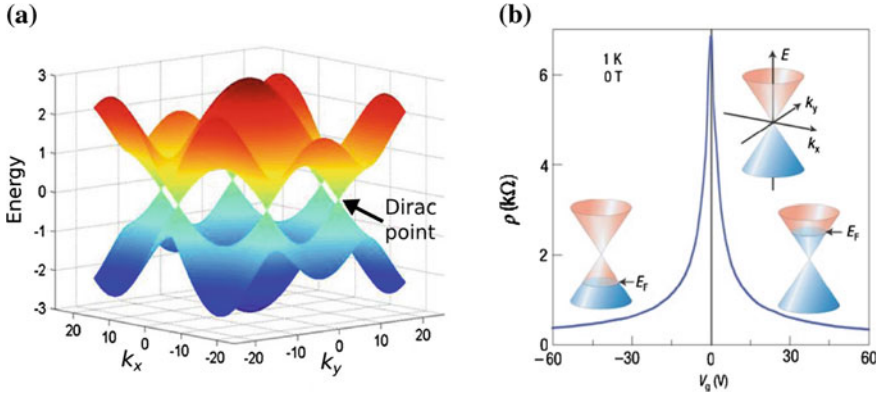


Fig. 2.7 **a** The valence and conduction bands around the Brillouin zone for graphene. The bands exactly meet at the Dirac point. Close to the Dirac points the bands have a linear dependence between E and $\mathbf{k}$. **b** Ambipolar electric field effect in graphene. The Fermi energy is shifted using a gate voltage, V_G , leading to a symmetrical resistivity around $V_G = 0$. The resistivity, ρ , has a maximum of 6.4532 $k\Omega$ that occurs when the Fermi energy is at the Dirac point. Figure reproduced from [13]

where $\mathbf{k}$ is the wave-number and v_F is the Fermi velocity. The linear dispersion between E and $\mathbf{k}$ is characteristic of massless particles and implies that graphene has charge carriers that have an effective rest mass of zero. This means that the charge carriers mimic relativistic particles and thus the Dirac equation can be employed to describe them.

The electrons are not moving at relativistic speeds, but the way in which they interact with the periodic potential of graphene's honeycomb lattice gives rise to quasi particles that are best described by the relativistic Dirac equation where $v_F = 10^6 \text{ ms}^{-1}$ is substituted for c [13].

The valence and conduction bands exactly touch at the critical Dirac point. The Fermi level intrinsically sits at this point. However in fabricating devices a gate voltage, V_G , can be used to apply a potential that shifts the Fermi level up or down. Due to the symmetry of the system graphene exhibits an ambipolar electric field effect, Fig. 2.7b. This means that shifting the gate voltage to a negative or positive value gives the same change in resistivity. The charge carriers can be tuned continuously between electrons and holes in concentration as high as 10^{13} cm^{-2} and with mobilities in excess of $150,000 \text{ cm}^2 \text{ Vs}^{-1}$ at room temperature [13].

Another fascinating feature of graphene is that when $V_G = 0$ the Fermi energy is at the Dirac point but the conductivity does not tend to zero, as it would in a semiconductor, instead it tends to a minimum conductivity value that is the same for all samples, regardless of size. It tends to multiple of a conductivity quantum, $4e^2/h$, which gives a maximum resistance, or resistivity as it is size independent, of 6.4532 $k\Omega$. Further it is temperature independent from 100 to 10 K. The maximum resistivity can be seen in Fig. 2.7b when $V_G = 0$.

The minimum conductivity is a double edge sword. On the one hand it is fascinating and exciting for physics as it is a direct consequence of the massless Dirac fermions which leads to many other interesting physics including graphene's room temperature integer quantum hall effect [38].

However for those wishing to utilize graphene's high mobility for use in devices such as transistors it becomes a major obstacle. The minimum conductivity means that graphene's electrical conduction cannot be turned off. Thus in making graphene transistors the on-off ratio will always low, with ratios only of the order 30 [11].

For bilayer graphene the presence of the additional layer enables a change in the band structure such that instead of a Dirac point and a minimum conductivity, it is possible to induce a band-gap through the use of a transverse electric field across the layers. This then allows for significantly higher on-off ratios.

2.2.3 Bilayer Graphene

Graphite posses an overlap between its valence and conduction bands around the K–H axis, making it a semi-metal. While graphene has valence and conduction bands that are exactly degenerate at the K point and linear at low energies close to the K point, thus making graphene a zero band-gap semiconductor.

Clearly the interactions between many stacked graphene layers leads to a dramatic change in the band structure from just a single layer. What happens when there is just one additional layer, bilayer graphene, has been a topic of intense research for the last 5 years [23].

It has been shown that bilayer graphene is a zero band-gap semiconductor, without the linear dispersion of graphene, and in the presence of an electric field across the layers a band-gap is opened up [39]. Thus making bilayer graphene a tunable band-gap semiconductor with a band-gap that is approximately proportional to the difference in potential across the layers.

Edward McCann can be considered the pioneering theoretician with regard to bilayer graphene. He predicted that it would be able to exhibit a *tunable band-gap* between the conduction and valence bands in 2006 [39]. He described the use of a parametrized tight binding model, similar to the one used earlier for graphite, to describe the band structure of bilayer graphene as the gap is opened up [15, 40]. This will be summarized next before going on to briefly summarise some of the impressive experimental work undertaken to fabricate bilayer graphene devices and measure this tunable band-gap.

In a similar way to the structure of graphite shown in Fig. 2.3, bilayer graphene has two coupled hexagonal lattices arranged according to Bernal stacking AB. The unit cell contains 4 atoms on inequivalent sites A, B, A', B' with A and B on the lower layer and A', B' on the top layer. The A, A' atoms lie directly on top of one another while A' lies below the center of a hexagon of the upper layer and B' lies above the centre of a hexagon from the lower layer.

