Theory, Experiment and Applications of Graphene Nano-Flakes

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Abstract

Although considerable attention has been given to the unique properties of graphene membranes and graphene nanoribbons, graphene nano-flakes offer a greater range of structural configurations and potential for a range of applications. In contrast, far fewer studies have focused on these tiny quasi-zero dimensional materials, but preliminary work is showing great promise. In this review, research on the structure, stability, properties and prototypes and graphene nano-flakes has been gathered and compared, to outline the current understanding in the field, and highlight the various questions that remain to be answered.

1. Introduction

The experimental isolation of graphene[1] was one of the greatest discoveries in materials physics for many years, although it had been first envisaged over 60 years ago [2]. From a physical perspective graphene is a large 2-D sheet or membrane of sp^2 bonded carbon atoms, which we will term graphene membranes (GMBs). The basic structure of GMBs is that of fused hexagonal rings of aromatic benzene, with a nearest neighbour distance of 1.42 Å and bond angles of 120º, so one may also regard GMBs as giant aromatic molecules. If the edges are hydrogenated, these are often termed polycyclic aromatic hydrocarbons (PAH's) [3,4]. Another useful way of thinking about at these structures is as two interpenetrating trigonal lattices, labeled A- and B-. But the important point here is that all of these descriptions and metaphors are referring to the same thing.

Since this experimental discovery there has been an enormous amount of theoretical and experimental interest in graphene, because graphene has been found to exhibit an array of exceptional properties, including very fast electron transport, room temperature quantum hall effect, the highest mechanical strength and greatest thermal conductivity yet measured [5,6]. In particular its fascinating electrical properties have led to the speculation that graphene may one day replace silicon as the material of choice for most electronic applications [7]. Despite having many exceptional properties GBMs have one very severe limitation from the point of view of electronics applications; they have no band-gap and a vanishingly small density of states at the Fermi level, making them a semi-metal [5,6]. Several methods have been suggested to induce a band gap in graphene and thus overcome this fundamental limitation.

One method is to cut a GMB into nanoribbons GNRs, which may produce a band-gap, depending on the width [5,6,8]. The reason for the appearance of a gap is that along with the finite width edge states begin to play a significant role in modifying the electronic properties, and a significant number of atoms reside at the edges. There are two major types of idealized edge states, zigzag (ZZ) and armchair (AC), as can be seen on the tops and sides respectively of the structure represented in figure 1. It has been shown that GNRs can be metals, semiconductors, half-metals, feromomagnets and antiferomagnets depending on their edge structures, width, shape and chemical termination [5,6,9,10,11]. However, this critical dependence of their properties on their edge states also leads to new limitations in terms of fabrication (for use in electronic devices) because it is difficult to consistently and reliably produce GNRs with edge states of a particular type. Another limitation

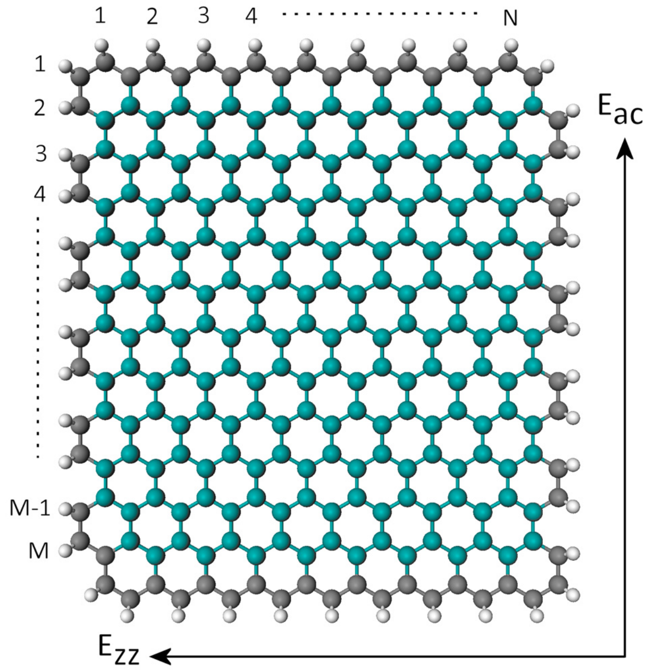

Figure 1. The basic type of structure of GNFs, showing zigzag edges (E_{zz}) and armchair edges (E_{ac}), passivated with hydrogen atoms.

is that the cutting of GMBs into GNRs leads to electron mobility degradation and loss of performance in devices.

The zero-dimensional (0-D) form of graphene, which may be called graphene nano-flakes (GNFs) or graphene nano-dots (GNDs) has also been produced, but has been much less extensively studied than GMBs or GNRs. This is surprising given that preliminary studies indicated they have a range of properties which differ from those of 2-D and 1-D graphene, and offer great potential for a variety of electronic and magnetic applications. Their desirable properties arise because GNFs possess corner states in addition to edge states, and may also be cut into a much larger variety of different shapes. GNFs have a much larger number of configurational degrees of freedom. In figure 2 we see some examples of different shapes which are possible with GNFs, and the different types of corners that can be introduced via simple combinations of zigzag and armchair edges.

