

RANDOM WALK TO GRAPHENE

Nobel Lecture, December 8, 2010

by

ANDRE K. GEIM

School of Physics and Astronomy, The University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom.

If one wants to understand the beautiful physics of graphene, they will be spoiled for choice with so many reviews and popular science articles now available. I hope that the reader will excuse me if on this occasion I recommend my own writings [1–3]. Instead of repeating myself here, I have chosen to describe my twisty scientific road that eventually led to the Nobel Prize. Most parts of this story are not described anywhere else, and its timeline covers the period from my PhD in 1987 to the moment when our 2004 paper, recognised by the Nobel Committee, was accepted for publication. The story naturally gets denser in events and explanations towards the end. Also, it provides a detailed review of pre-2004 literature and, with the benefit of hindsight, attempts to analyse why graphene has attracted so much interest. I have tried my best to make this article not only informative but also easy to read, even for non-physicists.

ZOMBIE MANAGEMENT

My PhD thesis was called “Investigation of mechanisms of transport relaxation in metals by a helicon resonance method”. All I can say is that the stuff was as interesting at that time as it sounds to the reader today. I published five journal papers and finished the thesis in five years, the official duration for a PhD at my institution, the Institute of Solid State Physics. *Web of Science* soberly reveals that the papers were cited twice, by co-authors only. The subject was dead a decade before I even started my PhD. However, every cloud has its silver lining, and what I uniquely learned from that experience was that I should never torture research students by offering them “zombie” projects.

After my PhD, I worked as a staff scientist at the Institute of Microelectronics Technology, Chernogolovka, which belongs to the Russian Academy of Sciences. The Soviet system allowed and even encouraged junior staff to choose their own line of research. After a year of poking in different directions, I separated research-wise from my former PhD supervisor, Victor Petrashov, and started developing my own niche. It was an experimental system that was both new and doable, which was nearly an oxymoron, taking into account the scarce resources available at the time at Soviet research

institutes. I fabricated a sandwich consisting of a thin metal film and a superconductor separated by a thin insulator. The superconductor served only to condense an external magnetic field into an array of vortices, and this highly inhomogeneous magnetic field was projected onto the film under investigation. Electron transport in such a microscopically inhomogeneous field (varying on a submicron scale) was new research territory, and I published the first experimental report on the subject [4], which was closely followed by an independent paper from Simon Bending [5]. It was an interesting and reasonably important niche, and I continued studying the subject for the next few years, including a spell at the University of Bath in 1991 as a postdoctoral researcher working with Simon.

This experience taught me an important lesson: that introducing a new experimental system is generally more rewarding than trying to find new phenomena within crowded areas. The chances of success are much higher where the field is new. Of course, the fantastic results one originally hopes for are unlikely to materialise, but, in the process of studying any new system, something original inevitably shows up.

ONE MAN'S JUNK, ANOTHER MAN'S GOLD

In 1990, thanks to Vitaly Aristov, director of my Institute in Chernogolovka at the time, I received a six month visiting fellowship from the British Royal Society. Laurence Eaves and Peter Main from Nottingham University kindly agreed to accept me as a visitor. Six months is a very short period for experimental work, and circumstances dictated that I could only study devices readily available in the host laboratory. Available were submicron GaAs wires left over from previous experiments, all done and dusted a few years earlier. Under the circumstances, my experience of working in a poverty-stricken Soviet academy was helpful. The samples that my hosts considered practically exhausted looked like a gold vein to me, and I started working 100 hours per week to exploit it. This short visit led to two *Phys. Rev. Letters* of decent quality [6,7], and I often use this experience to tease my younger colleagues. When things do not go as planned and people start complaining, I provoke them by proclaiming 'there is no such thing as bad samples; there are only bad postdocs/students'. Search carefully and you will always find something new. Of course, it is better to avoid such experiences and explore new territories, but even if one is fortunate enough to find an experimental system as new and exciting as graphene, meticulousness and perseverance allow one to progress much further.

The pace of research at Nottingham was so relentless and, at the same time so inspiring, that a return to Russia was not an option. Swimming through Soviet treacle seemed no less than wasting the rest of my life. So at the age of thirty-three and with an *h*-index of 1 (latest papers not yet published), I entered the Western job market for postdocs. During the next four years I moved between different universities, from Nottingham to Copenhagen to Bath and back to Nottingham. Each move allowed me to get acquainted with

yet another topic or two, significantly broadening my research horizons. The physics I studied in those years could be broadly described as mesoscopic and involved such systems and phenomena as two-dimensional electron gases (2DEGs), quantum point contacts, resonant tunnelling and the quantum Hall effect (QHE), to name but a few. In addition, I became familiar with GaAlAs heterostructures grown by molecular beam epitaxy (MBE) and improved my expertise in microfabrication and electron-beam lithography, technologies I had started learning in Russia. All these elements came together to form the foundation for the successful work on graphene a decade later.

DUTCH COMFORT

By 1994 I had published enough quality papers and attended enough conferences to hope for a permanent academic position. When I was offered an associate professorship at the University of Nijmegen, I instantly seized upon the chance of having some security in my new post-Soviet life. The first task in Nijmegen was of course to establish myself. To this end, there was no start-up and no microfabrication to continue any of my previous lines of research. As resources, I was offered access to magnets, cryostats and electronic equipment available at Nijmegen's High Field Magnet Laboratory, led by Jan Kees Maan. He was also my formal boss and in charge of all the money. Even when I was awarded grants as the principal investigator (the Dutch funding agency FOM was generous during my stay in Nijmegen), I could not spend the money as I wished. All funds were distributed through so-called 'working groups' led by full professors. In addition, PhD students in the Netherlands could formally be supervised only by full professors. Although this probably sounds strange to many, this was the Dutch academic system of the 1990s. It was tough for me then. For a couple of years, I really struggled to adjust to the system, which was such a contrast to my joyful and productive years at Nottingham. In addition, the situation was a bit surreal because outside the university walls I received a warm-hearted welcome from everyone around, including Jan Kees and other academics.