The tight binding model is used to calculate the band structure using a SWMC parametrization, as before for graphite. Clearly not all seven parameters will be required as there are only two layers, with less interaction, therefore for bilayer graphene we can define [40]:

- γ_0 The in-plane nearest neighbour interaction.
- γ_1 The strongest inter-layer interaction between A and A', atoms that lie directly above and below one another.
- γ_3 The weak inter-layer coupling between A and B' (or B and A'). This term gives rise to trigonal warping however it does not have a major significance in the opening of the band-gap and therefore for a first approximation it is often set to zero.
- Δ The on-site energy difference between the lower and upper layer, which we define as ε_1 and ε_2 with $\Delta = \varepsilon_2 - \varepsilon_1$ where $\varepsilon_2 = \frac{1}{2}\Delta$ and $\varepsilon_1 = -\frac{1}{2}\Delta$.

The Hamiltonian that describes the four π bands is as follows [40]:

$$\hat{H} = K_v \begin{pmatrix} -\frac{1}{2}\Delta & H_3 & 0 & H_0^\dagger \\ H_3^\dagger & \frac{1}{2}\Delta & H_0 & 0 \\ 0 & H_0^\dagger & \frac{1}{2}\Delta & H_1 \\ H_0 & 0 & H_1 & -\frac{1}{2}\Delta \end{pmatrix} \quad (2.4)$$

with,

$$\begin{aligned} H_0 &= \sqrt{3/2} \frac{a\gamma_0}{\hbar} (p_x + ip_y), \\ H_1 &= K_v \gamma_1, \\ H_3 &= \sqrt{3/2} \frac{a\gamma_3}{\hbar} (p_x + ip_y), \end{aligned} \quad (2.5)$$

where $H^\dagger$ denotes the Hermitian conjugate of H , $p = (p_x, p_y) = \hbar|\mathbf{k}|$ is the momentum with respect to the K point and $K_v = +1(-1)$ labels valley K ($\tilde{K}$). To simplify, we take $\gamma_3 = 0$ as this term has little effect on the size of the band-gap opened up. This allows us to write the equation that describes all four π bands as,

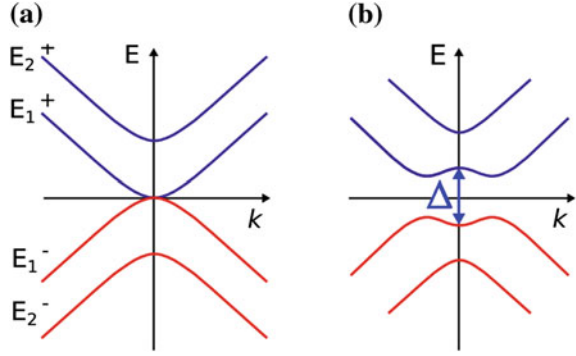
$$E_\alpha^\pm \approx \sqrt{\frac{\gamma_1^2}{2} + \frac{\Delta^2}{4} + v^2 p^2 + (-1)^\alpha \sqrt{\frac{\gamma_1^4}{4} + v^2 p^2 (\gamma_1^2 + \Delta^2)}}, \quad (2.6)$$

where $\alpha = 1, 2$ and $v = \sqrt{3/2} \frac{a\gamma_0}{\hbar}$. Exactly at the K point $p = 0$ and so we can further simplify,

$$E_1^\pm = \pm \frac{|\Delta|}{2}, \quad (2.7)$$

and,

Fig. 2.8 **a** The band structure of bilayer graphene close to the K point for $\Delta = 0$. The $E_1^\pm$ bands are degenerate at the K point, while $E_2^\pm$ are separated by γ_1 . **b** The band structure for bilayer graphene when a potential has been applied across the layer and $\Delta \neq 0$. The $E_1^\pm$ bands are now separated by Δ at the K point



$$E_2^\pm = \pm \sqrt{\gamma_1^2 + \frac{\Delta^2}{4}}. \quad (2.8)$$

The band structure of Eq. (2.6) is shown in Fig. 2.8a for $\Delta = 0$. As can be seen from Eqs. 2.7 and 2.8, the $E_1^\pm$ bands are degenerate at the K point, where they exactly touch, $\Delta = 0$. The $E_2^\pm$ bands do not touch at the K point and instead are separated by an energy γ_1 , the split due to the inter layer coupling. The band dispersions are not linear and thus the effective mass, unlike graphene, is non zero. The effective mass is light with $m^* = \frac{\gamma_1}{2v^2} \approx 0.054m_e$ [40].

When we apply a potential across the layers such that $\Delta \neq 0$. The $E_1^\pm$ bands no longer touch at the K point, instead they are separated by an energy gap, Δ , thus Δ is not just the difference in on-site energies it is also equal to the size of the *induced band-gap*. The higher bands $E_2^\pm$ will still be separated predominately by γ_1 with just a small contribution from Δ . This is plotted Fig. 2.8b. At large values of Δ , when $\Delta \approx \gamma_1$, a ‘Mexican hat’ structure begins to form in the $E_1^\pm$ bands. The band-gap becomes indirect and puts a maximum on the induced band-gap value of about 400 meV.

Theoretically, it is possible to induce a *band-gap* in bilayer graphene up to a value of 400 meV [40]. When the Fermi level is shifted into the band-gap there is an induced *semi-metal to insulator* transition. Experimentally this can be achieved by using electric fields to break the symmetry between the layers and cause a substantial change in conductivity.

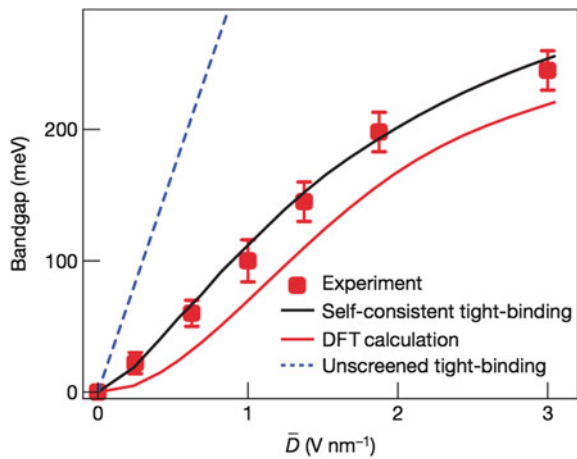
In 2006, Ohta et al. used angle-resolved photoemission spectroscopy (ARPES) to demonstrate that through potassium doping of the upper layer of a bilayer graphene it is possible to directly manipulate the size of the band-gap between the valence and conduction band [41]. The use of potassium doping is crude and the size of the field applied through the doping across the layers is of the same order of magnitude as an electric field that could be applied between a top and bottom gate and was the next obvious development.

