Graphene: Materials in the Flatland (Nobel Lecture)**

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carbon · graphene · materials science · monolayers · Nobel lectures

Much like the world described in Abbott's "Flatland", graphene is a two-dimensional object. And, as "Flatland" is "A Romance of Many Dimensions", graphene is much more than just a flat crystal. It possesses a number of unusual properties which are often unique or superior to those in other materials. In this brief lecture I would like to explain the reason for my (and many other people's) fascination with this material, and invite the reader to share some of the excitement I've experienced while researching it.

From the Contents

> " *I call our world Flatland ...* "
> Edwin Abbott Abbott, *Flatland. A Romance of Many Dimensions*

Biography

> " *Now, here, you see, it takes all the running you can do, to keep in the same place. If you want to get somewhere else, you must run at least twice as fast as that!* "
> Lewis Carroll, *Through the Looking Glass*

> " *Everything's got a moral...* "
> Lewis Carroll, *Alice's Adventures in Wonderland*

I was born in 1974 in Nizhnii Tagil, a middle-sized industrial city in the Ural mountains in Russia. My mother, Tatiana Novoselova, was an English teacher at my school (though, in spite of all her efforts, I only started to speak, not even proper, but *any* English after I moved to the Netherlands), and my father, Sergey Novoselov, was an engineer at the local Factory.

The Factory—a huge enterprise the size of the city itself—was central to our life, even at the most basic level: every morning there would be a whistle loud enough to wake people several miles away at 7.00am, two at 7.30am to get people out of their homes, three at 8.00am as a signal to start working and another at 4.30pm when the workers could go home. It produced railway carriages and tanks, including the legendary T-34 (it was moved from the occupation zone of Kharkov during the Second World War), a fact I was very proud of despite the trouble it brought to our family (my granddad Gleb Komarov, a tank test-driver who was evacuated from

Kharkov with the Factory, lost his legs in an accident in his tank in 1944).

Having such high-technology industry in the vicinity meant there were large numbers of highly qualified engineers and specialist technicians around, and inevitably, our hobbies were rather technical as well. So, along with cross-country skiing, I was seriously into carting, mainly due to my father, who was himself into auto-sports, and many parts of the cars were produced or modified by our own hands. Through this hobby, I learned bits of lathing, milling, and welding, skills which I also put to use during summer placements at the Factory.

I had always been quite technical. When I was eight, my father gave me a German model railway, and the part I used most was its variable DC power source, which came in handy in experiments from electrolyses to building electromagnets. With my parents working full time, and my seven-years-younger sister Elena in the nursery, I had a few hours after school each day to do "research", such as looking for gunpowder recipes or casting metals and then cleaning up the kitchen afterwards.

The load on our kitchen was significantly reduced when I reached the higher grades, and my passion for such experiments was supported by my physics teacher, Ljudmila Rastorgueva, who allowed me free rein with the equipment in our school physics laboratory. She also, together with my math teachers Valentina Filippova and Ljudmila Bashma-

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Figure 1. Myself (steering) and my friend Dima Zamiatin racing on ice track (approx. 1980).

kova, introduced me to the Moscow Institute of Physics and Technology (Phystech)'s Distance Learning School, as well as pushing me to participate in physics and math Olympiads of various levels. Other great sources of information and encouragement at this time were the monthly journal *Quant*, a series of fantastic books by the same publisher, and translated texts by Martin Gardner. But, it would be wrong to suggest that I limited myself to physics and math literature; quite a keen reader, my school-time favorites included Pasternak, Pushkin, Jack London, H. G. Wells, Jerome K. Jerome, Lewis Carroll, and Mark Twain (though my tastes changed dramatically over time).

My participation in the Distance Learning School and Olympiads made entering Phystech in 1991 fairly straightforward. I chose the Faculty of Physical and Quantum Electronics and experienced an amazing and bizarre combination of the highest standards of education and rather tough living conditions. The curriculum was also quite intense, especially during the third year, when one could easily spend ten straight hours a day in the lectures, tutorials, and research labs, but, with our courses given by the leading actively working scientists, we felt privileged and extremely proud to study there.

The Phystech students formed a very close and friendly community, and these connections helped us survive the turbulent times of 1991–95 in Russia. I remember, during one of the blackouts which were unfortunately very regular (especially during winter), Sasha Zhuromskii reading something from Tolkien using the last candle we could find, and a good dozen people hanging around on the double-decker beds in our hostel room, which was small even for the four of us who lived there. Another source of entertainment, despite a continuous shortage of money on all of our parts, were

regular visits to the Bolshoi theater, where we traded work as *claqueurs* (paid applauders) for a chance to see the performances.

Of course, there were quite a few temptations outside science and many alternative paths to take. In 1993, I participated in the October Putsch in Moscow, and it was quite an experience. I still feel lucky that they refused to give me a gun, despite my strong insistence. As a consequence, I decided that my revolutions would be in physics, definitely not politics—in fact, I decided to stay as far away as possible from any politics at all. My romance with business was somewhat longer-lasting: for about three years I was heavily involved with a construction company in parallel with my study (luckily the work was mostly during my summer breaks), and for some time it was good fun to learn another profession, meet new people, and earn good money. But, after a while, I got bored, and when the question of science or business arose, I chose science; it is absolutely impossible to do "part-time science", and I feel lucky that I realized that quite early in my career.

Figure 2. At this moment we were "heavily" involved in construction business in Moscow city (1993). Left to right: Danil Melnikov, Konstantin Antipin, Kostya Novoselov, Vladimir Ryabenko, Sergey Lemekhov with Taras Taran pressing the button on the camera.

Figure 3. At the military camp (1996). The first lesson in the camp is to learn how to put the foot-binding properly (wearing boots requires foot-binding rather than socks). Left to right: Kostya Novoselov, Alexander Fedichkin, Sergey Zhukov, Yurii Kapin, Misha Meleshkevich, Alexey Sobolev.

Phystech is rather different from other Russian universities. The science in the country is traditionally concentrated in research institutes, and Phystech uses these as so-called 'bases', where students can follow specialized courses and get involved in research projects. Typically, students spend about a day a week on a "base" during their third year, with the proportion reaching 100% by their sixth year. My first base was Astrophysica, the State Research Center originally focused on research into powerful laser systems and their use in military applications, but within a year I'd decided that it was not what I wanted and moved to Chernogolovka's Institute of Microelectronics Technology.

Chernogolovka is a very small town in the middle of a forest about sixty kilometers east of Moscow, with 20 000 people and a dozen research institutes. I loved everything about it: the place itself looked amazing, especially during the winter (I would have to walk through the forest for a good half-hour each day to get to the institute), the people were enthusiastic and passionate about science, and the range of courses we were offered was excellent. In addition, the lectures were given by the leading scientists in the Institute of Solid State Physics, the Landau Institute for Theoretical Physics, and the Institute of Microelectronics Technology: Vsevolod Gantmakher, Vladislav Timofeev, and Mikhail Trunin, to name just three.

At Chernogolovka, I started to learn microelectronics technology (now it would be happily called "nanotechnology") from Sergey Dubonos and worked with Zhenia Vdovin, Yura Khanin, and Sergey Morozov on tunneling spectroscopy[1] in the laboratory of the late Yura Dubrovskii. I learned so much from these people, from basic human communication skills to the most complicated experimental techniques. I remember that I so envied the skills with which Yura Khanin and Zhenia Vdovin handled the most miniscule samples that I asked a good friend of mine, Marina Dvinianina, to get me a cut-throat razor to develop the steadiness of my hands when shaving—it was quite a painful and bloody experience, but I soon achieved a less dangerous level of expertise.