Still, the research opportunities in Nijmegen were much better than in Russia and, eventually, I managed to survive scientifically, thanks to help from abroad. Nottingham colleagues (in particular Mohamed Henini) provided me with 2DEGs that were sent to Chernogolovka, where Sergey Dubonos, a close colleague and friend from the 1980s, microfabricated requested devices. The research topic I eventually found and later focused on can be referred to as mesoscopic superconductivity. Sergey and I used micron-sized Hall bars made from a 2DEG as local probes of the magnetic field around small superconducting samples. This allowed measurements of their magnetisation with accuracy sufficient to detect not only the entry and exit of individual vortices but also much more subtle changes. This was a new experimental niche, made possible by the development of an original technique of ballistic Hall micromagnetometry [8]. During the next few

years, we exploited this niche area and published several papers in *Nature* and *Phys. Rev. Letters* which reported a paramagnetic Meissner effect, vortices carrying fractional flux, vortex configurations in confined geometries and so on. My wife Irina Grigorieva, an expert in vortex physics [9], could not find a job in the Netherlands and therefore had plenty of time to help me with conquering the subject and writing papers. Also, Sergey not only made the devices but also visited Nijmegen to help with measurements. We established a very productive modus operandi where he collected data and I analysed them within an hour on my computer next door to decide what should be done next.

A SPELL OF LEVITY

The first results on mesoscopic superconductivity started emerging in 1996, which made me feel safer within the Dutch system and also more inquisitive. I started looking around for new areas to explore. The major facility at Nijmegen's High Field Lab was powerful electromagnets. They were a major headache, too. These magnets could provide fields up to 20 T, which was somewhat higher than 16 to 18 T available with the superconducting magnets that many of our competitors had. On the other hand, the electromagnets were so expensive to run that we could use them only for a few hours at night, when electricity was cheaper. My work on mesoscopic superconductivity required only tiny fields ($< 0.01\text{T}$), and I did not use the electromagnets. This made me feel guilty as well as responsible for coming up with experiments that would justify the facility's existence. The only competitive edge I could see in the electromagnets was their room temperature (T) bore. This was often considered as an extra disadvantage because research in condensed matter physics typically requires low, liquid-helium T . The contradiction prompted me, as well as other researchers working in the lab, to ponder on high-field phenomena at room T . Unfortunately, there were few to choose from.

Eventually, I stumbled across the mystery of so-called magnetic water. It is claimed that putting a small magnet around a hot water pipe prevents formation of scale inside the pipe. Or install such a magnet on a water tap, and your kettle will never suffer from chalky deposits. These magnets are available in a great variety in many shops and on the internet. There are also hundreds of articles written on this phenomenon, but the physics behind it remains unclear, and many researchers are sceptical about the very existence of the effect [10]. Over the last fifteen years I have made several attempts to investigate "magnetic water" but they were inconclusive, and I still have nothing to add to the argument. However, the availability of ultra-high fields in a room T environment invited lateral thinking about water. Basically, if magnetic water existed, I thought, then the effect should be clearer in 20 T rather than in typical fields of $< 0.1\text{T}$ created by standard magnets.

With this idea in mind and, allegedly, on a Friday night, I poured water inside the lab's electromagnet when it was at its maximum power. Pouring

water in one's equipment is certainly not a standard scientific approach, and I cannot recall why I behaved so 'unprofessionally'. Apparently, no one had tried such a silly thing before, although similar facilities existed in several places around the world for decades. To my surprise, water did not end up on the floor but got stuck in the vertical bore of the magnet. Humberto Carmona, a visiting student from Nottingham, and I played for an hour with the water by breaking the blockage with a wooden stick and changing the field strength. As a result, we saw balls of levitating water (Figure 1). This was awesome. It took little time to realise that the physics behind was good old diamagnetism. It took much longer to adjust my intuition to the fact that the feeble magnetic response of water ($\sim 10^{-5}$), billions of times weaker than that of iron, was sufficient to compensate the earth's gravity. Many colleagues, including those who worked with high magnetic fields all their lives, were flabbergasted, and some of them even argued that this was a hoax.

I spent the next few months demonstrating magnetic levitation to colleagues and visitors, as well as trying to make a 'non-boffin' illustration for this beautiful phenomenon. Out of the many objects that we had floating inside the magnet, it was the image of a levitating frog (Figure 1) that started the media hype. More importantly, though, behind all the media noise, this image found its way into many textbooks. However quirky, it has become a beautiful symbol of ever-present diamagnetism, which is no longer perceived to be extremely feeble. Sometimes I am stopped at conferences by people exclaiming "I know you! Sorry, it is not about graphene. I start my lectures with showing your frog. Students always want to learn how it could fly." The frog story, with some intricate physics behind the stability of diamagnetic levitation, is described in my review in *Physics Today* [11].

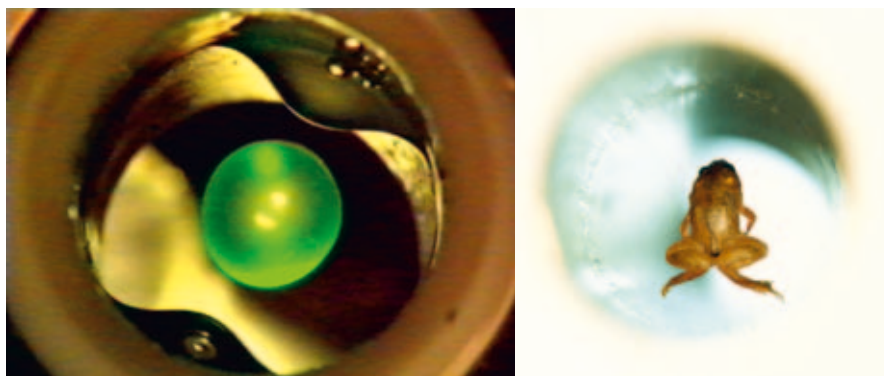


Figure 1. Levitating moments in Nijmegen. Left – Ball of water (about 5 cm in diameter) freely floats inside the vertical bore of an electromagnet. Right – The frog that learned to fly. This image continues to serve as a symbol showing that magnetism of 'nonmagnetic things', including humans, is not so negligible. This experiment earned Michael Berry and me the 2000 Ig Nobel Prize. We were asked first whether we dared to accept this prize, and I take pride in our sense of humour and self-deprecation that we did.