Furthermore, in contrast to GNRs, GNFs can potentially range in size from molecular to semi-infinite 2-D structures, and consequently their electronic structures will vary from having discrete molecular levels to being band-like as their dimensions are made larger. This leads to the potential of spanning the range of electronic and magnetic properties from molecular to 2-D by using GNFs of different dimensions. Of course, just as we see in GMBs and GNRs, GNFs also have their own inherent limitations, as we shall see in later sections.

In this review we give an outline of how GNF structures may be created, give a theoretical description of structure and stability, the electronic structure and basic characteristics. We then outline some of the potential applications of GNFs in the areas of electronic and magnetic devices. Where there exists a large literature which is particularly the case for GMBs and GNRs but also in

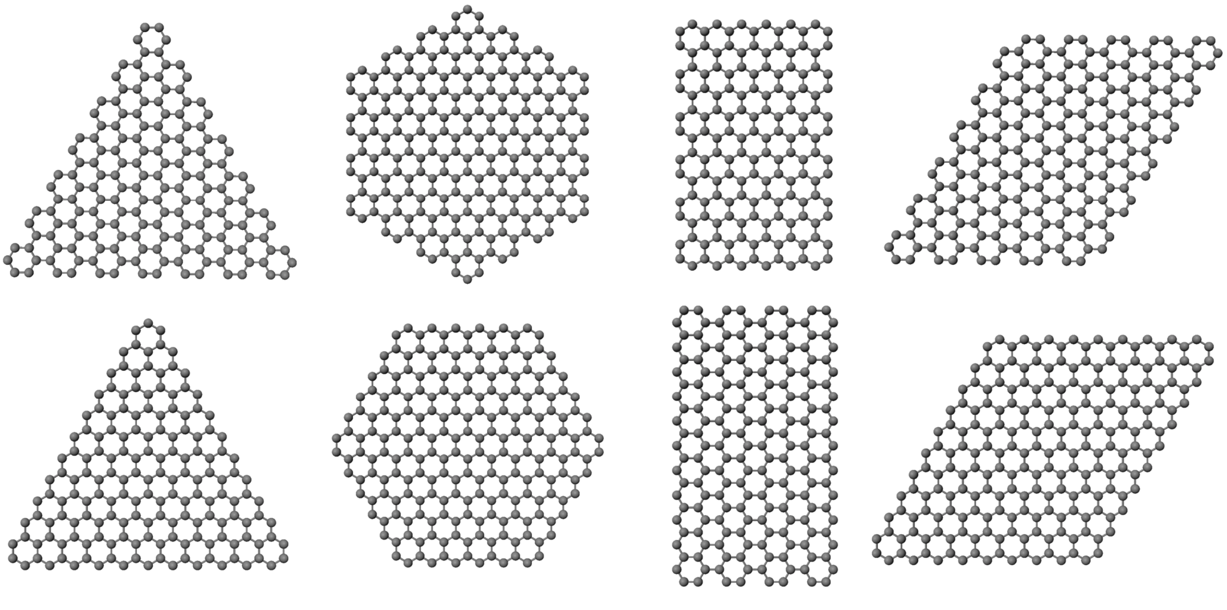

Figure 2. This shows a variety of possible GNF shapes which might be produced with different geometries and corners, but always terminated with either zigzag or armchair edges.

some areas on GNFs (particularly in the area of synthesis) we have attempted to reference comprehensive and up-to-date reviews in order to keep this review within reasonable limits.

2. The production of GNFs

As stated in the introduction graphenes consist of fused, combinations of hexagons of sp^2-bonded carbon atoms referred to as rings. Therefore, the lower end of the graphene length scale is naturally occupied by a benzene radical, or if terminated by hydrogen atoms, benzene. At the extreme upper end of the length scale we have an infinite 2-D graphene membrane. These limiting cases are usually treated by chemists or materials engineers, respectively, with materials physics spanning the sizes in between [12]. Depending on perspective, two different approaches have been used to make GNFs, referred to as *bottom-up* and *top-down*.

2.1 Bottom-up production of GNFs

As suggested above, these are essentially chemical methods of production that draw upon the well established chemistry of aromatic molecules. Small molecular units are combined form large aromatic hydrocarbons by a large variety of chemical reactions [3,4]. To date, the largest structure produced via this route is a GNF consisting of 222 rings. A variety of terminations have been added to these structures, including hydrogen and alkyl groups [3,4], and GNFs have been combined and assembled into complex structures and films. Bottom-up synthesis is usually performed in solution by mechanical extrusion, zone casting/refining, aligned substrate, magnetic field alignment and thermal annealing [3,4], but can also be achieved in vacuum using soft-landing mass spectrometry [13].