In 1997, I was doing my PhD in the same lab[2] (and still shaving with the same razor, which I use to this day), when I got an opportunity to go to Nijmegen in the Netherlands to work with Andre Geim. Andre already had a reputation for being an innovative and creative experimentalist, so I didn't think twice. During the spring of 1999, I spent a couple of months in Nijmegen as a probation period, where I did everything possible to disappoint Andre, once forgetting to close the lid on the helium dewar (which has never happened to me before or since) and using a "u" instead of an "a" in the phrase "*last* opportunity" when Andre asked me to write to a journalist for him from his e-mail account. Yet, despite all my "efforts" to sabotage my chances, I started my PhD with Andre in Professor Jan Kees Maan's high magnetic field laboratory in August 1999.

This was quite a different experience for me. The laboratory was large, international, had a huge variety of projects running simultaneously,[3,4] and always had visitors coming in for measurements on the high magnetic field installation. It certainly broadened my horizons in terms of science but unfortunately not with regards to Dutch: with our

Figure 4. High magnetic field installation in Nijmegen is a huge enterprise and requires rather radical moves if something needs to be fixed (2000).

Figure 5. Back to the beginning. At the first-ever graphite mines (Seathwaite, near Keswick, Lake District, England, 2009). After reaching Great Gable in a nice, blasting Lake District weather, we finally got to the mines (just 50 meters away from the main road) to find plenty of graphite in the mine hillock.

community being so international (my closest friends were Igor Shkliarevskii, Fabio Pulizzi, and Cecilia Possanzini), we spoke quite a weird dialect of English, with a smattering of Italian, French, Dutch, and Russian words and grammar lifted from Guy Ritchie's movies *Lock, Stock…* and *Snatch* (kindly and patiently explained to us by A. Keen and A. Quinn).

In 2001, as many people finished their PhDs and postdocs, the community started to break up. Andre himself moved to Manchester early that year, and I didn't hesitate for a moment when he invited me to join him, even though it meant leaving my PhD unfinished for the second time in a row. When I arrived in Manchester, it was to an empty room with one lock-in (still working), a turbo-pump (still there), and Sergey Morozov (still around), measuring 'magnetic water' while on

a short visit to Andre. It was my third lab in less than three years and a different experience again: everything had to be built from scratch both there and in the clean rooms (though I had less involvement with the latter), but this did allow for plenty of fun as everything was bespoke to our specific requirements.

Despite the fact that the lab then included only Andre, Irina Grigorieva, myself, and a couple of other postdocs and visitors, the number of projects (in comparison to what I was exposed to in Nijmegen) hadn't dropped. Probably even otherwise, besides mainstream projects like Irina's cryogenic Bitter decoration[5] and mine and Andre's domain wall motion in garnets,[6] we were all involved in several others, including the mentioned "magnetic water", mesoscopic superconductivity,[7] gecko tape,[8] scanning tunneling micros-copy (STM) with a gate electrode … the list was endless. In between the projects, I also managed to convince Irina Barbolina to marry me (over the phone, she was in Nijmegen at the time), and, with a PhD in microbiology, she joined the group for a few months, helping with bio-related experiments. We all enjoyed watching the turbulent life of yeast and other microorganisms under a microscope during a project we dubbed "the last fart of a living cell".[9]

One of our projects, initiated by Andre, was an attempt to make a metallic field-effect transistor. The choice of material, quite naturally, fell to graphite, mostly due to its low carrier concentration. I'll skip giving a detailed description of the first stage of the project, as Andre Geim describes the process in his lecture, but I would just like to mention that we thought we'd have to drop it altogether when Andre's PhD student Da Jiang enthusiastically polished a piece of very expensive graphite into dust. The unexpected solution to the problem came from the scanning tunneling microscopy project which was led by Oleg Shkliarevskii.

At that time, I was doing very long measurements on domain walls, with magnetic field sweeps easily taking a day or more, so I was often hanging around the cold STM. Oleg was doing the first scans and showed me the way he cleaned graphite, by cleaving it with Scotch tape. With the Scotch tape (with the residual flakes on it) taken literally from the dustbin, it took me less than an hour to produce a device which immediately demonstrated some miserable field effect; but, however small the effect—it was clear we had stumbled upon something very big (though I doubt at that time I realized how far it would go). We got onto it, and within a few months we had our first graphene device (sample ZYH-K51).[10]

The results we were getting were quite puzzling though, and I admit we got a great deal of help from theorists. I was organizing our group seminars at the time and invited Dima Khmelnitsky from Cambridge to visit us. The seminar was due to start at 3 pm and Dima arrived at 7 in the evening, arguing that he calculated it should have taken him 3.5 h to reach Manchester. Obviously, the seminar had to be cancelled, but we were able to spend the rest of the evening chatting about our recent results. When he heard about graphite, Dima immediately told us about the linear spectrum and pointed out (off the top of his head) that the Landau level quantiza-tion for such a spectrum was considered in the problem to the

paragraph on "Dirac equation for an electron in external field", on page 148 of *Quantum Electrodynamics* (book four of the Russian edition of the Landau and Lifshitz course)—information which came just in time. Another piece of useful information came from Dima the very next morning, when he called me to confirm that his theory was correct and that he had reached Cambridge within 3.5 h after having left Man-chester at 4am.

By 2004, my first postdoc was coming to an end, and I was actively searching for funding to allow me to continue in Manchester. I was granted a fellowship from the Leverhulme Trust, but they pointed out something unfortunate in the fine print: the recipient must have a PhD. I started running around like a headless chicken, searching for a body which would give me a degree within three months—with my project finishing soon, and I'm being close to be kicked out of the country. I was extremely close to buying a so-called "life experience" PhD on the internet, but circumstances came together, and I was awarded a PhD from Nijmegen—though even then things were touch-and-go, as the company I was flying with went bust and my passport got stuck at the Foreign Office. Finally, after months of havoc, I was able to proudly phone the Leverhulme Trust to ask where to send my certificate. "We don't want to see it", they replied, "If you say you've got it, you've got it". I was absolutely charmed with this kind of attitude.

In 2009, Irina and my bio-mechanical experiments paid off, and we produced a pair of amazingly good-looking samples: Sophia and Victoria. I sincerely hope that they will continue to work for many, many, many years.

Finally, the promised moral. Four of us (Andre Geim, Volodia Falko, Boris Altshuler, and I) were sitting in a seminar room in Lancaster discussing our recent experiments on weak localization in graphene. Volodia was telling us that it was unlikely that there was no weak localization at all, and that we should measure better, and we were insisting that those were the facts and encouraging everyone to discuss the real physical situation and try to understand it. The truth, as usual, appeared to be somewhere in the middle, but the discussion became rather heated and even personal (as it often does between Andre and Volodia). Eventually Boris jumped up, ran away, and brought back a poorly copied paper by Stark. It is really a bizarre reading on "*The Pragmatic and the Dogmatic Spirit in Physics*".[11] It starts with, probably, the most concise description of how the science should be done, and you are ready to sign under every single word until you turn the page, where … . Well, let's say Volodia turned out to be a bad guy (in the illustrious company of Einstein, Schrodinger, and Heisenberg).

The moral is that it is impossible to learn the spirit of science from a textbook or article. They may be able to teach us physics and chemistry and many other disciplines at university, but it is up to us to develop a gut-feeling for how best to "do science". I'm extremely lucky that I've worked with and learned from Andre Geim, who is highly innovative and broad in his perspective but, at the same time, very truthful and critical of himself, with manic attention to details. It's so easy to lose sight of the bigger picture underpinning the details or get carried away with your "beautiful theory" and

stop paying attention to the facts; Andre is a master of finding the narrow path between these extremes, and, if there's one thing I'm proud of in my life, it's that I have learned a little of this style.