FRIDAY NIGHT EXPERIMENTS

The levitation experience was both interesting and addictive. It taught me the important lesson that poking in directions far away from my immediate area of expertise could lead to interesting results, even if the initial ideas were extremely basic. This in turn influenced my research style, as I started making similar exploratory detours that somehow acquired the name ‘Friday night experiments’. The term is of course inaccurate. No serious work can be accomplished in just one night. It usually requires many months of lateral thinking and digging through irrelevant literature without any clear idea in sight. Eventually, you get a feeling – rather than an idea – about what could be interesting to explore. Next, you give it a try, and normally you fail. Then, you may or may not try again. In any case, at some moment you must decide (and this is the most difficult part) whether to continue further efforts or cut losses and start thinking of another experiment. All this happens against the backdrop of your main research and occupies only a small part of your time and brain.

Already in Nijmegen, I started using lateral ideas as under- and post-graduate projects, and students were always excited to buy a pig in a poke. Kostya Novoselov, who came to Nijmegen as a PhD student in 1999, took part in many of these projects. They never lasted for more than a few months, in order not to jeopardise a thesis or career progression. Although the enthusiasm inevitably vanished towards the end, when the predictable failures materialised, some students later confided that those exploratory detours were invaluable experiences.

Most surprisingly, failures sometimes failed to materialise. Gecko tape is one such example. Accidentally or not, I read a paper describing the mechanism behind the amazing climbing ability of geckos [12]. The physics is rather straightforward. Gecko’s toes are covered with tiny hairs. Each hair attaches to the opposite surface with a minute van der Waals force (in the nN range), but billions of hairs work together to create a formidable attraction sufficient to keep geckos attached to any surface, even a glass ceiling. In particular, my attention was attracted by the spatial scale of their hairs. They were submicron in diameter, the standard size in research on mesoscopic physics. After toying with the idea for a year or so, Sergey Dubonos and I came up with procedures to make a material that mimicked a gecko’s hairy feet. He fabricated a square cm of this tape, and it exhibited notable adhesion [13]. Unfortunately, the material did not work as well as a gecko’s feet, deteriorating completely after a couple of attachments. Still, it was an important proof-of-concept experiment that inspired further work in the field. Hopefully, one day someone will develop a way to replicate the hierarchical structure of gecko’s setae and its self-cleaning mechanism. Then gecko tape can go on sale.

BETTER TO BE WRONG THAN BORING

While preparing for my lecture in Stockholm, I compiled a list of my Friday night experiments. Only then did I realise a stunning fact. There were two dozen or so experiments over a period of approximately fifteen years and, as expected, most of them failed miserably. But there were three hits: levitation, gecko tape and graphene. This implies an extraordinary success rate: more than 10%. Moreover, there were probably near-misses, too. For example, I once read a paper [14] about giant diamagnetism in FeGeSeAs alloys, which was interpreted as a sign of high- T superconductivity. I asked Lamarches for samples and got them. Kostya and I employed ballistic Hall magnetometry to check for giant diamagnetism but found nothing, even at 1 K. This happened in 2003, well before the discovery of iron pnictide superconductivity, and I still wonder whether there were any small inclusions of a superconducting material which we missed with our approach. Another miss was an attempt to detect “heartbeats” of individual living cells. The idea was to use 2DEG Hall crosses as ultrasensitive electrometers to detect electrical signals due to physiological activity of individual cells. Even though no heartbeats were detected while a cell was alive, our sensor recorded huge voltage spikes at its “last gasp” when the cell was treated with excess alcohol [15]. Now I attribute this near-miss to the unwise use of yeast, a very dormant microorganism. Four years later, similar experiments were done using embryonic heart cells and – what a surprise – graphene sensors, and they were successful in detecting such bioelectrical activity [16].

Frankly, I do not believe that the above success rate can be explained by my lateral ideas being particularly good. More likely, this tells us that poking in new directions, even randomly, is more rewarding than is generally perceived. We are probably digging too deep within established areas, leaving plenty of unexplored stuff under the surface, just one poke away. When one dares to try, rewards are not guaranteed, but at least it is an adventure.

THE MANCUNIAN WAY

By 2000, with mesoscopic superconductivity, diamagnetic levitation and four *Nature* papers under my belt, I was well placed to apply for a full professorship. Colleagues were rather surprised when I chose the University of Manchester, declining a number of seemingly more prestigious offers. The reason was simple. Mike Moore, chairman of the search committee, knew my wife Irina when she was a very successful postdoc in Bristol rather than my co-author and a part-time teaching lab technician in Nijmegen. He suggested that Irina could apply for the lectureship that was there to support the professorship. After six years in the Netherlands, the idea that a husband and wife could officially work together had not even crossed my mind. This was the decisive factor. We appreciated not only the possibility of sorting out our dual career problems but also felt

touched that our future colleagues cared. We have never regretted the move.

So in early 2001, I took charge of several dilapidated rooms storing ancient equipment of no value, and a start-up grant of £100K. There were no central facilities that I could exploit, except for a helium liquefier. No problem. I followed the same routine as in Nijmegen, combining help from other places, especially Sergey Dubonos. The lab started shaping up surprisingly quickly. Within half a year, I received my first grant of £500K, which allowed us to acquire essential equipment. Despite being consumed with our one year old daughter, Irina also got her starting grant a few months later. We invited Kostya to join us as a research fellow (he continued to be officially registered in Nijmegen as a PhD student until 2004 when he defended his thesis there). And our group started generating results that led to more grants that in turn led to more results.

By 2003 we published several good-quality papers including *Nature*, *Nature Materials* and *Phys. Rev. Letters*, and we continued beefing up the laboratory with new equipment. Moreover, thanks to a grant of £1.4M (research infrastructure funding scheme masterminded by the then science minister David Sainsbury), Ernie Hill from the Department of Computer Sciences and I managed to set up the Manchester Centre for Mesoscience and Nanotechnology. Instead of pouring the windfall money into bricks-and-mortar, we utilised the existing clean room areas (~250 m²) in Computer Sciences. Those rooms contained obsolete equipment, and it was thrown away and replaced with state-of-the-art microfabrication facilities, including a new electron-beam lithography system. The fact that Ernie and I are most proud of is that many groups around the world have more expensive facilities but our Centre has continuously, since 2003, been producing new structures and devices. We do not have a posh horse here that is for show, but rather a draft horse that has been working really hard.