In 2007, Oostinga et al. achieved the formidable task of placing a top gate onto bilayer graphene [42]. They mounted bilayer graphene samples onto a 285 nm SiO_2 layer with p-doped silicon underneath to form the bottom gate. A 15 nm SiO_2 layer, followed by titanium and gold, was patterned on top of the graphene bilayer to form a top gate. The double gated structure allows simultaneous and independent control of the charge density in the system, the effective Fermi level, and the electric field perpendicular to the graphene layers.

Oostinga et al. demonstrated that through the use of two gates, a band-gap in bilayer graphene could be induced while at the same time the charge neutrality point (CNP) could be shifted to lie within the band gap, causing the resistance to increase. However the size of band-gap induced was only of the order 10 meV. Which due to thermal activation necessitates temperatures of the order of just a few Kelvin to experimentally measure the induced band-gap.

In 2009, Zhang et al. extended the work of Oostinga et al. [43]. Zhang et al. also used a top and bottom gate to control independently the electronic band-gap and the carrier doping concentrations, the effective Fermi level. The difference is that Zhang et al. used infrared spectroscopy to directly measure the band-gap, using optical transitions from the π to the π^* bands. The optical determination of the band-gap is less affected by defects and any external doping effects, than the electrical measurement of the band-gap. They succeeded in measuring a clear band-gap in the bilayer graphene of up to 250 meV induced through an electric field applied across the layers. They further demonstrated that through fine adjustment of the top and bottom gates the band-gap could be tuned between 0 and 250 meV at room temperature [43]. A plot of the band-gap induced as a function of the applied electrical field $\bar{D}$ is shown in Fig. 2.9. The tight binding model, derived previously, gives a linear dependence between the field across the bilayer and the size of the induced band-gap and can be seen to be a good first approximation.

Fig. 2.9 Zhang et al. were able to use electrical gating to tune a band gap in bilayer graphene up to 250 meV that follows closely the predicted band-gap from the tight-binding model when screening is included. $\bar{D}$ is the electric field across the bilayer. Figure reproduced from [43]



2.2.4 Summary

We have seen that bilayer graphene, intrinsically a zero-band semiconductor, can have an induced band-gap that is tunable in the presence of an electric potential *perpendicular* to the layers. There has been a lot of interest regarding bilayer transistors and Zhang et al. was able to demonstrate a two atomic layer thick switch. However the interactions between the two layers means that some of the special electrical properties of graphene due to the, massless Dirac fermions, are lost for bilayer graphene where the dispersion is not linear. Thus the exceptionally high mobility seen for a suspend single layer graphene, up to $200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is an order of magnitude smaller, $\simeq 15,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in bilayer graphene [44]. The technical challenges involved in creating the double gated structures required are certainly not trivial. However the idea of having a electrically tunable band-gap is still very exciting and may have some applications for novel nanophotonic devices for infrared light generation, amplification and detection [43].

2.3 Graphite Nanoparticles

In the previous section, we have considered graphite as a perfect crystalline form of AB stacked graphene planes. In the real world graphite does not always come as this perfectly stacked structure. There are in fact many different forms of graphite and in the literature there is a huge range of terminology that depends on the exact degree of graphitisation and the original source of the graphite, i.e whether it is synthetic or natural. There is also a substantial grey area between the different types and with graphite used in such a huge range of industrial applications it is natural that for different industries to each have their own definitions and terminology. Graphite's industrial uses include: conductive coatings, glass manufacturing, lubricant formation, metallic alloys, nuclear reactors, powder metallurgy, structural materials, steel making, brake linings, zinc-carbon batteries, electric motor brushes and this is to name but a few [16, 18–21].

For the purposes of simplification all the different types of graphite can be generally split into three categories of increasing levels of crystallinity, amorphous carbon (AC), pyrolytic carbon (PC) and HOPG.

AC Amorphous carbon does not have any crystalline structure. There is no long range order such as stacking although there may be small clumps of carbon joining together to form small hexagonal segments and thus it is possible to observe some short range order. There will be a range of sp^2 and sp^3 bonding, the ratio of which can be used to characterise the amorphous carbon. Carbon black is a good example of a processed amorphous carbon and it is used extensively as a filler in rubber and in printing [45].

PC Pyrolytic carbon has a good degree of crystalline structure with groups of graphite layers but that have completely random orientations about the

layer. This is probably the most broad group as the degree of crystallinity can vary so much. PC can be either: grown through chemical vapor deposition; formed through annealing AC at temperatures between 1,000 and 2,500°C that restores some long range order; or mined as natural graphite [16].

HOPG Highly oriented pyrolytic graphite has the strictest definition of the three types as it lies close to the ideal graphite crystal with an angular spread between the C-axis of crystallites of less than 1°. It is usually formed through an annealing process of pyrolytic graphite through heating at over 2,700°C whilst under pressures of several atmospheres. This induces further ordering between the planes and stress relieving within each plane. It can also be mined naturally where similar high temperature and high pressure processes have occurred naturally deep underground [16].

Lastly there has recently, with the advent of graphene, become another form available referred to as graphene nano-platelets (GNP). These are normally some form of expanded graphite where a chemical method has been used to break apart the HOPG into small particles that have just 5–20 layers of stacked graphene sheets. In some ways these could still be considered graphite nanoparticles but what sets them aside is their aspect ratio with widths of up to 20 µm but thickness of just 2–10 nm. Providing that the particles do not aggregate they are able to provide unprecedented surface to volume ratios and are being rapidly developed for use in a new generation of supercapacitors for electric cars. The high surface area means that the GNP based supercapacitor can be rapidly charged whilst having a high energy density [46, 47].