1. Graphene and Its Unusual Properties

Graphene is a two-dimensional (2D) atomic crystal which consists of carbon atoms arranged in a hexagonal lattice (Figure 6). Although sporadic attempts to study it can be
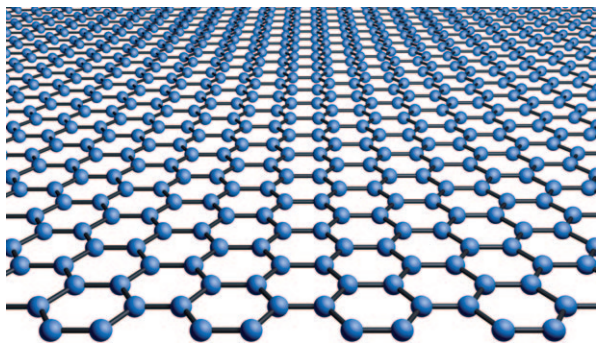
Figure 6. The crystal structure of graphene—carbon atoms arranged in a honeycomb lattice.

traced back to 1859,[12] active and focused investigation of this material started only a few years ago, after a simple and effective way to produce relatively large isolated graphene samples was found.[13,14] The original "Scotch tape method"[13,14] appeared to be so simple and effective that this area of science grew extremely quickly, and now hundreds of laboratories around the world deal with different aspects of graphene research. Also known as the micromechanical cleavage technique, the Scotch tape method has a low barrier to entry in that it doesn't require large investments or complicated equipment, which has helped considerably to broaden the geography of graphene science.

Another source of graphene's widespread popularity is that it appeals to researchers from a myriad of different backgrounds. It is the first example of 2D atomic crystals, whose properties from the thermodynamics point of view are significantly different from those of 3D objects. It is also a novel electronic system with unprecedented characteristics.[15] It can be thought of as a giant molecule which is available for chemical modification[16,17] and is promising for applications[18,19] ranging from electronics[18–20] to composite materials.[19,21–22] These factors allow for true multi- and cross-disciplinary research. Thanks to these attributes, within seven years of the first isolation of graphene we have accumulated as many results and approached the problem from as many different perspectives as other areas of science would more commonly achieve over several decades.

The major draw to people in the field, though, is graphene's unique properties, each of which seems to be superior to its rivals. This material is the first 2D atomic crystal ever known to us;[14] the thinnest object ever obtained; the world's strongest material;[23] its charge carriers are massless Dirac fermions;[18,24–25] it is extremely electrically[26] and thermally[27] conductive; very elastic; and impermeable to any molecules[28]—the list goes on. Even a simple inventory of graphene's superlative qualities would require several pages, and new entries are being added on a monthly basis.

As it is not possible to give a comprehensive overview of all of graphene's properties in one lecture, I will limit myself to just three, which, in my opinion, give the best possible impression of graphene: it is the first example of a 2D atomic crystal (see Section 2), it demonstrates unique electronic properties, thanks to charge carriers which mimic massless relativistic particles (see Section 3), and it has promise for a number of applications (see Section 4).

2. Two-Dimensional Crystals

2.1. Stability of 2D crystals

Intuitively, one can easily discern the difference between two- and three-dimensional objects: restrict the size or motion of an object to its width and length and forget (or reduce to zero) its height, and you will arrive in "flatland". The consequences of subtracting one (or more) dimensions from our 3D world are often severe and dramatic. To give just a few examples: there are no knots in 2D space; the probability of reaching any point in d-dimensional space by random walking is exactly unity for $d=1$ and $d=2$ and smaller than 1 in higher dimensions;[29] the problem of bosons with repulsive potential in 1D is exactly equivalent to that of fermions, since particles can't penetrate each other and can't be swapped[30,31] (the Tonks–Girardeau gas and fermionization of bosons in 1D problem); and it is impossible to have thermodynamic equilibrium between different phases in 1D systems.[32]

Many of the peculiar properties that one can expect in 2D systems are present due to so-called "logarithmic divergences", with the most well-known example being the weak localization quantum corrections to the conductivity in 2D. In particular, a series of reports by Peierls,[33–34] Landau,[32,35] Mermin,[36] and Wagner[37] demonstrated the theoretical impossibility of long-range ordering (crystallographic or magnetic) in 2D at any finite temperatures. The stability of 2D crystals (here the theory has to be expanded to take flexural phonons or out-of-plane displacements into account[38–40]) is a simple consequence of divergences at low k vectors, when the integration of the atomic displacements is taken over the whole 2D k space.

It is important to mention that such instabilities are the result of thermal fluctuations and disappear at $T=0$. Also, strictly speaking, at any finite temperature the fluctuations diverge only for infinitely large 2D crystals ($k\rightarrow0$); as the divergences are weak (logarithmic), crystals of limited sizes might exhibit infinitely small fluctuations, at least at low temperatures.

These fluctuations place a fundamental restriction on the existence and synthesis of low-dimensional crystals. Growth

or synthesis generally requires elevated temperatures—at which only crystallites of very limited size can be stable in the flat form—and, as the bending rigidity of such crystals is usually low, they would generally crumple and fold easily and form 3D structures (which might also help in reducing the energy of unsaturated dangling bonds at the perimeter). The largest flat molecule synthesized to date therefore is C_{222},[41] and the method used to create it is the *low (room)-temperature* cyclodehydrogenation of a 3D precursor molecule.

A possible way around the problem of 2D crystals' instability is synthesis as part of a 3D structure, with subsequent extraction of the 2D part of the system at low temperatures (in fact, such a strategy is the basis of all methods of graphene synthesis available to date).[18] The fluctuations, which might diverge at high temperatures, are quenched during the synthesis due to the interaction with the 3D matrix (substrate) whenever the extraction of 2D crystals could be done at low temperatures where the fluctuations are suppressed.

2.2. Graphene Creation

The simplest implementation of this method for graphitic materials is to use bulk graphite and exfoliate it into individual planes. Graphite is a layered material and can be considered as a stack of individual graphene layers. High-quality graphite typically requires growth temperatures of above 3000 K, but exfoliation can be done at room temperature—an order of magnitude lower than the growth temperatures. In fact, many of us have performed this procedure numerous times while using pencils, as drawing with a pencil relies on exfoliation of graphite (though not up to the monolayer limit, which would be practically invisible to the naked eye).

Graphite exfoliation techniques slightly more elaborate than writing with a pencil have been attempted by several groups[42–48] and thin graphitic films obtained. But even graphitic films only 20 layers thick would generally behave similarly to bulk graphite, so the real breakthrough came when monolayer films of graphene large enough to be studied by conventional techniques were prepared.[13,15] The technique used in those cases is known as the micromechanical cleavage or "Scotch tape" method (Figure 7). The top layer of the high-quality graphite crystal is removed by a piece of adhesive tape, which—with its graphitic crystallites—is then pressed against the substrate of choice. If the adhesion of the bottom graphene layer to the substrate is stronger than that between the layers of graphene, a layer of graphene can be transferred onto the surface of the substrate, producing extremely high-quality graphene crystallites via an amazingly simple procedure. In principle, this technique works with practically any surface which has reasonable adhesion to graphene.

However, especially in the first experiments, the process' yield was extremely low, and one would have to scan macroscopically large areas to find a micrometer-sized graphene flake (Figure 8). Needless to say, this search is a practically impossible task for conventional microscopy
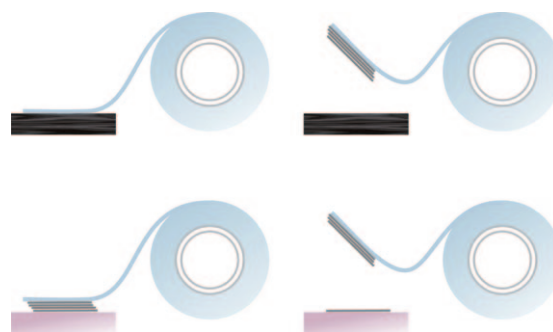
Figure 7. The micromechanical cleavage technique ("Scotch tape" method) for producing graphene. Top: Adhesive tape is used to cleave the top few layers of graphite from a bulk crystal of the material. Bottom left: The tape with graphitic flakes is then pressed against the substrate of choice. Bottom right: Some flakes stay on the substrate, even on removal of the tape.
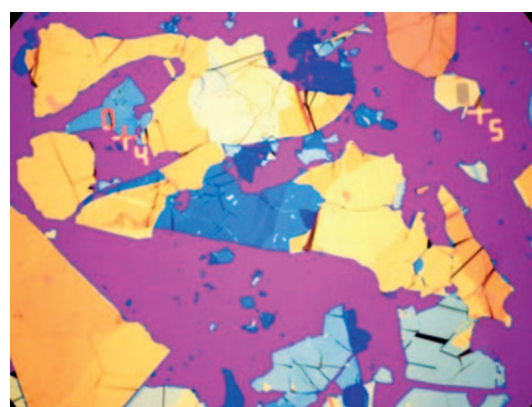
Figure 8. Thin graphitic flakes on a surface of Si/SiO$_2$ wafer (300 nm of SiO$_2$, purple). The different colors correspond to flakes of differing thicknesses, from approximately 100 nm (the pale yellow ones) to a few nanometers (a few graphene layers—the most purple ones). The scale is given by the distance between the lithography marks (200 μm).