Whenever I describe this experience to my colleagues abroad, they find it difficult to believe that it is possible to establish a fully functional laboratory and a microfabrication facility in less than three years and without an astronomical start-up grant. If not for my own experience, I would not believe it either. Things progressed unbelievably quickly. The University was supportive, but my greatest thanks are reserved specifically for the responsive mode of the UK Engineering and Physical Sciences Research Council (EPSRC). The funding system is democratic and non-xenophobic. Your position in an academic hierarchy or an old-boys network counts for little. Also, 'visionary ideas' and grand promises to 'address social and economic needs' play little role when it comes to the peer review. In truth, the responsive mode distributes its money on the basis of a recent track record, whatever that means in different subjects, and the funding normally goes to researchers who work both efficiently and hard. Of course, no system is perfect, and one can always hope for a better one. However, paraphrasing Winston Churchill, the UK has the worst research funding system, except for all the others that I am aware of.

THREE LITTLE CLOUDS

As our laboratory and Nanotech Centre were shaping up, I got some spare time for thinking of new research detours. Gecko tape and the failed attempts with yeast and quasi-pnictides took place during that time. Also, Serge Morozov, a senior fellow from Chernogolovka, who later became a regular visitor and invaluable collaborator, wasted his first two visits on studying magnetic water. In the autumn of 2002, our first Manchester PhD student, Da Jiang, arrived, and I needed to invent a PhD project for him. It was clear that for the first few months he needed to spend his time learning English and getting acquainted with the lab. Accordingly, as a starter, I suggested to him a new lateral experiment. It was to make films of graphite ‘as thin as possible’ and, if successful, I promised we would then study their ‘mesoscopic’ properties. Recently, trying to analyse how this idea emerged, I recalled three badly shaped thought clouds.

One cloud was a concept of ‘metallic electronics’. If an external electric field is applied to a metal, the number of charge carriers near its surface changes, so that one may expect that its surface properties change, too. This is how modern semiconductor electronics works. Why not use a metal instead of silicon? As an undergraduate student, I wanted to use electric field effect (EFE) and X-ray analysis to induce and detect changes in the lattice constant. It was naïve because simple estimates show that the effect would be negligible. Indeed, no dielectric allows fields much higher than 1V/nm, which translates into maximum changes in charge carrier concentration n at the metal surface of about 10^{14} per cm^2 . In comparison, a typical metal (e.g., Au) contains $\sim 10^{23}$ electrons per cm^3 and, even for a 1 nm thick film, this yields relative changes in n and conductivity of $\sim 1\%$, leaving aside much smaller changes in the lattice constant.

Previously, many researchers aspired to detect the field effect in metals. The first mention is as far back as 1902, shortly after the discovery of the electron. J. J. Thomson (1906 Nobel Prize in Physics) suggested to Charles Mott, the father of Nevill Mott (1977 Nobel Prize in Physics), to look for the EFE in a thin metal film, but nothing was found [17]. The first attempt to measure the EFE in a metal was recorded in scientific literature in 1906 [18]. Instead of a normal metal, one could also think of semimetals such as bismuth, graphite or antimony which have a lot fewer carriers. Over the last century, many researchers used Bi films ($n \sim 10^{18} \text{ cm}^{-3}$) but observed only small changes in their conductivity [19,20]. Aware of this research area and with experience in GaAlAs heterostructures, I was continuously, albeit casually, looking for other candidates, especially ultra-thin films of superconductors in which the field effect can be amplified in proximity to the superconducting transition [21,22]. In Nijmegen, my enthusiasm was once sparked by learning about nm-thick Al films grown by MBE on top of GaAlAs heterostructures but, after estimating possible effects, I decided that the chances of success were so poor it was not worth trying.

Carbon nanotubes were the second cloud hanging around in the late

1990s and early 2000s. Those were the years when nanotubes were at the peak of their glory. Living in the Netherlands, I heard talks by Cees Dekker and Leo Kouwenhoven and read papers by Thomas Ebbesen, Paul McEuen, Sumio Iijima, Pheadon Avouris and others. Each time, those exceptionally nice results inevitably triggered thoughts about entering this research area. But I was too late and needed to find a different perspective, away from the stampede.

As for the third cloud, I read a review of Millie Dresselhaus about intercalated graphite compounds [23], which clearly showed that, even after many decades, graphite was still a material little understood, especially in terms of its electronic properties. This influential review prompted me to look further into graphite literature. In doing so, I encountered papers by Pablo Esquinazi and Yakov Kopelevich, who reported ferromagnetism, superconductivity and a metal-insulator transition, all in the same good old graphite and at room T [24,25]. Those provocative papers left me with a distinct feeling that graphite was very much worth having a careful look at.

The three thought clouds (and maybe some more that I cannot recall) somehow merged into Da's project. I reckoned that if we were to succeed in making thin films of graphite, instead of Bi, they could exhibit some electric field effect and/or some other interesting properties resembling those of carbon nanotubes. In the worst-case scenario, our mesoscopic samples would be monocrystals and this could help to clarify those controversies about graphite. Why not try to poke in this direction for a few months, I thought.

LEGEND OF SCOTCH TAPE

To make thin graphite films, I provided Da with a tablet of pyrolytic graphite, which was several mm thick and an inch in diameter, and suggested using a polishing machine. We had a fancy one that allowed submicron flatness. A few months later, Da declared that he had reached the ultimate thickness and showed me a tiny speck of graphite at the bottom of a Petri dish. I looked at it in an optical microscope and, by focusing on the top and bottom surfaces, estimated that the speck was $\sim 10\ \mu\text{m}$ thick. Too thick, I thought and suggested trying a finer polishing liquid. However, it turned out that Da had polished away the whole tablet to obtain this one speck. It was actually my fault: Da successfully finished his PhD later, but at that time he was just a fresh foreign student with a huge language barrier. Moreover, by mistake I gave him high-density graphite instead of highly-oriented pyrolytic graphite (HOPG) as was intended. The former does not shed as easily as HOPG.