2.2 Top-down production of GNFs

Beginning with a large piece of graphene (or graphene related material such as graphene oxide) this approach involves cutting GNFs directly into desired sizes and shapes. These methods usually produce graphene islands in a membrane of graphene, which are effectively non-free standing GNFs that are often quite large. Such structures are then usually referred to as graphene quantum dots (GQDs) [14]. Naturally, top-down synthesis necessitates the initial production of GMBs, which may be done via micromechanical cleaving of a graphite single crystal [1], via chemical routes starting from graphite oxide [15], or by chemically “unzipping” carbon nanotubes or fullerenes [16,17].

Graphene layers have also been produced on surfaces, either by removal of layers from a SiC crystal surface [18] or by chemical vapour deposition [19]. Presumably some or all of these techniques could be adapted to produce graphene GNFs.

Once sheets of 2-D graphene are produced, GNFs have to be “cut”. This can be done my combined e-beam lithography and plasma etching [20,21,22,23], chemical stripping [24], scanning tunneling microscope lithography [25] and atomic force microscope lithography [23], hydrocarbon lithography [26] and catalytic cutting by atoms [27,28,29,30]. Standard e-beam lithography methods seem to be limited to producing features >10 nm, but scanning tunneling microscope lithography can produce much smaller features with pre-determined crystallographic orientations [25]. In contrast, catalytic cutting can produce GNFs with very clean edges with definite edge geometries. This method was first developed using Fe atoms for multi-layered structures [27] and later adapted [28,29,30] to produce single layer nanostructures. Being able to produce definite edge geometries is very important in determining the properties of GNFs so these techniques look very promising.

2.3 Production of GNFs by Functionalization

Processing graphene by traditional methods is challenging, as graphene is hydrophobic and is therefore difficult to solubilize or disperse in most liquids. For this reason chemists have spent considerable effort in functionalizing graphenes to improve solubility or dispersion, especially in water. GNFs produced using bottom-up approaches (above) have the advantage of being constructed from organic molecules which have solubilizing groups already attached before the GNF is synthesized. For example, it has been previously shown that during the chemical production of graphenes one can avoid using graphene oxide [31]. However, other methods have been developed to make larger top-down GNFs more soluble in a variety of solvents such as water and tetrahydrofurane [32]. Groups such as carboxyl epoxy and hydroxyl are commonly used to solubilize in water and long alkyl chains make GNFs soluble in many organic solvents.

Unfortunately, many of these methods produce heterogeneous, non-stoichiometric functionalized products which contain defects that usually degrade their properties. However, in some cases adsorbed groups may lead to the new and interesting behavior. For example, the optical properties of GNFs may be tailored by use of different attached groups, and this may open up the possibility of using graphene in optical applications [32].

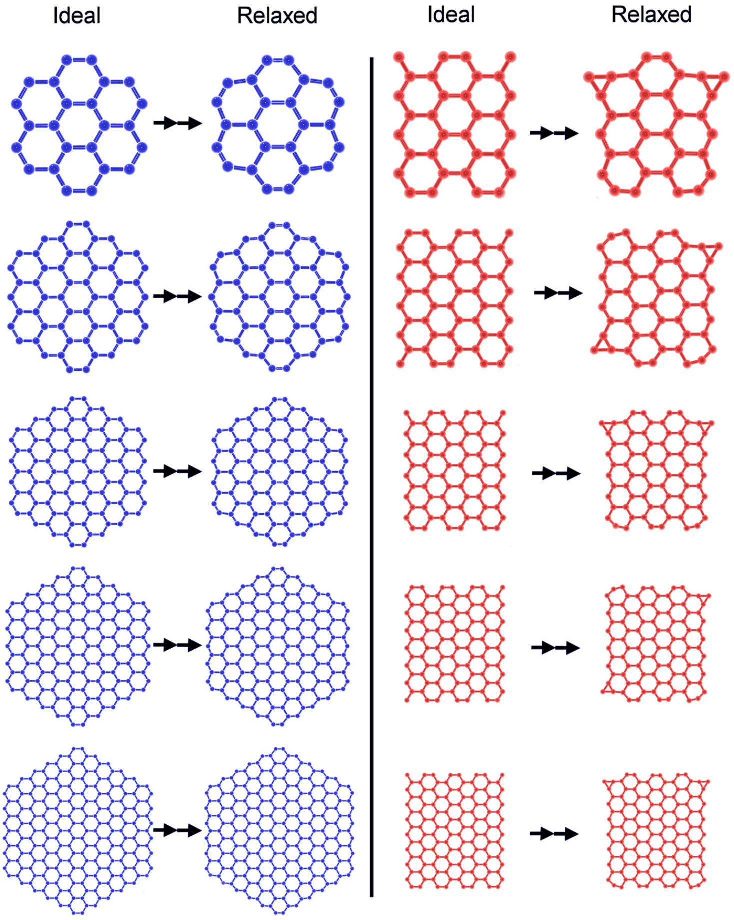

Figure 3. The initial (ideal) structures on the left and final relaxed structures on the right for all symmetric (left) and asymmetric (right) structures obtained by DFT [33].