2.4 Percolation in Composites

Composites combine two or more materials of differing desirable characteristics to engineer the resulting composite properties for specific applications. Often this involves incorporating a reinforcement filler into a binding matrix. The filler may have the desirable strength, electrical or colour characteristics, while the matrix enables the composite to have the desired shape, flexibility or viscosity to support or bind the filler.

Carbon black, an amorphous carbon, can be used to form many interesting types of composites as it has a range of particle sizes and structures that readily disperses into polymers, resins, plastics and rubbers. Carbon black is a by-product of combustion and being easily available has found applications in a wide variety of industries. For instance carbon black is added to natural rubber to form tyres with better wear characteristics, it is dispersed in printing inks for its dark colour and it is incorporated in high concentrations into polymers to form anti-static coating materials [45].

Due to carbon black being widely used in industry there is a vast amount of literature regarding its composite forms. This enables a detailed discussion of its percolation behaviour and we will use carbon black as an example. Furthermore

carbon black composites share many similarities with the composite used in this thesis and therefore it is a good starting point to discussing the expected electrical characteristics. As our interest is in the electrical conduction behaviour of composites when the filler is highly conductive and the matrix is a completely insulating medium that binds the filler. These highly conductive composites are explained with the use of percolation theory.

2.4.1 Percolation Theory

Percolation is a critical concept for the understanding of transport systems in disordered systems [48]. Percolation theory deals with the process of fluid flow in a random media, where the fluid could be water, electrons, or microbes and the media could be coffee granules, atomic structures or human populations. It has been used to successfully describe physical phenomena such as: how a solvent percolates through a solute; electron transport in an atomic lattice; or a disease infecting a community [49]. The pioneers for the mathematical description of percolation processes were Broadbent and Hammersley in the late 1950s [50].

The simplest way to picture a percolation network is to take a regular square lattice and randomly occupy sites with a probability, p . At a critical threshold, p_c , the first long range connection will occur called the *percolation threshold*. Now, imagine that each occupied sites is a wire with a resistance R and there are two contact points on each side of the lattice, A and B. Below the percolation threshold the total resistance, R_T , will be infinitely large as no current can flow (Fig. 2.10a). At the percolation threshold current can first start to flow and the resistance will be at a finite maximum, some multiple of R (Fig. 2.10b). As further sites are occupied more paths will be created that are in parallel to each other and therefore lowering R_T (Fig. 2.10c). This continues up to a maximum filling fraction, $p = 1$, where R_T will now be less than R .

2.4.2 Electrical Percolation

It was Kirkpatrick who first formally took the percolation theorems of Broadbent and Hammersley and applied them specifically to the problem of conductive particles in an insulating matrix [51]. In composites we can readily apply percolation theory as the conductive particles have conductances which are many orders of magnitude greater than the insulating matrix. At low filling fractions of filler, p , there are no current paths through the material and the resistance is high, if not infinite. As the conductive particles are added to the matrix at some critical volume filling fraction, which we also call p_c , the material makes a transition from being an insulator to conductor. As further particles are added the resistance quickly decreases. Eventually the matrix is saturated with particles and no more can be added. The conduction

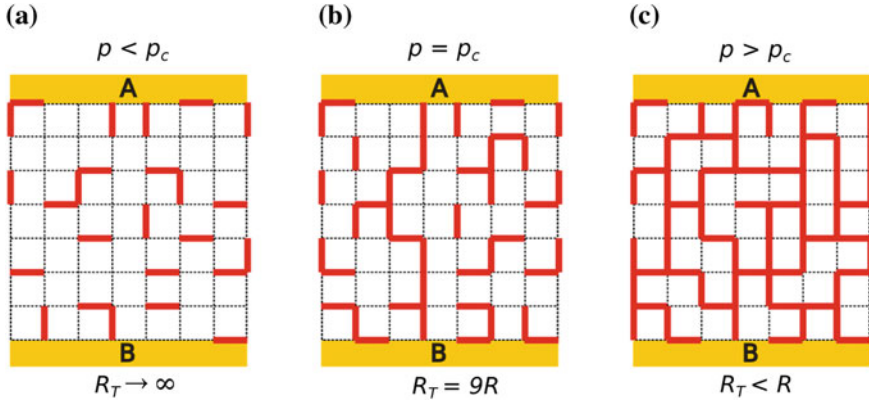


Fig. 2.10 As the probability, p , that a site is occupied increases, the total resistance, R_T , decrease from an infinite value for (a) with $p < p_c$; to a finite but large value at (b) with $p = p_c$; and then tends to a value less than R at (c) with $p > p_c$, as parallel conduction paths occur

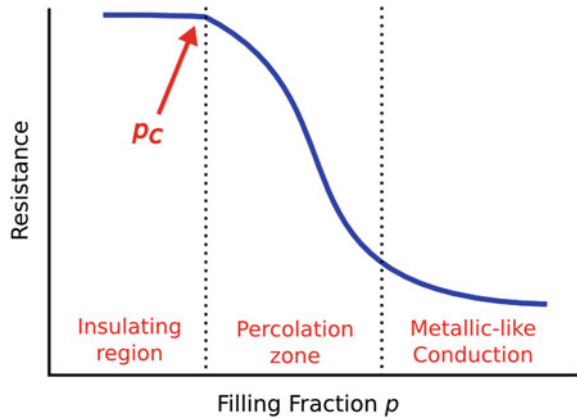
becomes almost metallic-like as the resistance tends to a minimum. This evolution is shown in Fig. 2.11.

Kirkpatrick was specifically interested in the conductance of 2D and 3D resistor networks and at what critical volume fraction they crossed the percolation threshold [51]. His work led to a simple power law dependence that could describe the DC electrical conductivity close to and above the percolation threshold,

$$\sigma \propto (p - p_c)^t, \quad (2.9)$$

where σ is the bulk composite conductivity, p the volume filling fraction of filler to insulating matrix, p_c the critical filling fraction and t the conduction coefficient.