Oleg Shklyarevskii, a senior fellow from Kharkov, Ukraine was working nearby and had to listen to the typical flow of my teasing remarks, this time about polishing a mountain to get one grain of sand. Oleg was an expert in scanning tunnelling microscopy (STM) and worked on a project that later turned out to be another bad 'Friday night' idea of mine. He interjected by bringing over a piece of cellotape with graphite flakes attached to it. Allegedly, he just fished out the tape from a litter bin. Indeed, HOPG is

the standard reference sample for STM, where a fresh surface of graphite is normally prepared by removing a top layer with sticky tape. We used this technique for years but never looked carefully at what was thrown away along with the tape. I looked in the microscope at the remnants of graphite (Figure 2) and found pieces much thinner than Da's speck. Only then did I realise how silly it was of me to suggest the polishing machine. Polishing was dead, long live Scotch tape!

This moment was not a breakthrough yet, but things started to look promising and required more people to get involved. Oleg did not volunteer to take on yet another project but Kostya did. 'Volunteer' is probably not the right word. Everyone in our lab has always been welcome to move around and participate in whatever project they want. At that time, Kostya was working on a nicely-moving project on ferromagnetism [26]. He was also our 'caretaker' when things went wrong, especially with measuring equipment. As for me, at that time I used to spend a few hours a day in the lab preparing samples, doing measurements and analysing results. It was only after 2006 that I turned into a paper-writing machine combined with a data analyser. I have always loved the latter but hated to write papers. Unfortunately, no lab can survive without its Shakespeare.

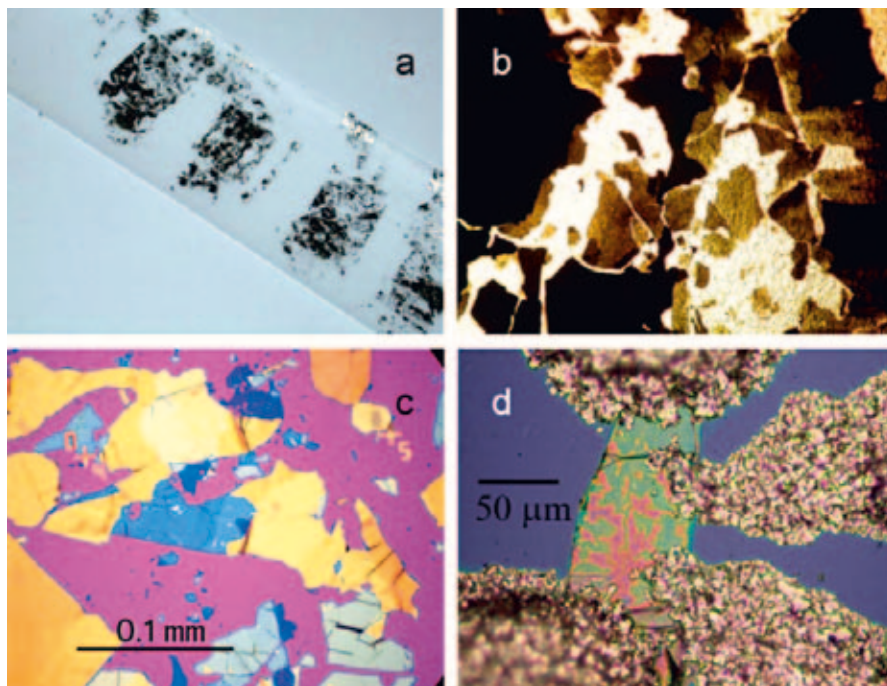


Figure 2. In hindsight, thin crystals of graphite are easy to obtain. **a** – Remnants of HOPG left attached to Scotch tape. **b** – Some of the crystals are optically transparent if viewed in an optical microscope or just with a magnifying glass. **c** – If placed on an oxidised Si wafer, transparent crystals give rise to various shades of blue. **d** – One of our very first devices made by using 'a shoestring and sealing wax': in this case, tweezers, a toothpick and silver paint.

Kostya and I decided to check out the electrical properties of the graphite flakes found on the cello tape and, to this end, he started transferring them onto glass slides, initially by using just tweezers. A few days later and keeping in mind the initial motivation, I brought in oxidised Si wafers in order to use them as substrates and detect the EFE. This delivered an unexpected bonus. Placing thin graphite fragments onto those wafers allowed us to observe interference colours that indicated that some of the fragments were optically transparent. Moreover, the colours provided us with a very intuitive way of judging which flakes were thin (Figure 2c). We quickly found that some of them were just a few nm thick. This was our first real breakthrough.

EUREKA MOMENT

In graphene literature and especially in popular articles, a strong emphasis is placed on the Scotch tape technique, and it is hailed for allowing the isolation and identification of ultra-thin graphite films and graphene. For me, this was an important development but still not a Eureka moment. Our goal always was to find some exciting physics rather than just observing ultra-thin films in a microscope.

Within a couple of days after Oleg prompted the use of Scotch tape, Kostya was already using silver paint to make electrical contacts to graphite platelets transferred from the Scotch tape. To our surprise, they turned out to be highly conductive and even the painted contacts exhibited a reasonably low resistance. The electronic properties could be studied, but we felt it was too early to put the ugly-looking devices (see Fig. 2d) in a cryostat for proper measurements. As a next step, we applied voltage, first, through the glass slides and, a bit later, to the Si wafer, using it as a back gate to check for the field effect. Figure 2 shows a photograph of one of our first devices. The central part is a graphite crystal that is ~ 20 nm thick, and its lateral size is comparable to the diameter of a human hair. To transfer the crystal by tweezers from the tape and then make four such closely-spaced contacts by using just a toothpick and silver paint is the highest level of experimental skill. These days, not many researchers have fingers green enough to make such samples. I challenge readers to test their own skills against this benchmark!