2.4 Production of GNFs by Confinement

As an alternative to producing regions of a material with actual physical boundaries (as discussed above), one of the standard methods of producing semiconducting nanodots is to confine a region of a bulk material by using an electrostatic potential (a gate potential) to produce a confined structure. The confinement of electrons in such regions of graphene, by use of potentials, is not straightforward as the relativistic nature of the electronic excitations leads to Klein tunneling where these electrons can tunnel unimpeded through such barriers [5,6]. Methods such as creating a confinement potential within the graphene layer to trap an electron for a finite time, the introduction of a finite gap by coupling with the substrate or by using a bilayer, or the use of a magnetic confinement potential have been suggested to overcome this problem. The review by Abergel et al. gives an excellent and comprehensive summary and explanation of such methods [6].

3. Structure and stability of GNFs

In the introduction we discussed the idealized structures of GNFs, however, in practice real structures may differ considerable from these idealizations. In this section we will discuss some more realistic features of the structure of GNFs.

3.1 Edge and corner reconstructions

The first factor one must consider when studying realistic GNFs is that, if the edges and corners of the GNF are un-terminated, then reconstructions will occur, breaking the aromaticity and lowering the total energy of the flake. Depending on the shape, the effects can be minimal, or quite extreme, as we can see from the relaxed structures of the GNFs obtained by density functional theory (DFT) calculations [33] shown in figure 3. Reconstructions are generally more severe at highly under-coordinated feature such as corners, and differ on zigzag and armchair edges. Moreover, although rarely observed, other types of reconstructed zigzags and armchairs edges are possible [34,35,36] as well as *chiral* edges arising from unconventional "cuttings" [37]. Far from being an unavoidable hindrance, unique reconstructions may be developed, by controlling the ratio of edges and corners, and can offer further potential to tailor the edge states of different shaped GNFs.

3.2 Defects, adsorption, impurities and doping

It was recognized very early on in the study of graphene nanomaterials that defects occur with remarkable frequency, and that they may perturb the properties of the material [34,38]. In many cases the effect of defects has been shown to be detrimental, but in some cases they may be useful and introduce new properties (such as magnetism) or improve performance [38]. Native vacancy defects have a non-zero probability of occurring naturally, as a consequence of the fabrication processes, or through interaction with the substrate and with the environment, but may also be deliberately produced by an electron or ion beam.

In addition to native vacancy defects, several types of defects have been predicted and/or observed [39]. Some of the earliest defects types identified in graphene were point defects and Stone-Wales (SW) defects [40], which consists of two pentagons adjacent to two heptagons. One of the most interesting recent developments is the suggestion that an extended one-dimensional defect made of paired pentagons and octagons may function as a conducting nano-wire, which could become very useful in the development of graphene-based electronics [39]. Defects may also be of use in creating spintronic devices, making microfluidic channels, forming porous membranes, and offering active sites where controlled chemical reactions could take place.

There is also theoretical and experimental evidence that SW-type defects represent preferred sites for atomic and molecular attachment and may be of benefit in modifying the properties of pure graphene structures. This may very well be a way of increasing the capacity of graphene to adsorb hydrogen, and ultimately lead to a solution to the long standing question of providing a viable way of storing hydrogen to be used as a fuel.

Other related "defects" include adsorbed atoms and molecules (which, as mentioned above, may "decorate" native defect sites), incidental impurities, and functional impurities such as dopants. One may also regard the attachment of functional groups to the periphery (or to defect sites) of graphenes as an "impurity", particularly when they are non-functional, as they have the potential to quell the properties of pure graphene structures. It should also be highlighted that adsorbates, defects and the attachment of functional groups to graphenes may change their structure (as well as their properties) and/or lead to non-planarity of the system. This will be particularly severe for small GNFs.

There is a growing literature on defects, doping and adsorption in graphene but most of this is concerned with GMBs and GNRs and not with GNFs, so there is a need and an opportunity for new research in this area. In particular, since GNFs are of finite size, the properties of a defect can dominate the structure, depending on the size and defect density. If the GNF is small, a high fraction of atoms will either participate in (or be in the vicinity of) a defect, and this may have a consequence for the thermal/chemical stability and structural integrity. In addition to this, while the opportunities for traditional defect patterning of GNFs may be limited by the finite size, new opportunities are introduced when one considers combinations of defects, edges and corners.

3.3 Vibrational states and ripples

When researching the properties and applications of graphenes, one must also remember that the structures outlined above are static in time (if computational), or represent a statistical average over time (if experimental), and that vibrational states occur around these values. These states have been well studied in GMBs and in GNRs [41,42] but do not appear to have been extensively studied for GNFs. This is a problem that needs to be addressed as these vibrational states lead to Raman and/or infrared spectra which are very useful in identifying the structure of graphenes. The characteristic Raman G-band of graphene has been extensively used to differentiate single, double and multi-layer graphenes [41,42], as has the low frequency breathing modes of carbon nanotubes. These are considered signatures of these materials, and are suggestive of a similar signature being possible for small fragments of graphene.