Fig. 2.11 As the filling fraction of particles in the composite is increased there is a transition at the critical volume (percolation threshold), p_c , from insulator to conductor. The resistance decreases many orders of magnitude through the percolation zone



Computational modelling of the process described above yields the universal percolation theory predictions that in a 3D systems $p_c = 0.16$ and $t = 2.0$ [45, 49, 52]. The universal percolation theory is a ‘touching’ model that assumes that particles have to be in contact to conduct but that when they do there is zero contact resistance between them.

The power law can be tested for real composites by fabricating samples of different amounts of filler into the same amount of matrix and measuring the resistance. It can be shown that t is a function of the system geometry and p_c is a function of particle geometry, dispersion and the nature of the conduction between particles. Thus finding the values of p_c and t enables conclusions to be drawn regarding the nature of the particle dispersions and the percolation processes.

2.4.3 Carbon Black Example

In studying different carbon black composites with varying sizes and geometries of filler incorporated into different insulating mediums it was found, by Balberg, Carmona and many others, that often the expected values of p_c and t did not conform with the calculated values from universal percolation theory [45, 48, 52–55]. Much work has gone into understanding where the discrepancy arises and interpreting the values of t and p_c with respect to the conduction mechanisms in the composite and the nature of the particle dispersion.

To enable easy comparisons between different carbon black types they are categorised according to their structure. With a *low structure* corresponding to spherical well dispersed isolated particles and a *high structure* meaning either geometrically highly anisotropic particles that are long and thin, or particles with a tendency to agglomerate in large anisotropic clumps (Fig. 2.12).

It is found that generally the high structure particles have p_c and t values close to that of 0.16 and 2.0, following universal percolation theory. However the low structure particles tend to have t values as high as 6.4 [54], many times greater than predicted [49].

This is counter intuitive as the low structure particles should conform most closely to the universal percolation theory as they most closely resemble the theoretical ideal of an even dispersion. However, the universal percolation theory makes a central assumption that the conduction between particles is either on, touching, or off, not touching. This binary approach is not valid as electrons are able to tunnel, and hop, between particles that are not actually in physical contact.

If we examine our composites more closely we find that the particles dispersed in the insulating medium are likely to be encased in a thin layer of insulating medium. Experimental evidence shows that providing the medium is capable of a high degree of wetting and the particles have a tendency to disperse, then a surrounding insulating layer will *encapsulate* the particles [53]. Therefore true particle–particle contact will not occur due to the insulating buffer, unless p_c approaches 0.7 which is the maximum packing fraction of spheres. However, composites with the insulating buffer present

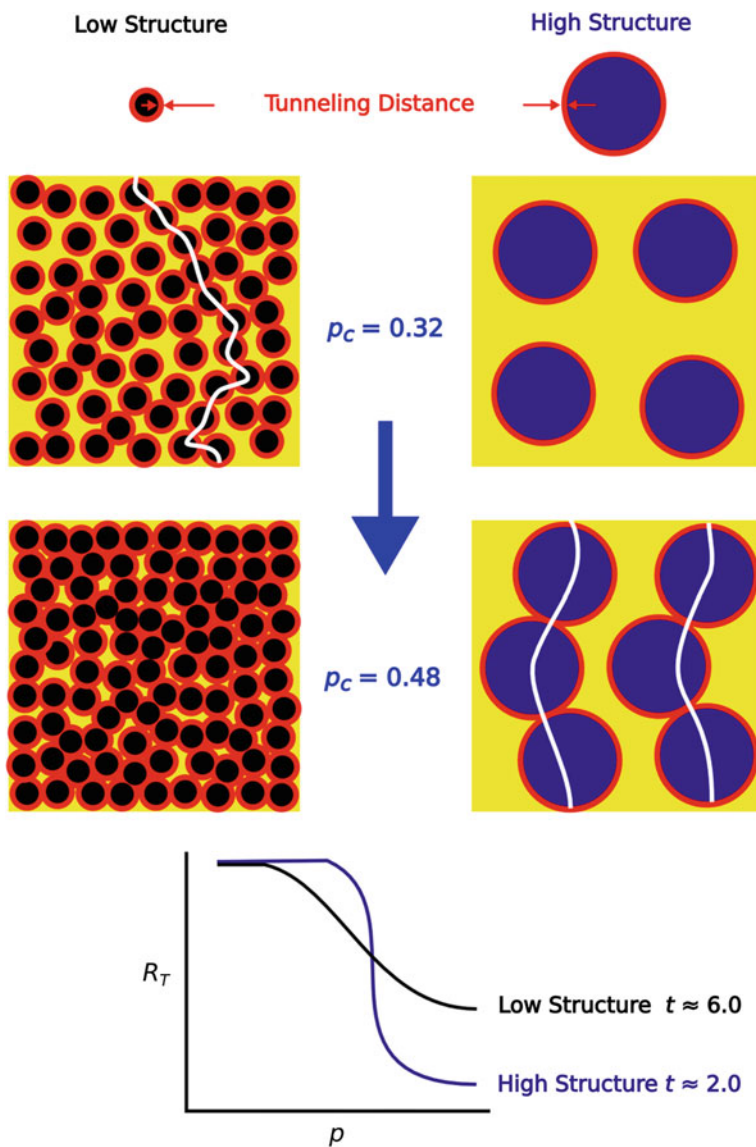


Fig. 2.12 A schematic to show the difference between low and high structure fillers in a composite. At two representative filling fractions, the low and high structure fillers clearly show very different behaviours. The low structure is able to reach the percolation threshold for a lower p however the high structure once it reaches the percolation threshold decreases in resistance at a much sharper rate. This is due to the resistance being less dependant on the tunneling between particles

around the filler are still able to conduct at much lower filling fractions than this. This means our mechanism for conduction, that underpins the percolation theory, is not ‘touching’. We must take into account the ability of the electrons to *tunnel* between particles to form conduction lines.