The very first hand-made device on glass exhibited a clear EFE such that its resistance could be changed by several per cent. It may sound small and of marginal importance but, aware of how hard it was previously to detect any EFE at all, I was truly shocked. If those ugly devices made by hand from relatively big and thick platelets already showed some field effect, what could happen, I thought, if we were to use our thinnest crystallites and apply the full arsenal of microfabrication facilities? There was a click in my head that we had stumbled onto something really exciting. This was my Eureka moment.

What followed was no longer a random walk. From this point, it was only logical to continue along the same path by improving procedures for cleaving and finding thinner and thinner crystals and making better and

better devices, which we did. It was both painstaking and incredibly rapid, depending on one's viewpoint. It took several months until we learned how to identify monolayers by using optical and atomic force microscopy. On the microfabrication side, we started using electron-beam lithography to define proper Hall bar devices and started making contacts by metal evaporation rather than silver painting. The microfabrication development was led by Dubonos, aided by his PhD student Anatoly Firsov. Initially, they employed facilities in Chernogolovka but, when our new postdoc Yuan Zhang got fully acquainted with the recently-installed lithography system at our Nanotech Centre, the process really speeded up.

The move from multilayers to monolayers and from hand-made to lithography devices was conceptually simple but never straightforward. We took numerous detours and wasted much effort on ideas that only led us into dead ends. An example of grand plans that never worked out was the idea to plasma-etch graphite mesas in the form of Hall bars which, after cleavage, would provide readily shaped devices, or so I thought. Later, we had to return to the unprocessed graphite. The teething problems we experienced at that time can also be illustrated by the fact that initially we believed that Si wafers should have a very precise thickness of oxide (within several nm) to allow hunting for monolayers. These days we can find graphene on practically any substrate. Crystal sizes also went up from a few microns to nearly a millimetre, just by tinkering with procedures and using different sources of graphite.

The most essential part of our 2004 report [27] was the electrical measurements, and this required a lot of work. For several months, Kostya and Serge Morozov were measuring full time, and I was around as well, discussing and analysing raw data, often as soon as they appeared on the screen. The feedback to our microfabrication guys was almost instantaneous. As always in the case of encountering a new system where one does not know what to expect, we had to be particularly careful in those first experiments. We disregarded any curve, unless it was reproducible for many devices and, to avoid any premature conclusions, we studied more than 50 ultra-thin devices. Those were years of hard work compressed into just a few months, but we were excited as every new device got better and better, and we could work 24x7, which typically meant fourteen hour days and no breaks for the weekends.

Finally, by the end of 2003, we got a reliable experimental picture ready for publication. Between that moment and the end of my timeline when the *Science* paper was accepted in September 2004, there is a lengthy gap. Those nine months were consumed by excruciating efforts to publish the results in a high-profile journal. We continuously added data and polished the presentation. Irina's help was invaluable in this time-consuming process, which can be fully appreciated only by those readers who ever published in such glossy journals. First, we submitted the manuscript to *Nature*. It was rejected and, when further information requested by referees was added, rejected again. According to one referee, our report did "not constitute a sufficient scientific advance." *Science* referees were more generous (or more knowledgeable?),

and the presentation was better polished by that time. In hindsight, I should have saved the time and nerves by submitting to a second-tier journal, even though we all felt that the results were ground-breaking. Readers aspiring to get published in those glossy magazines and having their papers recently rejected can use this story to cheer up: Their papers may also be prize winning!

DEFIANT EXISTENCE

One of the most surprising results of our *Science* report was the observation that, after being isolated, atomic planes remained continuous and conductive under ambient conditions. Even with hindsight, there are many reasons to be surprised.

First, for many decades researchers studied ultra-thin films, and their collective experience proves that continuous monolayers are practically impossible to make (see, e.g., [28,29]). Try to evaporate a metal film a few nm in thickness, and you will find it discontinuous. The material coagulates into tiny islands. This process, called island growth, is universal and driven by the fact that a system tries to minimise its surface energy. Even by using epitaxial substrates that provide an interaction working against the surface energy contribution and cooling them down to liquid-helium T , which prevents migration of deposited atoms, it is hard to find the right conditions to create continuous nm thick films, let alone monolayers [28,29].

The second reason to be surprised is that theory unequivocally tells us that an isolated graphene sheet should be thermodynamically unstable. Calculations show that 'graphene is the least stable [carbon] structure until about 6000 atoms' [30]. Until $\sim 24,000$ atoms (that is, a flat sheet with a characteristic size of ~ 25 nm), various 3D configurations are energetically more favourable than the 2D geometry [30,31]. For larger sizes, theory shows again that a graphene sheet is unstable but now with respect to scrolling. The latter conclusion is based on considering competing contributions from the bending and surface energies [32,33]. These calculations are specific to carbon, but the underlying physics is conceptually connected to the surface energy mechanism that leads to island growth.

Third, 2D crystals cannot be grown in isolation, without an epitaxial substrate that provides an additional atomic bonding. This follows from the Landau-Peierls argument that shows that the density of thermal fluctuations for a 2D crystal in the 3D space diverges with temperature [1]. Although the divergence is only logarithmic, crystal growth normally requires high T such that atoms become sufficiently mobile. This also implies a softer lattice with little shear rigidity. The combination of the two conditions sets a limit on possible sizes L of 2D atomic crystals. One can estimate L as $\sim a \exp(E/T_G)$ where $a \sim 1\text{\AA}$ is the lattice spacing, $E \sim 1\text{eV}$ the atomic bond energy and T_G the growth temperature. This consideration should not be applied to graphene at room T , which would yield astronomical sizes. T_G is usually comparable to the bond energy, which renders the disorder-generating mechanism irrelevant

at much lower T . Note that, in principle, self-assembly may allow growth of graphene at room T but, so far, this has been achieved only for nm-sized graphene sheets [34].

The fourth and probably the most important reason to be surprised is that graphene remains stable under ambient conditions. Surfaces of materials can react with air and moisture, and monolayer graphene has not one but two surfaces, making it more reactive. Surface science research involves ultra-high vacuum facilities and, often, liquid-helium T to keep surfaces stable and away from reactive species. For example, gold is one of the most inert materials in nature but, even for Au, it is hard to avoid its near-surface layer being partially oxidised in air. What then are the chances for a monolayer exposed to ambient conditions to remain unaffected?