methods like atomic force microscopy or scanning electron microscopy; realistically only optical microscopy, which relies on the high sensitivity, speed, and processing power of the human eye and brain, can do the job. So it came as a pleasant surprise that monolayers of graphite on some substrates (Si/SiO$_2$ with a 300 nm SiO$_2$ layer, for instance) can produce an optical contrast of up to 15% for some wavelengths of incoming light. The phenomenon is now well understood[49,50] and made Si/SiO$_2$ with an oxide layer either 100 or 300 nm thick the substrate of choice for a number of years for most experimental groups relying on the micromechanical cleavage method of graphene production.

Similar techniques (growth at high temperatures as a part of a 3D system, with subsequent extraction of the 2D part at low temperatures) have been used in other graphene preparation methods. Probably the closest to the micromechanical exfoliation method is chemical exfoliation, which can be traced back to the original work of Professor Brodie,[12] who

treated graphite with acids and arrived at "Graphon" (or graphite oxide as we now know it). Graphite oxide can be thought of as graphite intercalated with oxygen and hydroxy groups, which makes it a hydrophilic material and easily dispersible in water. This technique produces extremely thin, sometimes even monolayer, flakes of this material,[51–55] which can then subsequently be reduced, producing low-quality graphene.[16,21,56–58]

One can imagine an even simpler path for chemical exfoliation. Although graphene is hydrophobic, it can be dispersed in other, mostly organic, solvents.[59,60] By repeating the exfoliation and purification (centrifugation) process several times one can obtain 50% and higher fractions of graphene in suspension.

There are also well-known graphene-growing recipes from surface science. Catalytic cracking of hydrocarbons, or precipitation of dissolved carbon on a metal surface with subsequent graphitization, has long been known to produce high-quality graphene layers.[61–68] A similar process is the graphitization of excess carbon atoms after sublimation of silicon from the surface of silicon carbide.[69,70] One should note that it is also true in these cases that graphene must be a part of the 3D structure, as the underlying substrate aids in quenching the diverging fluctuations at high temperatures.

2.3. Other 2D Crystals

Thus far we've been talking mainly about graphene, but the 2D materials family is of course not limited to carbonic crystals, although similar problems are faced when attempts are made to synthesize other 2D materials. At least two possible methods of obtaining other 2D crystals come immediately to mind.

One possibility is to apply the same recipes we saw working for graphene to other chemical compounds. Micromechanical or chemical exfoliation can be successfully applied to other layered materials (Figure 9) such as $Bi_2Sr_2CaCu_2O_x$,[14] $NbSe2$,[14] BN,[14] MoS_2,[14,71] Bi_2Te_3,[72] and other dichalcogenides, and epitaxial growth has been applied

Figure 9. Optical micrographs of various 2D crystals (top) and their crystal structures (bottom). Left: Flakes of boron nitride on top of an oxidized Si wafer (290 nm of SiO_2, the image taken using narrow band yellow filter, $\lambda = 590$ nm). The central crystal is a monolayer. Center: A device prepared from mono- and bilayer $NbSe_2$ crystals on an oxidized Si wafer (290 nm of SiO_2). Right: Flakes of MoS_2 on top of an oxidized Si wafer (90 nm of SiO_2). The piece at the bottom-right corner is a monolayer. Color coding for the crystal structures at the bottom: yellow spheres = boron, purple = nitrogen; large white spheres = niobium, red = selenide, blue = molybdenum, small white spheres = sulfur.
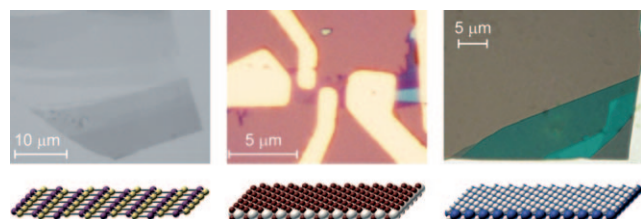
to grow monolayers of boron nitride.[73,74] As with graphene, the crystal quality of the obtained monolayer samples is very high. Many of the 2D materials conduct and even demonstrate field effects (changes of the resistance with gating). The properties of the obtained 2D materials might be very different from those of their 3D precursors. For example, the overlapping between the valence and conduction bands in graphene is exactly zero, while it is finite in graphite,[13] and a monolayer of molybdenum disulfide is a direct-band semiconductor while the bulk material has an indirect band gap.[71]

A second approach is to start with an existing 2D crystal and modify it chemically to obtain a new material. One can think of graphene, for instance, as a giant molecule. All the atoms of this molecule are, in principle, accessible for chemical reaction (as opposed to the 3D case, where atoms in the interior of the crystal cannot participate in such reactions).
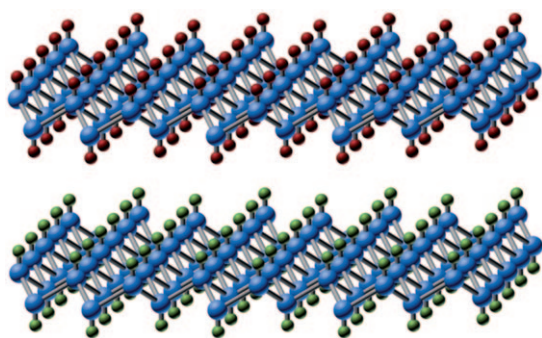
Graphene, due to the versatility of carbon atoms, is a particularly good candidate for such modification. Depending on the environment, the electron configuration of a carbon atom (which has four electrons in the outer shell) might change dramatically, allowing it to bond to two, three, or four other atoms. Bonding between the carbon atoms is exceptionally strong (the strongest materials on Earth are all carbon-based), whereas bonding to other species, though stable, can be changed by chemical reactions. To give an example of such versatility: a backbone of two carbon atoms each can accept one, two, or three hydrogen atoms, forming ethyne (also known as acetylene), ethene (ethylene), or ethane, respectively. It is possible to convert any one of those into another by adding or removing hydrogen, thus changing the electron configuration of carbon atoms between so-called sp, sp^2, and sp^3 hybridizations.

Carbon atoms in graphene are sp^2-hybridized, meaning that only three electrons form the strong σ bonds, and the fourth has a communal use forming the so-called π bonds. So graphene is a zero-overlap semimetal and conducts electricity very well (in contrast to diamond, where each carbon atom is in sp^3 hybridization and therefore has four neighbors. In that case, all four electrons in the outer shell are involved in forming σ bonds, so a huge gap appears in the electronic band structure, making diamond an insulator). The versatility of carbon atoms, then, gives us an idea of how to create novel 2D crystals: one can attach something to carbon atoms, creating a new material with a different chemical composition and exciting properties.