Thus the central assumption of the universal percolation theory of particle–particle touching must be adapted to include the effects of tunneling. At first the inclusion of tunneling might appear to completely undermine the idea of percolation. Instead of a system where particles are only electrically connected when they touch we now have the entire system of particles that are theoretically electronically connected to every other particle via tunneling. How these two apparently conflicting ideas are reconciled is that the probability of tunneling *exponentially decays* with separation distance. Therefore the tunneling is only likely to happen between particles that are closely separated. Typically tunneling distances are of the order 5–50 nm depending on the nature of the barrier and the materials that form it.

Percolation theory is still effective as only nearest neighbours are assumed to be able to tunnel but with an adjustment required to take into account tunneling which is a function of the distribution of distances between the particles. If we consider the resistance of a conduction line in the composite we must now sum the resistance of all the particles in the conduction path, R and sum the resistance of all the tunneling barriers between the particles:

$$R_T = \sum_{i=0}^n R + \sum_{i=0}^n R_c, \quad (2.10)$$

where R_c is a function describing the resistance encountered to tunneling. Simply put we can expect the universal percolation theory to hold when the sum of R_c is negligible compared to R , while for percolation systems where the resistance is dominated by R_c then we can expect non-universal percolation and $t > 2.0$.

In low structure systems, where the particles are small and well dispersed, we can expect that percolation will start at low filling fractions as tunneling will enable particles to connect without physically touching. However the resistance will only decrease slowly as with the addition of more particles the tunneling distances only decrease by a small amount and the medium surrounding the particles forces tunneling to always take place. Due to there being many particles in a percolation path there will always be many contacts, R_c , to include. Thus t will tend to a larger value as the conductivity only increases slowly but starts increasing at a lower threshold p_c (Fig. 2.12).

On the other hand for the high structure particles such as large agglomerates or highly anisotropic particles, the first percolation path will not occur until a higher critical volume fraction as there is a greater distance between the particles. However above the percolation threshold, as the particles are large, there are less tunneling barriers to be overcome in a percolation path and so the total resistance is not so dependant on tunneling. Thus t will tend towards values of 2.0, as for the universal percolation theory.

This situation is shown in Fig. 2.12, comparing equal filling fractions of large (high structure) and small (low structure) particles. The high structure has a much sharper percolation region, that onsets at a higher p_c and reaches a lower resistance. While the low structure reaches the percolation threshold sooner but cannot reach such a low resistance due to more numerous resistance critical tunneling barriers. The simple schematic in Fig. 2.12 has actually been confirmed experimentally by Hong through comparing like composites but with nano-sized fillers and micron sized filler [56]. Hong found that the percolation threshold of the nano-sized filler was 14 and 30 % for the micron sized particles. The onset of percolation is also shown to occur at the same average inter-particle distance, $\bar{b} = 45$ nm, calculated from:

$$\bar{b} = l \left[\left(\frac{\pi}{6p} \right)^{1/3} - 1 \right], \quad (2.11)$$

where l is the length of the particle and p is the filling fraction [56]. This gives a typical tunneling distance in these types of composites of 45 nm.

In summary the power law dependence from percolation theory is shown to be a good starting point for describing the conductivity in composites. However the impact of tunneling yields greater values of t in low structure composites. If the tunneling distance is large compared to the particle size then universal percolation theory doesn't apply; if the particle size is much greater than the tunneling distance then universal percolation theory does apply. We now consider the tunneling processes between the particles more closely.

2.5 Tunneling

Tunneling is a quantum mechanical process by which a particle can penetrate through a classically forbidden region. In considering electrons of energy, E , incident on a one dimensional rectangular barrier of height, ϕ , and width, b , classical mechanics dictates that when $E < \phi$ electrons will be unable to pass through the barrier. However in quantum mechanics while most electrons incident on the barrier are reflected, some are in fact transmitted through the barrier. The probability of electron transmission is given by $|T|^2$. The transmission probability for a one dimensional rectangular barrier when $E_z < \phi$ is,

$$|T|^2 = \frac{16E(\phi - E)}{\phi^2} \exp(-2bk_z) \quad (2.12)$$

where k_z is the value of the wave-vector through the barrier,

$$k_z = \sqrt{\frac{2m(\phi - E_z)}{\hbar^2}}. \quad (2.13)$$

The tunneling probability decays exponentially with barrier width, b . The importance of this has been discussed in the previous section where the average distance between particles in a composite strongly effects the overall resistance. Further the tunneling probability is also a function of the effective barrier height and the temperature, T .

We wish to calculate the overall current density through a single barrier system when the barrier is biased between the emitter and collector contacts by a potential, eV . The bias causes the barrier to become trapezoidal, shown in Fig. 2.13, and become increasingly *transparent* as electrons are able to more readily cross the barrier via thermionic emission.

We proceed by first finding an expression for the tunneling current through a metal-insulator-metal (M-I-M) barrier as a function of the available electronic states and the tunneling probability. The Wentzel-Kramers-Brillouin (WKB) approximation is utilized to obtain the transmission coefficient of the biased barrier and we eventually arrive at the generic Tsu-Esaki tunneling equation. We apply this in Chap. 4 to derive the I-V characteristics for a single graphite-silicone-graphite barrier.