Graphene flouts all the above considerations. It is instructive to analyse how. First, any existing method of obtaining graphene starts with 3D rather than 2D growth. Graphene sheets are initially formed either within the bulk or on top of an epitaxial substrate, which quenches the diverging thermal fluctuations. The interaction can be relatively weak, as in the case of graphene grown on graphite [35], but it is always present. This allows graphene to dodge the Landau-Peierls argument and, also, to avoid coagulation into islands and 3D carbon structures. Second, if graphene is cleaved or released from a substrate, the process is normally carried out at room T so that energy barriers remain sufficiently high. This allows atomic planes to persist in an isolated, non-scrolled form without any substrate [36], even though this is energetically unfavourable. If placed on a substrate, the van der Waals interaction may also be sufficient to prevent a graphene sheet from scrolling. Third, graphite is even more chemically inert than gold. Although graphene is more reactive than graphite and weakly reacts with air and pollutants at room T , this does not destroy its crystal lattice and high conductivity [37,38]. It requires T twice as high as room T to irreversibly damage graphene in air. Our ambient conditions appear fortuitous enough for the graphene lattice to survive.

REQUIEM FOR BRILLIANT IDEAS

Science literature is full of brilliant ideas that did not work. Searching the literature for those is not a good idea at all. At a start of a new project, a couple of decent reviews usually do the job of making sure that one does not reinvent the wheel. The alternative can be truly detrimental. I have met many promising researchers who later failed to live up to their promise because they wasted their time on searching literature, instead of spending it on searching for new phenomena. What's more, after months of literature search, they inevitably came to the same conclusion: Everything they planned had been done before. Therefore, they saw no reason to try their own ideas and, consequently, began a new literature search. One should realise that ideas are never new. However brilliant, every idea is always based on previous knowledge and, with so many smart people around, the odds are that some-

one somewhere had already thought of something similar before. This should not be used as an excuse for not trying because local circumstances vary and, moreover, facilities change with time. New technologies offer a reasonable chance that old failed ideas may work unpredictably well the next time round.

In 2002–2003, the merged thought clouds that I would not even call a brilliant idea were sufficient to instigate the project. They also provided us with an Ariadne’s thread that helped with choosing specific directions. Literature search was done in due course, after we roughly scouted the new area and especially when the results were being prepared for publication. In addition to the literature relevant to the thought clouds, our *Science* paper cited the challenges of obtaining isolated 2D crystals, their thermodynamic instability, the observation of nanoscrolls and papers on epitaxial growth. Those references were important to show the experimental progress we achieved. The first review of earlier literature was done in our 2007 progress article [1]. Since then, I updated my conference presentations whenever a historically important paper came to light. This is the first opportunity to update the history chapter in writing by adding several new references. Furthermore, my recent call for further historical insights [39] was answered by a number of researchers and, for completeness, I want to acknowledge their early ideas and contributions, too.

GRAPHENE INCARNATIONS

Looking back at graphene history, we should probably start with an observation by the British chemist Benjamin Brodie [40]. In 1859, by exposing graphite to strong acids, he obtained what he called ‘carbonic acid’ (Figure 3a). Brodie believed that he discovered ‘graphon’, a new form of carbon with a molecular weight of 33. Today we know that he observed a suspension of tiny crystals of graphene oxide, that is, graphene sheets densely covered with hydroxyl and epoxide groups [41]. Over the next century, there were quite a few papers describing the laminated structure of graphite oxide, but the next crucial step in graphene history was the proof that this ‘carbonic acid’ consisted of floating atomic planes. In 1948, G. Ruess and F. Vogt used transmission electron microscopy (TEM) and, after drying a droplet of a graphene-oxide suspension on a TEM grid, they observed creased flakes down to a few nm in thickness [42]. These studies were continued by the group of Ulrich Hofmann. In 1962, he and Hanns-Peter Boehm looked for the thinnest possible fragments of reduced graphite oxide and identified some of them as monolayers [43] (Figure 3b).

This remarkable observation received little attention until 2009–2010. I have to mention that the 1962 identification relied on a relative TEM contrast, an approach that would not stand today’s scrutiny because the contrast strongly depends on focusing conditions [44]. For example, Rahul Nair and I tried but predictably failed to distinguish between monolayers and somewhat thicker flakes by using only their TEM contrast. Graphene

monolayers were unambiguously identified in TEM only forty years after the 1962 paper by counting the number of folding lines [45–47]. Nonetheless, the Boehm-Hofmann work should, in my opinion, stand as the first observation of graphene because monolayers should have been present among the residue, and the idea was correct. Furthermore, it was Boehm and his colleagues who in 1986 introduced the term graphene, deriving it from the combination of the word ‘graphite’ and the suffix that refers to polycyclic aromatic hydrocarbons [48].