Another important contribution from vibrational effects is to the thermal conductivity of graphene. While one can argue that this is more important for GMBs because of their large thermal conductivity, the importance for GNFs remains largely unexplored.

Finally, at finite temperature (T), graphene structures develop ripples [5,6,43] in addition to normal modes. This was first seen in GMBs, and has now been shown theoretically [44] to be a fundamental characteristic of graphene. A truly 2-D crystal with harmonic forces is unstable for T > 0K, so this rippling is presumably the mechanism by which this instability is overcome. Although these structures are still composed of a single layer of C atoms, planarity is no longer preserved, and the structures is no longer mathematically 2-D. It has also been shown by *ab initio* molecular dynamics calculations that similar large scale vibrational modes occur in GNFs [33,45] as shown in figure 4.

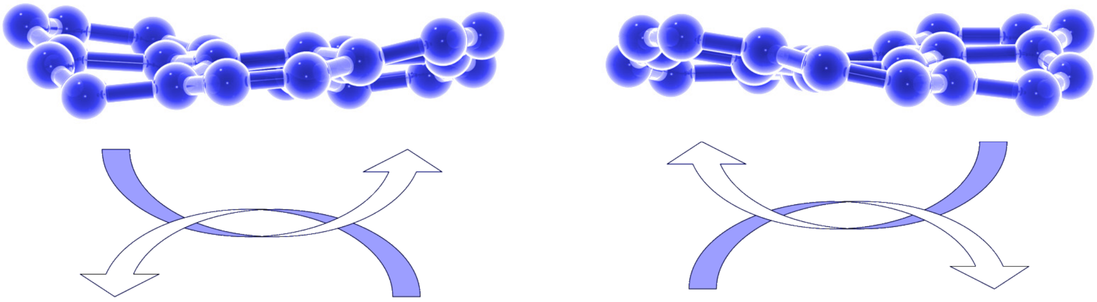

Figure 4. Examples of the saddle-like distortions of the symmetric C_{24} flake, annealed at 900 K. A dynamical rocking between these structures is observed following equilibration [33].

4. Electronic structure and magnetic behavior of GNFs

One of the first and continuing interests in graphene membranes is in their fascinating electronic properties which we will only briefly outline here as there exists a large and growing literature on this topic [5,6]. In this review we will only give a brief outline of some of the fundamental aspects and their consequences for the particular case of GNFs.

4.1 The electronic structure of GMBs

As mentioned above, the 2-D hexagonal lattice structure of GMBs may be looked on as two triangular lattice A- and B- , the reason for this is (as Wallace ^{2} used a Huckel model to show) that the highest electronic states can be described by occupied π and and unoccupied π* bands which meet only at the K and K* points in reciprocal space on the Fermi surface. This is why no band gap exists and as there is also a vanishing density of states at these points making 2-D graphene a semi-metal (or zero-bandgap semiconductor). The elementary excited electronic states show a linear dispersion relationship similar to massless, chiral, relativistic particles and are now termed *Dirac Fermions*. This leads to the electron intrinsic mobility being much higher than in silicon, and suggests that faster electronics can be made from graphene, but the zero-gap restricts graphene from replacing the majority of current Si-based electronic devices.