A wide variety of chemicals can be attached to graphene. So far only two crystallographically ordered chemical modifications of graphene have been predicted and achieved: graphane (when one hydrogen atom is attached to each of the carbon atoms)[75,76] and fluorographene (Figure 10).[77–80] Both derivatives are insulators (exhibiting large band gaps) of very high crystallographic quality and are very stable at ambient temperatures (though it should be mentioned that fluorographene generally exhibits more robust properties, probably due to stronger C−F bonding in comparison to C−H). Graphane and fluorographene open the floodgates for the chemical modification of graphene and for the appearance of novel two-dimensional atomic crystals with predetermined

Figure 10. Chemically modified graphene. One can add different species (like hydrogen or fluorine) to graphene scaffolding. Carbon atoms are represented by blue spheres.

properties. It would be interesting to see other derivatives, probably filling the gap between graphene and graphane in terms of electrical conductance (the size of the band gap).

Clearly then, the importance of graphene is not only that it has unique properties but also that it has paved the way for, and promoted interest in, the isolation and synthesis of many other 2D materials. We can now talk about a whole new class of materials, 2D atomic crystals, and already have examples with a large variety of properties (from large-band-gap insulators to the very best conductors, the extremely mechanically strong to the soft and fragile, and the chemically active to the very inert). Further, many of the properties of these 2D materials are very different from those of their 3D counterparts. Given that, even after seven years' intensive research, graphene still regularly delivers surprises, and it seems reasonable to expect a huge influx of breathtakingly interesting results from the field of 2D atomic crystals.

2.4. Out to Spaceland: 2D-Based Heterostructures

As has been mentioned earlier, the properties of 2D crystals can be very different from their 3D counterparts. Even bilayer graphene[81,82] (two graphene layers stacked on top of each other in special, so-called Bernal or A–B, stacking), is remarkably different from graphene. The latter is a zero-overlap semimetal, with linear dispersion relations whenever the bands are parabolic in bilayer graphene, and a gap can be opened in the spectrum if the symmetry between

the layers is broken (say by applying an electric field between the layers).[83–86] However, the properties of multilayered materials depend not only on the number of layers[13,87] but also on how those layers are stacked. For instance, in the case of graphite, consider Bernal stacking versus rhombohedral versus hexagonal versus turbostratic, and, in bilayer, a small rotation between the individual layers leads to the appearance of van Hove singularities at low energies.[88–91]

As we have full control over the 2D crystals, we can also create stacks of these crystals according to our requirements. Here, we are not merely talking about stacks of the same material: we can combine several different 2D crystals in one stack. Insulating, conducting, probably superconducting and magnetic layers can all be combined in one layered material as we wish; the properties of such heterostructures depend on the stacking order and are easily tunable.

Thus a completely new world of "materials on demand" is opening up to us. Because the pool of the original 2D crystals is very rich, the properties of such heterostructures can cover a huge parameter space, combining characteristics which previously we would not even dare to think of being found together in one material.

The first members of this huge family are already there. By combining (alternating) monolayers of insulating boron nitride and graphene, one can get weakly coupled graphene layers whose coupling would depend on the number of BN layers between the graphene planes (Figure 11). The level of interaction between the graphene planes ranges from tunneling (for single or double BN layers in between) to purely Coulomb (for thick BN spacers).

3. Chiral Quasiparticles and the Electronic Properties of Graphene

3.1. Linear Dispersion Relation and Chirality

What really makes graphene special is its electronic properties. Graphene is a zero-overlap semimetal, with valence and conduction bands touching at two points (K and K') of the Brillouine zone[92–94] (Figure 12). This is a consequence of the hexagonal symmetry of graphene's lattice (which is not one of the Bravais lattices): it has two atoms per unit cell and can be conceptualized as two interpenetrating triangular lattices. The p_z orbitals from the carbon atoms
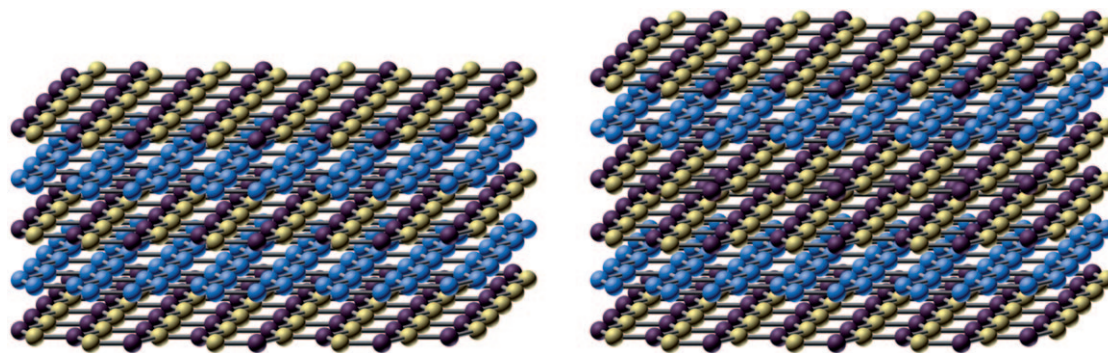
Figure 11. Graphene/BN heterostructures. Blue spheres = carbon atoms, yellow = boron, purple = nitrogen.
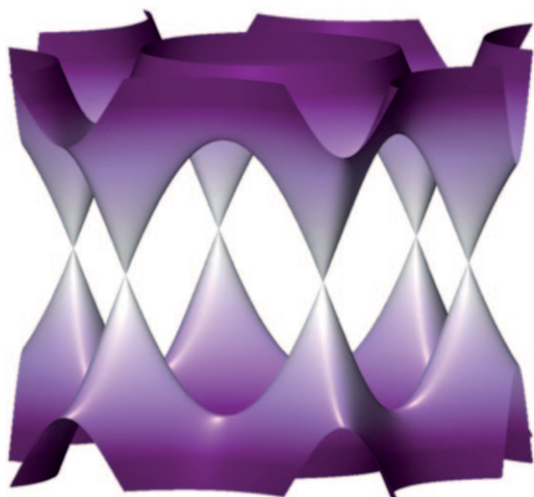
Figure 12. The low-energy band structure of graphene.

hybridize to form π and π* bands, whose crossing at the K and K′ points guarantees a gapless spectrum with linear dispersion relation. Thus, the absence of a gap between the valence and the conduction bands in graphene makes for a very robust phenomenon and is a consequence of the symmetry between the sublattices[94] (in boron nitride, where the symmetry between the sublattices is broken [one consists of boron, another of nitrogen], a large gap is opened in the electronic spectrum[95]).

The linear dispersion relation already makes graphene special, but there is more to it than that. States in the valence and conduction bands are essentially described by the same spinor wave function, so electrons and holes are linked via charged conjugation. This link implies that quasiparticles in graphene obey chiral symmetry, similar to that which exists between particles and antiparticles in quantum electrodynamics (QED). This analogy between relativistic particles and quasiparticles in graphene is extremely useful and often leads to interesting interpretations of many phenomena observed in experiment.[96]

3.2. The Klein Paradox

Probably the most striking result of the quasiparticles' chiral symmetry is the prediction[97] and observation[98–99] of the Klein paradox in graphene (to explore which the p–n junction is a natural venue[100]). The paradox refers[101,102] to the enhanced tunneling probability of a relativistic particle, which approaches unity as the height of the potential barrier exceeds $2m_0c^2$ (where m_0 is the rest mass of the particle and c is the speed of light) and is exactly 1 for massless particles. It can be seen as a result of suppressed backscattering (massless relativistic particles, like photons, always move with constant velocity—the speed of light—whereas backscattering requires velocity to become zero at the turning point) or as particle–antiparticle pair production and annihilation due to Schwinger[103] mechanism in the areas of high electric field.