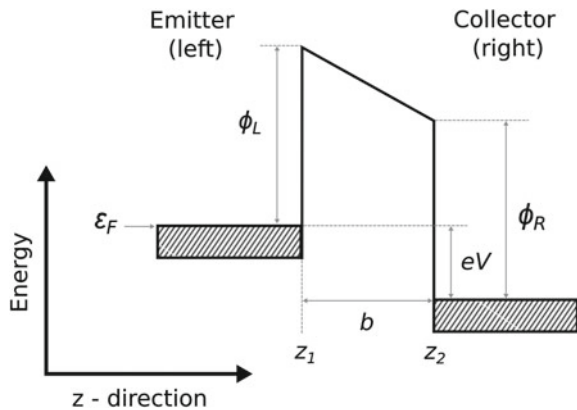
2.5.1 Current Density Through a Barrier

Current density, J , is defined as the product of the number of electrons per unit volume, n , the electronic charge, e , and the electron velocity, v , with,

$$J = nev. \quad (2.14)$$

Applying this for the tunneling barrier, shown in Fig. 2.13, the number of electrons per unit volume is given through summing over all the allowed electron states in k -space with a certain probability that each state is occupied, $f_L(E)$, given by the Fermi-Dirac distribution. The electron is only able to cross the insulator if there

Fig. 2.13 A one dimensional MIM barrier. Electrons are able to tunnel through the barrier of height, ϕ , and width, b , with probability $Z(E_z)$. The barrier is sloped due to the applied potential eV



is a corresponding unfilled allowed state on the the other side and so we multiply by $1 - f_R(E)$. For tunneling to occur we also need to account for the tunneling probability which we define as $Z(E_z) = |T|^2$. Thus our current density from left to right, emitter to collector, is given by,

$$J_{L \rightarrow R} = e \sum_k f_L(E)(1 - f_R(E))Z(E_z)v_z, \quad (2.15)$$

where v_z is the electron velocity in the z-direction over the barrier. Rather than taking the sum of all k-states, instead we integrate over the volume element of k-space using the three dimensional density of electron states per unit volume, $\frac{d^3k}{8\pi^3}$. We also take account of the two possible spin states of the electrons by multiplying by 2. Thus,

$$J_{L \rightarrow R} = 2e \int \frac{d^3k}{8\pi^3} f_L(E)(1 - f_R(E))Z(E_z)v_z. \quad (2.16)$$

Substituting in the electron velocity in the z-direction,

$$v_z = \frac{1}{\hbar} \frac{dE_z}{dk_z}, \quad (2.17)$$

and splitting k into its three elemental components $d^3k = dk_x dk_y dk_z$,

$$J_{L \rightarrow R} = \frac{2e}{8\pi^3} \int \int \int dk_x dk_y dk_z f_L(E)(1 - f_R(E))Z(E_z) \frac{1}{\hbar} \frac{dE_z}{dk_z}. \quad (2.18)$$

As the k_x and k_y states are symmetric and equivalent integrating over dk_x and dk_y is equivalent to integrating over a cross-section of the Fermi sphere, $k_{\parallel} 2\pi dk_{\parallel}$. Then by cancelling the dk_z terms gives,

$$J_{L \rightarrow R} = \frac{2e}{8\pi^3 \hbar} \int \int k_{\parallel} 2\pi dk_{\parallel} f_L(E)(1 - f_R(E))Z(E_z) dE_z. \quad (2.19)$$

From the kinetic energy relation for $k_{\parallel}$ we find,

$$\frac{dE_{\parallel}}{dk_{\parallel}} = \frac{\hbar^2 k_{\parallel}}{m}, \quad (2.20)$$

which leads to,

$$J_{L \rightarrow R} = \frac{em}{4\pi^2 \hbar^3} \int \int f_L(E)(1 - f_R(E))Z(E_z) dE_{\parallel} dE_z. \quad (2.21)$$

Next, we find the total current density over the barrier by subtracting the current going right to left, $J_T = J_{L \rightarrow R} - J_{R \rightarrow L}$. We assume that any directional dependence of $Z(E_z)$ is negligible to find:

$$J_T = \frac{2em}{(2\pi)^2 \hbar^3} \int \int (f_L(E) - f_R(E)) Z(E_z) dE_{\parallel} dE_z. \quad (2.22)$$

The total current density over the barrier has a double integral both over the energy in the z-direction, over the barrier, and the energy perpendicular to the barrier. The total energy of the system is given by the sum of these, $E_T = E_z + E_{\parallel}$. To evaluate J_T we first integrate the Fermi–Dirac functions for $E_{\parallel}$.

2.5.2 Supply Function

The Fermi–Dirac equation describes the probability that a state of energy E_T is occupied,

$$f = \frac{1}{1 + \exp(\beta(E_T - \epsilon_F))}, \quad (2.23)$$

where $\beta = \frac{1}{k_B T}$ and ϵ_F is the Fermi-energy. To evaluate the integrals of f_L and f_R over $E_{\parallel}$ we take the limits from the minimum energy to infinity,

$$F_L = \int f_L dE_{\parallel} = \int_{\epsilon_F}^{\infty} \frac{1}{1 + \exp(\beta(E_{\parallel} + E_z - \epsilon_F))} dE_{\parallel} \quad (2.24)$$

$$F_R = \int f_R dE_{\parallel} = \int_{\epsilon_F + eV}^{\infty} \frac{1}{1 + \exp(\beta(E_{\parallel} + E_z - \epsilon_F))} dE_{\parallel}. \quad (2.25)$$

Using the identity,

$$\int \frac{1}{1 + \exp(x)} dx = \ln \left(\frac{1}{1 + \exp(-x)} \right), \quad (2.26)$$

we can integrate f_L over $E_{\parallel}$,

$$\begin{aligned} F_L &= \frac{1}{\beta} \left[\ln \left(\frac{1}{1 + \exp(-\beta(E_{\parallel} + E_z - \epsilon_F))} \right) \right]_{\epsilon_F}^{\infty} \\ &= 0 - \frac{1}{\beta} \ln \left(\frac{1}{1 + \exp(-\beta E_z)} \right). \end{aligned} \quad (2.27)$$

We do a similar operation for f_R ,

$$\begin{aligned} F_R &= \frac{1}{\beta} \left[\ln \left(\frac{1}{1 + \exp(-\beta(E_{\parallel} + E_z - \epsilon_F))} \right) \right]_{\epsilon_F + eV}^{\infty} \\ &= 0 - \frac{1}{\beta} \ln \left(\frac{1}{1 + \exp(-\beta(E_z + eV))} \right). \end{aligned} \quad (2.28)$$

We then subtract left from right as from Eq. (2.22),

$$F_L - F_R = \frac{1}{\beta} \ln \left(\frac{1}{1 + \exp(-\beta(E_z + eV))} \right) - \frac{1}{\beta} \ln \left(\frac{1}{1 + \exp(-\beta E_z)} \right) \quad (2.29)$$

$$= \ln \left(\frac{1 + \exp(-\beta E_z)}{1 + \exp(-\beta(E_z + eV))} \right). \quad (2.30)$$

We have integrated the distribution of states in the emitter, minus the states in the collector, that are perpendicular to the barrier to arrive at the *supply function*. The supply function describes the number of electrons in energy interval, E_z to $E_z + dE_z$ that are available to tunnel.