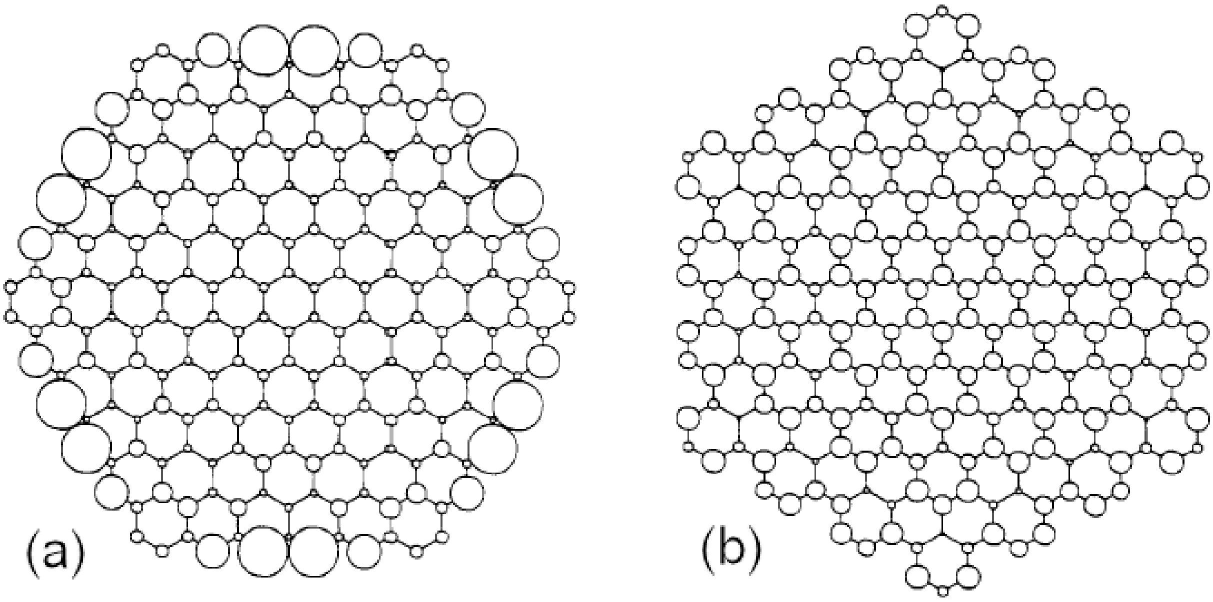

Figure 5. The spatial distribution of populations of the HOMO level for GNFs having (a) zigzag edges and (b) having armchair edges (adapted from reference 58).

4.2 The effect of edges on the electronic structure of graphene

As we have discussed, the simplest way to modify the electronic structure of GMBs is the introduction of edges and corners. As we know there are two basic types of edge structures, zigzag and armchair as displayed in figures 1 and 2, and that these edges contain dangling ("unsatisfied") bonds. This introduces a mixture of sp^2 and sp hybridization into the basic sp^2 graphene lattice unless the edges are chemically bonded to non-carbon atoms or functional groups (see figure 1). Both un-terminated and terminated edge structures can alter the basic electronic structure and play a crucial role in determining the electronic and magnetic properties of finite structures (see figure 5).

Since GNFs have a higher fraction of atoms residing at edges and corners, this effect is magnified. In particular, corner states are unique to GNFs and are likely to be invaluable for a variety of purposes. However, since far fewer atoms reside at or near corners and (even in complicated shapes) the corner-to-edge ratio is very low, it is imperative that the nano-flakes be kept small. The effect of edge states on electronic and magnetic behaviour has been most extensively studied for GNRs (which have a finite band gap), so at this stage we will selectively summarize some findings of relevance to GNFs [5,6,9,10,46,46].

GNRs are semiconducting although the origin of the gap is different in each case, and depends on the type of edges. Zigzag edges introduce localized states, but since opposite edges of such a GNR belong to different sub-lattices so the spin ordering is different on each edge. Zigzag edges can create ferromagnetic (FM) or antiferromagnetic (AFM) phases, and large magnetic moments occur at ZZ edges. There are no localized states at AC edges, and magnetic phases. Zigzag terminated GNRs may be useful in the field of spintronics, whereas AC edges may not. It has also been found theoretically that AC edged GNRs can be metallic but this has been suggested to be due to the limitations of the tight binding model used in these studies to describe their electronic structure.

Of course, functionalization (or passivation) of edges can significantly change the properties of GNRs with either AC or ZZ edges, and in the latter case this can generate a fully spin polarized state. In an applied electric field ZZ terminated GNRs can produce a ½ metallic states.

Finally, in this review we have ignored few layered GNFs and large stacks of GNFs both of which have been the subject of theoretical and experimental interest. Such structures can have properties which differ from those of single GNFs, and of graphite nanocrystals, often in a beneficial way [6,47]. For example, bilayer GNFs have a different band gap than single layer GNDs and electrons in such structures may be confined with potential barriers in contrast to single layer GNFs [6].

4.3 The transition from discrete to band-like electronic states in GNFs

Small GNFs have discrete, molecular electronic energy levels, so the energy of the highest occupied molecular orbital (HOMO) takes the place of the Fermi energy (E_f) and the difference in the energies of the HOMO and that of the lowest unoccupied molecular orbital (LUMO) corresponds to the energy gap (E_g). GNFs only have a continuous band structure when their dimensions are very large [48]. Along with this basic change in the nature of the electronic levels there is also a consequent change in electrical character from insulator to semiconductor, and then to small or zero energy gap material. In the case of very small GNFs the details of this discrete electronic structure can vary strongly with their shape and dimensions, and can be heavily influenced by passivation or functionalization.

4.4 Some interesting results for simple geometric shapes

There have been a small but growing number of studies of the electronic states of GNFs using a variety of techniques such as tight binding models (TBMs), Hubbard models (HM), density functional theory (DFT) and the Dirac equation (DE). In these studies a variety of different shapes have been investigated including squares, rectangles, circles, triangles, disks, hexagonal, polygonal and disordered non-symmetric shapes.

4.4.1 Squares and rectangles

It has been shown for square and rectangular shaped GNFs (GNRs of finite length) that the band gap may be readily manipulated by altering the width of the GNF [49]. A study GNFs with AC edges showed that unlike infinite GNRs they can be metallic [50] and half-metallic states have also been predicted by DFT calculations with ZZ edges in the presence of an electric field [46,51]. The smallest rectangular GNFs consisting of a chain of *n*- fused benzene rings (acenes) have been shown to have an AFM ground state for $n > 7$ [52].