The Klein paradox for chiral quasiparticles in graphene leads to perfect electron-to-hole conversion at a potential barrier, and an equal to unity probability of tunneling through such a barrier at least for the normal incidence.[97,100,104–105] This guarantees the absence of localization[106–107] and finite minimum conductivity,[18] even in relatively disordered graphene, which—in the limit of nominally zero carrier concentration—splits into electron–hole puddles.[108] The absence of backscattering, which leads to the Klein paradox, also ensures that quantum (interference) corrections to the conductivity are positive (at least if we neglect the intervalley scattering and the effect of trigonal warping),[15,109] resulting in weak antilocalization, which has indeed been observed experimentally.[110,111]

3.3. Half-Integer Quantum Hall Effect

The charge conjugation symmetry between electrons and holes also guarantees that there should always be an energy level exactly at $E = 0$. In the magnetic field this symmetry results in a sequence of the Landau levels as $E_n = \pm\sqrt{2e\hbar v^2 B(n + 1/2 \pm 1/2)}$ (here e is an electron charge, $\hbar$ the Plank constant, B the magnetic field, v the Fermi velocity and $n = 0,1,2\ldots$), rather different from that for normal massive particles. The $\pm 1/2$ term is related to the chirality of the quasiparticles and ensures the existence of two energy levels (one electron- and one hole-like) at exactly zero energy, each with degeneracy two times smaller than that of all the other Landau levels.[112–118]

Experimentally such a ladder of Landau levels exhibits itself in the observation of a "half-integer" quantum Hall effect (Figure 13).[24,25] The two-times-smaller degeneracy of the zero Landau level is revealed by the $\pm 1/2(4e^2/h)$ plateaus in Hall conductivity at filling factors ± 2. Furthermore, due to linear dispersion relation and the relatively high value of the Fermi velocity ($v \approx 10^6$ m s^{-1}), the separation between the zero and first Landau levels is unusually large (it exceeds the room temperature even in a modest magnetic field of 1 T).
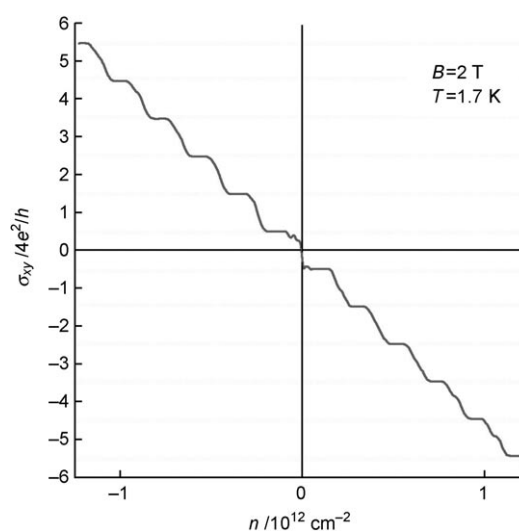

Figure 13. Hall conductivity as a function of the carrier concentration.

This, in conjunction with the low broadening of the zero Landau level,[119] makes it possible to observe the quantum Hall effect even at room temperature.[120] This is rather exciting news for people working in metrology, as it should allow much simpler realization of quantum resistance standard (no need for ultralow temperatures), an idea which has recently been supported by several experiments.[121,122]

3.4. Effect of Mechanical Deformation

It is important to remember that graphene is not just another 2D electronic system, similar to electrons on the surface of silicon MOSFET or in 2D quantum wells in GaAs/AlGaAs heterostructures. Graphene is a truly 2D atomic crystal and has electronic properties as in two dimensions. Essentially the thinnest possible fabric, it can be easily deformed mechanically and can be stretched,[23,28,123–127] compressed,[128] folded,[91,129] rippled[130]—even torn into pieces.[131] Needless to say, each of these mechanical manipulations would result in strong changes to the electronic structure.[132–134]

Furthermore, it can be demonstrated that strain is equivalent to the local magnetic field (of opposite directions for quasiparticles in the K and K′ valleys, to preserve the time-reversal symmetry)—a phenomenon used to explain the suppression of the weak localization[110,135] and additional broadening of all but zeroth Landau levels.[119] In principle, one can imagine engineering strain distribution of a special geometry so that the electronic band structure would be modified as if constant magnetic field was being applied to a particular area of the sample.[136,137] Since graphene is mechanically strong and very elastic,[23] the strains applied (and thus the pseudomagnetic fields which would be generated) can be extremely large, resulting in the opening of sizeable gaps in the electronic spectrum.[138] This allows us to talk about a completely new and unexplored direction in electronics: strain engineering of electronic structure[134] and valleytronics.[139–141]

3.5. Graphene Optics

Can one expect anything interesting from the optical properties of graphene? Rather counterintuitively, despite being only one atom thick, graphene absorbs quite a large fraction of light. In the infrared limit the absorption coefficient is exactly $\pi\alpha \approx 2.3\%$ (where $\alpha = e^2/\hbar c$ is the fine structure constant), and the corrections to this number in the visible range of the spectrum are less than 3%.[142–145] Such a significant absorption coefficient makes it possible to see graphene without the use of a microscope; thus, one can observe (literally) the most fundamental constant of this universe with the naked eye. At higher frequencies the absorption becomes even larger, reaching 10% due to the presence of the van Hove singularities at the zone edge.[146,147]

By changing the carrier concentration, one can shift the position of the Fermi level and change graphene's optical absorption due to Pauli blocking.[144] Since the density of states in graphene is relatively low (at least in the vicinity of the Dirac point), even electrostatic gating can be enough to shift the Fermi level as high as a few hundred meV,[148] so the Pauli blocking happens in the visible range of the spectrum. By executing such strong gating on several tens of graphene layers in series, it would be possible to control the light transmission in such structures to a large extent; an observation which might be promising for novel photonic devices.

3.6. Bilayer Graphene

Although the addition of one layer on top of graphene is all that is needed to arrive at bilayer graphene, the properties of the latter are not simply twice those of the monolayer crystal; this is one of those cases where "one plus one is greater than two". Bilayer graphene is remarkably different—sometimes even richer in its properties than its monolayer cousin—and fully deserves to be called a different material in its own right.

Two graphene layers, when placed together, do not like to lie exactly one on top of each other with each atom having a counterpart in the adjacent layer (unlike boron nitride, which does exactly that). Instead, bilayer graphene is mostly found[89] in so-called A–B or Bernal stacking[149] (named after the famous British scientist John Desmond Bernal, one of the founders of X-ray crystallography, who determined the structure of graphite in 1924). In such an arrangement, only half of the carbon atoms have a neighbor in another layer, and the other half don't (and so are projected right into the middle of the hexagon; Figure 14). The quantum mechanical hopping integral between the interacting atoms (generally called γ_1) is of the order of 300 meV, which gives rise to a pair of high-energy electronic sub-bands.[81,82,150] The offset from the zero energy (the postion of the Fermi level in undoped bilayer graphene) is exactly γ_1, so these sub-bands do not contribute to electronic transport unless a very high level of doping is achieved (though these sub-bands can be easily observed in optical experiments;[151,152] Figure 15).

The non-interacting atoms give rise to low-energy bands which are still crossing at zero energy (as in graphene), but are parabolic (Figure 15). The symmetry between the layers is
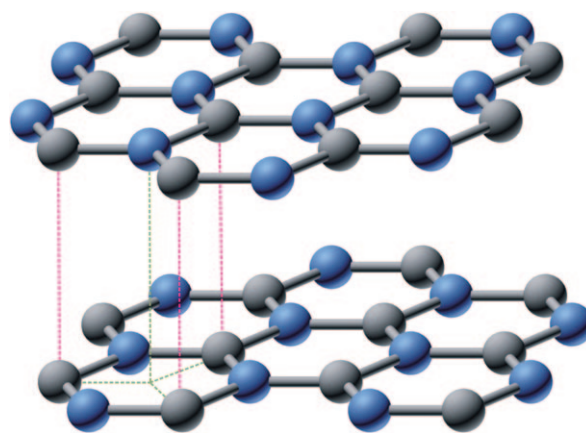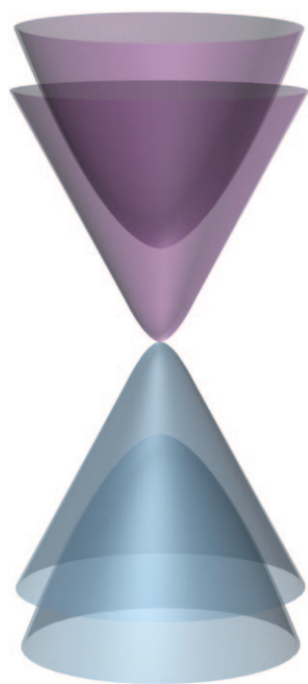

Figure 14. Crystal structure of bilayer graphene.

properties in them. Topological transitions at low electron energies,[157] excitonic effects,[158] and topological one-dimensional states[141] are among those which can be expected.