2.5.3 Tunneling Probability

Now we turn our attention to finding the tunneling probability, $Z(E_z)$, for which we utilize the WKB approximation. This is a semi classical approximation for the wave function through the barrier which provides a good solution provided that the potential varies slowly with z and that the barrier is not too thin [57]. For the sloped barrier in Fig. 2.13 the potential is a linear function of z and thus the WKB approximation states,

$$Z(E_z) \simeq \exp \left(-2 \int_{z_L}^{z_R} |k_z| dz \right), \quad (2.31)$$

where k_z is the value of the wave vector in the barrier from z_L to z_R . If barrier was rectangular we would easily find,

$$Z(E_z) \simeq \exp(-2bk_z), \quad (2.32)$$

where $b = z_R - z_L$, the barrier width. This is the same result as given in Eq. (2.12). However the applied potential eV means the barrier becomes sloped. We define $U(z)$ as the linear dependence of potential variation through the barrier with,

$$U(z) = \phi - \gamma(z - z_L). \quad (2.33)$$

Which makes the tunneling probability,

$$Z(E_z) \simeq \exp \left(\frac{-2\sqrt{2m}}{\hbar} \int_{z_L}^{z_R} (U(z) - E_z)^{1/2} dz \right). \quad (2.34)$$

If we now make a substitution with X where

$$X = \frac{2m(\phi - \gamma(z - z_L) - E_z)}{\hbar^2}, \quad (2.35)$$

and

$$\frac{dX}{dz} = \frac{-2m\gamma}{\hbar^2}, \quad (2.36)$$

we arrive at a single integral of,

$$Z(X) = \exp \left(\frac{\hbar^2}{m\gamma} \int_{X_1}^{X_2} X^{1/2} dX \right). \quad (2.37)$$

Integrating and replace X from the substitution yields,

$$Z(E_z) = \exp \left(\frac{2\hbar^2}{3m\gamma} \left[X^{3/2} \right]_{X_1}^{X_2} \right), \quad (2.38)$$

$$\begin{aligned} Z(E_z) = \exp \left(\frac{2\hbar^2}{3m\gamma} \left(\left[\frac{2m(\phi - \gamma(z_2 - z_1) - E_z)}{\hbar^2} \right]^{3/2} \right. \right. \\ \left. \left. - \left[\frac{2m(\phi - \gamma(z_1 - z_1) - E_z)}{\hbar^2} \right]^{3/2} \right) \right). \end{aligned} \quad (2.39)$$

As the slope of the barrier is linear $\gamma = eV/b$ and $\gamma(z_2 - z_1) = eV$ and so we find,

$$Z = \exp \left(\frac{-4(2m)^{1/2}b}{3eV\hbar} \left[(\phi - E_z)^{3/2} - (\phi - E_z - eV)^{3/2} \right] \right), \quad (2.40)$$

the *tunneling probability* in a linearly *sloped* barrier.

2.5.4 Tsu-Esaki Equation

Combining the Fermi–Dirac distributions integrated over $E_{\parallel}$ and the tunneling probability in the sloped barrier we arrive at,

$$J = \frac{2emk_B T}{(2\pi)^2 \hbar^3} \int_{\epsilon_F}^{\infty} Z(E_z) F(E_z) dE_z, \quad (2.41)$$

where

$$F(E_z) = \ln \left(\frac{1 + \exp(-\beta E_z)}{1 + \exp(-\beta(E_z + eV))} \right), \quad (2.42)$$

and

$$Z(E_z) = \exp \left(\frac{-4(2m)^{1/2} b}{3eV\hbar} \left[(\phi - E_z)^{3/2} - (\phi - E_z - eV)^{3/2} \right] \right). \quad (2.43)$$

This is a very general result that can be readily applied to many tunneling situations such as MIM systems and super-lattices with multiple barriers [58]. It is possible to find exact analytical solutions for certain situations through either assuming; low temperatures, $T \rightarrow 0$; a low applied potential; or a very high applied potential. In the instance of a high potential we have a triangular barrier and we arrive at the Fowler–Nordheim tunneling equation [57]. In the Sect. 4.3 we solve Eq. (2.41) numerically for a graphite-silicone-graphite barrier in order to model the theoretical I-V curves for a single barrier system and in the process extract the height of the silicone barrier.

2.6 Summary

The aim of this chapter was to discuss some of the underlying physics behind carbon and the nature of conduction in carbon-based composites.

Graphite was shown to be a semi-metal and graphene a zero band-gap semiconductor with the significance of its linear E - $\mathbf{k}$ dispersion briefly explained. The tight binding model was applied to bilayer graphene to show that it has an electric field *tunable band-gap*. This will certainly be of interest in the next chapter where we discuss the origins of the NDR mechanism.

Next we considered percolation theory in relation to conductive composites. The concept of electrons ‘percolating’ through a network of conductive particles, forming conduction lines, will be of particular interest in Sect. 5.4, where conduction line destruction through perturbations will be used in differential pressure detection.

Experimental work with carbon black composites was used to show that the universal percolation theory is not always correct. Instead a non-universal percolation theory is required that includes the ability of electrons to *tunnel* between particles due

to *encapsulation* of the insulation matrix. This highlights the importance of tunneling between particles in the conduction lines.

A general tunneling equation was derived, based on a MIM barrier, to describe the current through the barrier. We have included the effect of a potential that causes the barrier to become increasingly *transparent* for higher biases. We use this in Sect. 4.3 to model the I-V characteristics of single graphite-silicone-graphite barrier.

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