The effect of functionalization and doping rectangular GNFs by the H, N, O, F, V atoms and by groups such as –OH, $-CH_3$ has also been studied by means of DFT calculations which showed that the electronic and magnetic properties of GNFs may be readily manipulated by these means [51,53,54,55,56]. This leads to the expectation that they may be extremely useful in areas such as spintropics, sensors and transistors [57].

4.4.2 Nanodisks

The electronic structure of a variety of compact structures based highly symmetrical shapes such as large PAHs, triangular, hexagonal and other polygonal shapes, which are often referred to as *nanodisks*, have been studied by several groups [58,59,60,61,62,63]. The results show that their electronic and magnetic structure may be varied considerably by changing the shape and size of the nanodisk, or via suitable functionalization, which prompts interest from fields such as spintronics.

4.4.3 Complex shapes

Some research has begun into investigating the properties of more complicated shapes [64,65,66] and because of the variety of shapes that GNFs can exist in they are ideal candidates for such studies. However, a complication arises because the relative energies of the various possible phases (AFM, FM, metal, semiconducting, ½ metal, non-magnetic) have to be predetermined in order to find the most stable state. This is usually done by means of extensive and time consuming calculations so there have been various methods suggested to circumvent this problem using simple rules to predict these stabilities [66,67,68,69,70]. These methods are based on the underlying geometry and topology of the structures (utilizing the two A- and B- sub-lattices). Such methods are assumed to be invaluable in the design of GNF structures for spintronics applications [71,72,73,74], and is enhanced by work showing the magnetic behavior of GNFs is very robust to disorder [75,76].

5. Graphane nano-flakes

We have already introduced the simplest GNF; benzene, which is a planar six membered ring of C atoms each being terminated by a single H atom (monohydride). However, there is another stable six membered ring of C atoms; cyclohexane, which is a non-planar structure in which the C atoms are terminated by two H atoms (dihydride). If a GMB is completely hydrogenated on all carbon atoms on both sides of the sheet, then the resulting structure, called graphane, is non-planar and consists entirely of sp^3 bonded carbon atoms and two sigma bonded hydrogen atoms per C atom. This structure was predicted computationally by means of DFT calculations [77] and subsequently discovered experimentally [78,79]. As graphane is an insulator it may be an ideal material to use in combination with graphene to form hybrid graphene/graphane integrated electronic devices and detectors. However, there remains the problem of how to “connect” these two materials together in an integrated hybrid device. Two recent theoretical studies have suggested ways that this might be achieved.

In one study [80], tight binding density functional theory (DFTB) was used to show that if a graphene nano-flake were anionically charged by adding excess electrons (for example by means of an electron beam or space charging) then beyond a certain level of added charge regions of the GNF would transform into hydrogen-less graphane. A sample of these results are shown in figure 6, where we can see that the graphene/graphane ratio, and the graphane distribution is dependent on the level of charge and the shape of the flake. However, in each case graphene/graphane boundaries are produced. Further work revealed that the charge- induced graphene to graphane transformation can be predicted if the mass and the structure of the flake is known (or can be estimated), and that it can be conveniently be identified as a shift in the energy of the Fermi level [81]. If this can be realized experimentally then it will enable structures consisting of co-existing regions of graphene and graphane to be produced spontaneously, and in the absence of volatile or expensive chemical environments.