4. Graphene Applications

Fans of American sitcom *The Big Bang Theory* (splendidly produced by Chuck Lorre) might recall the episode "The Einstein Approximation" in which string theorist Sheldon tries to resolve "the graphene problem": why do quasiparticles in graphene behave like massless Dirac fermions? (Figure 16) The whole crew is great as usual,

Figure 15. The band structure of bilayer graphene in the vicinity of the K point.

Figure 16. Dr. Sheldon Cooper (Jim Parsons) "...either isolating the terms of his formula and examining them individually or looking for the alligator that swallowed his hand after Peter Pan cut it off". From *The Big Bang Theory*, series 3, episode 14 "The Einstein Approximation". Photo: Sonja Flemming/CBS ©2010 CBS Broadcasting Inc.

analogous to the sublattice symmetry in monolayer graphene, and it guarantees the chiral symmetry between electrons and holes. Thus we have a new type of quasiparticle in graphene—massive chiral fermions—which doesn't have an analogy in QED.[81,82] Similarly to graphene, the chirality reveals itself in the unusual quantum Hall effect. The sequence of the Landau levels in the magnetic field is now $E_N = \pm \hbar \omega_c \sqrt{N(N-1)}$; here $\omega_c = eB/m^*$ is the cyclotron frequency and $m^* = \gamma_1/2v^2$ is the cyclotron mass. It is easy to see that two Landau levels exist at zero energy ($N=0$ and $N=1$), which again ensures a peculiar sequence of the Hall plateaus and metallic behavior in the limit of zero filling factor (at least if we neglect the many-body effects).[81,82]

As has been said, the chiral symmetry in mono- and bilayer graphene is protected by the symmetry between the sublattices. In the case of graphene it is rather difficult to break this symmetry—one would have to diligently apply a certain potential to atoms which belong to one sublattice only while applying different potential to another sublattice—but in bilayer graphene, it is possible to do just that. By applying a gate voltage or by chemically doping from only one side, we can discriminate between the layers and thus between the sublattices (breaking the inversion symmetry). This results in lifting the chiral symmetry and opening a gap in the spectrum. Both strategies have been implemented in experiment and yielded a rather striking result: a gap as large as 0.5 eV could be opened.[83–85,151–154] Thus bilayer graphene is a rare case of a material where the band gap can be directly controlled by (and its size is directly propotional to) the electric field applied across the layers.

As the quality of bilayer graphene samples improves,[155–157] we will see more and more interesting

particularly actor Jim Parsons' grotesquely brilliant depiction of the tough but enjoyable process of searching for a solution to a scientific problem. It is also probably the best episode from a physics point of view (thanks to Chuck Lorre, other writers, and the scientific advisor David Saltzberg), as—unusually—the whole plot hinges on the scientific problem, rather than this serving merely to link its parts (the only other example I can recall of such an episode is the one about the paper on supersolid). I'd like to think that the reason for this is the simple and appealing physics of graphene, which is Sheldon sophisticated, Penny beautiful, Raj exotic, Leonard practical, and Howard intrusive. On the day the episode was shot, Professor Saltzberg wrote in his blog, "...graphene has captured the imagination of physicists with its potential applications", and, in fact, graphene applications are already here.

The point of this paragraph is not to advertise *The Big Bang Theory* but to demonstrate the kind of applications we are expecting from graphene. The fact that one of the first practical uses of this material was not in a high-expectation,

predictable field like transistors or photonics, but instead in the entertainment industry indicates its great potential and versatility. Indeed, in graphene we have a unique combination of properties which are not seen together anywhere else: conductivity and transparency, mechanical strength and elasticity. Graphene can successfully replace many materials in a great number of existing applications, but I would also like to see things going in the other direction, with the unique combination of properties found in graphene inspiring completely new applications.

4.1. Graphene Supports

I would like to start by talking about relatively simple graphene devices for quite a minute market: graphene supports to study biological and other samples in transmission electron microscopy (TEM).[159–161] It is appealing for the simple reason that graphene membranes are already available on the market and are sold by several companies in both Europe and the US.

Graphene is an ultimately thin, ultimately conductive, ultimately mechanically strong and crystallographically ordered material, and it would be strongly beneficial to use it as a support for nano-objects when observing them in TEM. Its mechanical strength provides rigidity and ease in sample preparation, and it has a very high radiation damage threshold (of the order of 80 keV). High conductivity eliminates the problem of charging of the support. As it is only one atom thick (and also made of a very light element), graphene ensures the highest possible contrast (one can only go higher in contrast if suspending the object). Finally, because it is highly crystallographically ordered, graphene produces few diffraction spots, and those that do appear can be easily filtered out, leaving the image completely unperturbed by the presence of support. Although graphene is already quite compatible with biomolecules, it could also be functionalized to achieve a certain surface potential (for example, changed from being hydrophobic to hydrophilic). Chemical modification of graphene is already well-developed, but there are still a large number of opportunities available in this area.[16,17]
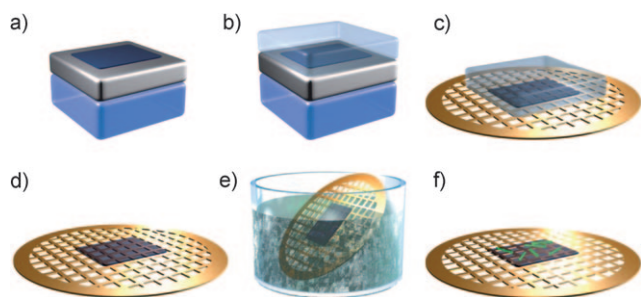
Figure 17. Production of graphene membranes for TEM support application. Graphene, grown on metal (a) is covered with a layer of plastic (b). The sacrificial metal layer is etched away, and graphene on plastic is fished on a standard TEM grid (c). Upon the removal of the plastic layer (d) the graphene membrane can be exposed to a solution of biomolecules (e), which adsorb on the surface of graphene (f) and can be studied in a TEM.

Initially, free-standing graphene membranes were produced from exfoliated graphene[162,163] and required several lithography steps during their manufacturing. With the availability of chemical vapor deposition (CVD)-grown graphene,[164,165] the technique became dramatically simpler, enabling production on an industrial scale. Graphene, epitaxially grown on the surface of a metal (either by precipitation of the dissolved carbon upon cooling or by direct catalytic cracking of the hydrocarbons on the hot surface of the metal, with subsequent graphitization), is covered by a sacrificial layer of plastic. The underlying metal is then removed by etching, and the plastic film (with graphene attached) can be transferred onto practically any surface. It can be placed, for example, on a metal grid with holes typically the size of few micrometers, where—upon the removal of the sacrificial plastic film—a free-standing graphene membrane is formed (Figure 17). This entire process is very reproducible and can result in a large total area of graphene membranes.

4.2. Transparent Conductive Coating

Another area which should benefit significantly from the availability of CVD-grown graphene is that of transparent conductive coatings. Graphene is unusually optically active[142–144,146] and absorbs a rather large fraction of incoming light for a monolayer (2.3%), but this is still significantly smaller than the typical absorption coefficient which could be achieved with a more traditional transparent conductive coating materials.[166] In conjunction with its low electrical resistivity, high chemical stability, and mechanical strength, this absorption coefficient makes graphene an attractive material for optoelectronic devices.