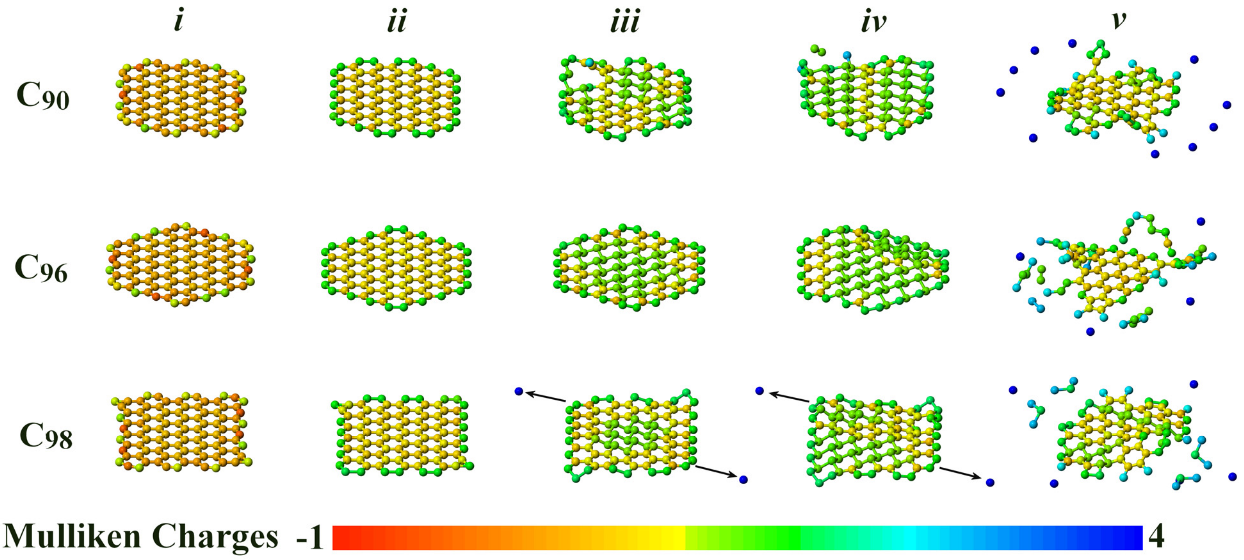

Figure 6. Structure and distribution of charges in C_{90} C_{96} and C_{98} anionic graphene nano-flakes at different stages of electron injection [80].

Yakobson et al. used DFT and DFTB methods to simulate graphene nanodots of various sizes embedded in a graphane sheet [82]. In this study it was found that the size *n*, shape and stability of the simulated dots were governed by the aromaticity of the dot and the interface between the two regions. Sizes corresponding to embedded aromatic molecules such as benzene and coronene were predicted to be stable, and hexagonal shapes were favoured for larger dots. The dots had large band gaps of about $15/\sqrt{n}$ eV with the size-dependence being characteristic of confined Dirac fermions. The authors also simulated some arrays of dots and found that the band gaps of these structures are similar to that of isolated dots.

6. Potential applications of graphene nano-flakes

Since GNFs may range in size from molecular to mesoscopic they have the potential to bridge the gap between molecular electronics and nano-electronics, and to integrate with existing technologies. Potential applications have been mentioned previously in this review, but here we will briefly mention how some of these ideas have resulted in real device prototypes, giving a few examples which will illustrate the extreme limits.

An example of the former class of devices is the use of coronenes to make a graphene field-effect transistor (FET) a "circuit diagram". This device consists of a coronene molecule with wires to the source and drain electrodes consisting of linker molecules which behaved electrically as a FET and thus this is a molecular graphene transistor. At the other end of the size scale there has been considerable interest in building devices such as single electron transistors [1,83,84]. The work outlined above, and that of others [22,84] shows that it is indeed possible to fabricate working electronic devices from graphene which contain GNFs and GQDs and this is set to become a growing area of research in the future. Currently the features of devices such as these are around 10 nm, but has been projected that dimensions should be able to be reduced to 1 nm quite soon [83].

In addition to this, it has been shown experimentally that GMBs, graphene oxide and GNFs [32,85,86,87] have interesting optical properties when functionalized. This leads to the interesting possibility of developing graphenes with optical properties which may be tuned by changing the functional groups [32]. It has been suggested that graphene composites may be used commercially for optical applications such as saturable absorbers for laser applications before they are for electronic ones. This may well be a promising area to investigate the optical properties of GNFs both theoretically and experimentally. Already it has been predicted that GNFs of different shapes can have a significant second hyperpolarizability which may be of use in non-linear optics applications.

7. Conclusions

As this review can testify, graphene has already proved to be an extremely exciting new material which has many fascinating properties. Much of the research on graphene has concentrated on 2-D graphene (graphene membranes, GMBs) and 1-D graphene (graphene nanoribbons, GNRs), because their interesting and potentially very useful properties have been relatively simple to isolate and address. It has already been shown that it is feasible to make working devices (albeit only at the laboratory level) using GMBs and GNRs for applications such as transistors, molecule detectors and flexible electrodes.

Less well studied is the 0-D form of graphene (graphene nano-flakes, GNFs) which presents a greater degree of complexity, but offers a greater potential for flexibility and selectivity (both literally and figuratively). In this review we have attempted to show that GNFs share many useful features in common with these 2-D and 1-D forms of graphene, but also possess a many unique properties of their own (such as interesting electronic and magnetic states) with a great degree of untapped potential. Many of these additional features arise because GNFs may be engineered to form many more shapes than GMBs and GNRs and, as has been pointed out, GNFs can also span the dimensional scale from molecular to macroscopic, enabling potentially great versatility in many applications. As the magnetic properties of GNFs are comparable with those of GNRs, while being far more amenable to manipulation, one of the most promising futures appears to be in the area of spintronics, but the opportunities do not stop there.

GNFs also offer many challenges to refine existing scientific knowledge of their preparation and properties including, their improved synthesis and assembly by bottom-up and top-down methods, the refinement of confinement methods for GQDs, and the exploration of their properties such as their vibrational spectra and magnetic behavior. Nevertheless, there are still a large number of unanswered questions, which highlights the enormous potential for further exploration and exploitation of the smallest members of the graphene family.

Acknowledgements

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