Transparent conductors are an essential part of many optical devices, from solar cells to liquid-crystal displays and touch screens. Traditionally metal oxides or thin metallic films have been used for these purposes,[166] but with existing technologies often complicated (thin metallic films require antireflection coating, for example) and expensive (often using noble or rare metals), there has been an ongoing search for new types of conductive thin films. Furthermore, many of the widely used metal oxides exhibit non-uniform absorption across the visible spectrum and are chemically unstable; the commonly used indium tin oxide (ITO, In_2O_3:Sn), for instance, is known to inject oxygen and indium ions into the active media of a device.

Graphene avoids all of these disadvantages. Moreover, it has recently been demonstrated that large areas of graphene can be grown by the CVD method[126,164–165] and transferred onto practically any surface. Prototype devices (solar cells and liquid-crystal displays) which use graphene as a transparent conductive coating have already been created.[59,167]

4.3. Graphene Transistors

Even the very first graphene field-effect transistors demonstrated remarkable quality: prepared using rather

humble methods in poorly controlled environments, they still showed reasonably high quasiparticle mobility (up to 20 000 cm^{2}V^{-1}s^{-1}, Figure 18).[13,14] Although the role of differ-
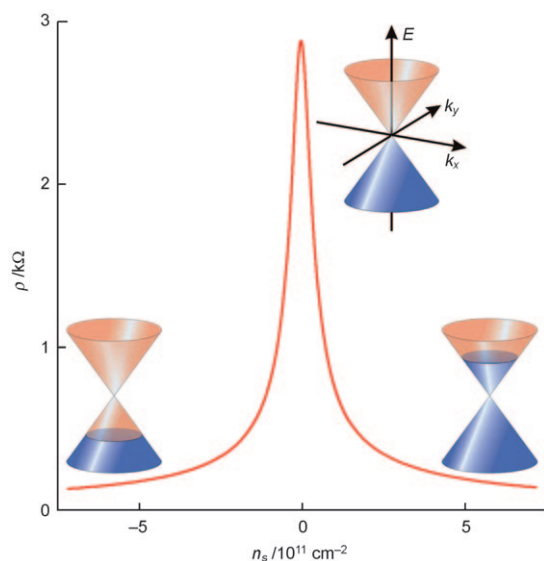
Figure 18. Ambipolar field effect in graphene.

ent scattering mechanisms is still debated[106,118,168–179] the careful elimination of Coulomb and resonant scatterers, as well as ripples, has allowed the achievement of mobilities of over 10^6 cm^{2}V^{-1}s^{-1} at low temperatures[180] in free-standing devices,[155–156] and offers hope that values above 10^5 cm^{2}V^{-1}s^{-1} can be achieved even at ambient temperatures.[181]

Such characteristics make graphene field-effect transistors extremely promising for high-frequency applications.[182,183] Additional benefits are also emerging from very favorable electrostatics of 2D films and high Fermi velocity (which is important in ballistic regimes). Even when using graphene with rather modest mobility (ca. 10^3 cm^{2}V^{-1}s^{-1}), current gain has been achieved at frequencies as high as 100 GHz for 240 nm gate length transistors (power gain for similar devices was achieved below 14 GHz),[184] which is better than for Si metal oxide semiconductor FETs of the same gate length.

The situation is not as bright for integrated circuits. The Klein paradox ensures a finite minimum conductivity for graphene (of the order of 4e^2/h) even within the limit of nominally zero carrier concentration. This is definitely too high for applications in logic elements, as it leads to high 'leakage' current in the "off" state and limits the possible on/off ratio of such transistors to about 10^3 even in very favorable circumstances.

There are several possible tricks one can play to increase the on/off ratio of graphene transistors, however. One is to utilize low-dimensional graphene nanostructures such as graphene nanoribbons,[185] quantum dots,[186] and single-electron transistors,[186,187] where a band gap can be engineered due to quantum confinement or Coulomb blockade. The smallest quantum dots (a few nanometers in size) demon-

strate a significant gap of the order of few hundred meV, which is enough for such transistors to achieve an on/off ratio of the order of 10^5 even at room temperatures.[186] The strong carbon–carbon bonds ensure the mechanical and chemical stability of such devices, which also can pass a significant current without diminishing their properties. Basically, we can think of it as top-down molecular electronics—one nanometer-sized graphene quantum dot contains only about 10^2 atoms. The major problem with implementing such quantum dots would be the limits of modern lithographic techniques, which do not currently allow true nanometer resolution. Also, one would have to control the roughness and chemistry of the edges with atomic precision, which is also beyond the capabilities of modern technology.

Although modern microelectronics relies on lithographic techniques, one can imagine using other approaches to form nanostructures which would eventually allow reproduction of fine details far beyond the resolution of lithography. One promising method would be the use of the self-organization properties of chemical reactions. Graphene nanostructures could be formed, for instance, by fluorination of the supposed-to-be-insulating parts. Partial fluorination or hydrogenation can result in the formation of self-organized structures on a graphene surface,[188,189] which, in principle, could be used to modify its transport and optical properties.

The other possible way to open a gap in the spectrum of quasiparticles in graphene is to use chemically modified graphene,[76–80] where the π electrons are participating in the covalent bond with foreign atoms attached to the carbon scaffolding. One could also use bilayer graphene, as a gap can be opened by applying a potential difference between the two layers.[83–85,151–154] An on/off ratio of 2000 has recently been achieved in dual-gated devices at low temperatures.[190]

4.4. Graphene Composites

The unique combination of graphene's electronic, chemical, mechanical, and optical properties can be utilized in full in composite materials. It is also relatively easy to prepare graphene for such an application: one can either use the direct chemical exfoliation of graphene,[59,60] which allows a rather high yield of graphene flakes in a number of organic solvents, or go through an oxidation process to prepare graphite oxide—which can be easily exfoliated in water—with subsequent reduction in a number of reducing media.[21]

The strongest and simultaneously one of the stiffest known materials, with a Young's modulus of 1 TPa, graphene is an ideal candidate for use as a reinforcement in high-performance composites.[22] There is a huge advantage in its being exactly one atom thick: it cannot cleave, giving it the maximum possible strength in the off-plane direction. Its high aspect ratio also allows graphene to act as an ideal stopper for crack propagation. As for interaction with the matrix—the central issue for all nanocomposite fillers like carbon fiber or carbon nanotubes—chemical modification of the surface or edges may significantly strengthen the interface between the graphene and polymer.

Using chemical derivatives of graphene would not only broaden the range of possible matrices but also widen the functionality of the possible composites. Given that the mechanical strength of fluorographene is only slightly smaller than that of pristine graphene,[77] one can obtain composites with similar mechanical properties but a range of other characteristics, from optically transparent to opaque, and from electrically conductive to insulating.

We should also benefit strongly from the possibility of optically monitoring the strain in graphene.[22, 123–125] The Raman spectrum of graphene[191–193] changes significantly with strain, so even mechanical distortions of a fraction of a percent can be easily detected. As the stress transfer between graphene and polymer is reasonably good,[22] and graphene's Raman signal is very strong (the strongest peaks in the Raman spectrum of graphene are due to either single or double resonant processes), one can easily detect stress build-up in the composite material under investigation by monitoring the position of the Raman peaks.

4.5. Other Applications

It is impossible to review all the potential applications of graphene in one lecture: with practically all the properties of this 2D crystal superior to those in other materials, and the combination of these properties unique, we are limited only by our own imaginations. In terms of electronic properties it is worth mentioning ultimately sensitive gas detectors[194] (graphene, being surface without bulk, can detect a single foreign molecule attached to it) and variable quantum capacitors.[195,196] In photonics, ultrafast photodetectors[197] (utilizing the high mobility and high Fermi velocity of quasiparticles in graphene) and extremely efficient mode lockers[198] must be noted. Additionally, its unprecedented mechanical strength and high crystallographic quality allow one to use graphene to provide the perfect gas barrier[28] and strain gauges.[126]

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