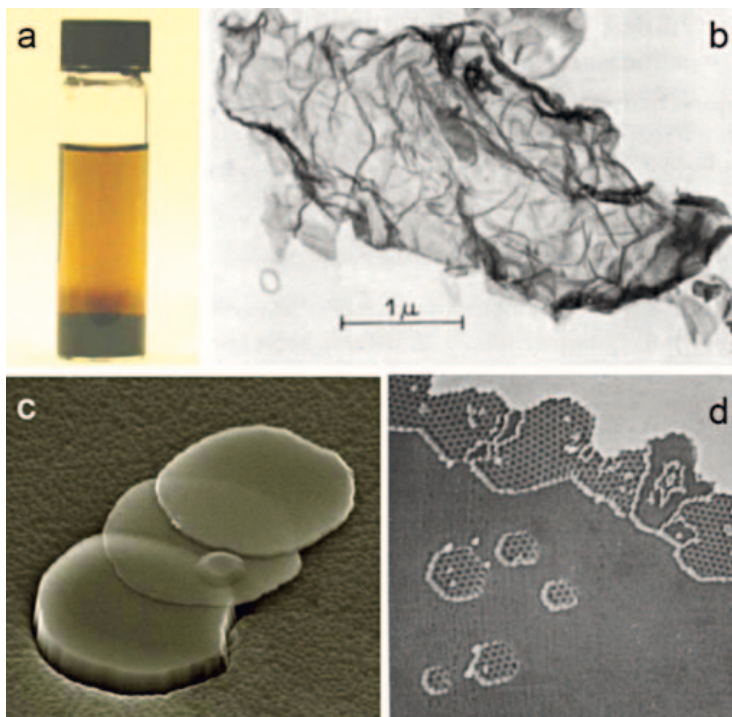


Figure 3. Prehistory of graphene. **a** – Graphene as probably seen by Brodie 150 years ago. Graphite oxide at the bottom of the container dissolves in water making the yellow suspension of floating graphenic flakes. **b** – TEM image of ultra-thin graphitic flakes from the early 1960s (copied with permission from ref. [43]). **c** – Scanning electron microscopy (SEM) image of thin graphite platelets produced by cleavage (similar to images reported in ref. [60]). **d** – STM of graphene grown on Pt (copied with permission from ref. [53]). The image is 100x100 nm² in size. The hexagonal superstructure has a period of ~22 Å and appears due to the interaction of graphene with the metal substrate.

In addition to the TEM observations, another important line in pre-2004 graphene research was its epitaxial growth. Ultra-thin graphitic films and, sometimes, even monolayers were grown on metal substrates [49–53], insulating carbides [54–57] and graphite [35] (see Fig. 3d). The first papers I am aware of go back to 1970 when John Grant reported graphitic films on Ru and Rh [49] and Blakely *et al.* on Ni [50]. Epitaxial growth on insulating substrates was first demonstrated by van Bommel *et al.* in 1975 [54] whereas

Chuhei Oshima found other carbides allowing graphene growth (for example, TiC) [55]. The grown films were usually analysed by surface science techniques that average over large areas and say little about the film's continuity and quality. Occasionally, STM was also used for visualisation and local analysis.

Even more relevant were earlier attempts to obtain ultra-thin films of graphite by cleavage, similar to what we did in 2003. In 1990, Heinrich Kurz's group reported 'peeling optically thin layers with transparent tape' (read Scotch tape), which were then used to study carrier dynamics in graphite [58]. In 1995, Thomas Ebbesen and Hidefumi Hiura described few-nm-thick 'origami' visualised by atomic force microscopy (AFM) on top of HOPG [59]. Rod Ruoff also photographed thin graphite platelets in SEM [60] (Fig. 3c). In 2003, monolayers were reported by Yang Gan who used STM for their cleavage on top of HOPG [61].

Finally, there were electrical studies of thin graphite films. Between 1997 and 2000, Yoshiko Ohashi succeeded in cleaving crystals down to ~20 nm in thickness, studied their electrical properties including Shubnikov – de Haas oscillations and, quite remarkably, observed the electric field effect with resistivity changes of up to 8% [62,63]. Also, Ebbesen's group succeeded in growth of micron-sized graphitic disks with thickness down to 60 layers and measured their electrical properties [64].

As for theory, let me make only a short note (for more references, see [1,65]). Theoretically, graphene ('a monolayer of graphite') was around since 1947 when Phil Wallace first calculated its band structure as a starting point to understanding the electronic properties of bulk graphite [66]. Gordon Semenoff and Duncan Haldane realised that graphene could provide a nice condensed-matter analogue of (2+1)-dimensional quantum electrodynamics [67,68] and, since then, the material served as a toy model to address various questions of QED (see, e.g., [69,70]). Many of the theories became relevant to experiment well before 2004, when electronic properties of carbon nanotubes (rolled-up graphene ribbons) were investigated. A large amount of important theoretical work on graphene was done by Tsuneya Ando, and Millie Dresselhaus and co-workers (see, e.g., [71–73]).

To complete the history of graphene, let me also acknowledge some earlier ideas. Thomas Ebbesen and Hidefumi Hiura envisaged a possibility of graphene-based nanoelectronics in 1995 (as an example, they referred to epitaxial graphene grown on TiC) [59]. In patent literature, speculations about "field effect transistors employing pyrolytic graphite" go back as far as 1970 [74]. Also, it was pointed out to me by Rod Ruoff and Reginald Little that their pre-2004 papers discussed possibilities and mentioned an intention of obtaining isolated monolayers [60,75]. Finally, the layered structure of graphite was known since early days of X-ray crystallography, and researchers certainly have been aware of graphite being a deck of weakly bonded graphene planes for an even longer time. This property has been widely used to create a variety of intercalated graphite compounds [23] and, of course, to make drawings. After all, we now know that isolated monolayers can be

found in every pencil trace, if one searches carefully enough in an optical microscope [2]. Graphene has literally been before our eyes and under our noses for many centuries but was never recognised for what it really is.

Πλανήτη GRAPHENE

The reader may find some of the cited ideas and historical papers irrelevant, but I tried my best to avoid any pre-2004 result, especially experimental, being overlooked. All the mentioned studies poked in the right direction, but there were no big surprises to spark a graphene gold rush. This is probably because the earlier experiments had one thing in common. They were observational. They observed ultra-thin graphitic films, and occasionally even monolayers without reporting any of graphene's distinguishing properties. The very few electrical and optical measurements cited above were done using thin films of graphite and could not assess the physics that graphene has brought to the fore since 2004.

Our *Science* paper provided a clear watershed. Of course, the article reported the isolation of graphene crystals large enough to do all sorts of measurements, beyond the observation in an electron or scanning probe microscope. The method of graphene isolation and identification it described was so straightforward and accessible that even schoolchildren could probably do it. This was important but, if we were to stop there, just with the observations, our work would only add to the previous literature and, I believe, disappear into oblivion. It is not the observation and isolation of graphene but its electronic properties that took researchers by surprise. Our measurements delivered news well beyond the Scotch tape technique, which persuaded many researchers to join in the graphene rush.

First, the 2004 paper reported an ambipolar electric field effect, in which resistivity changed by a factor of ~ 100 . This is thousands of times more than the few per cent changes observed previously for any metallic system and amounted to a qualitative difference. To appreciate the exquisiteness of this observation, imagine a nanometre thick Au film. No matter what you do with such a film by physical means, it will remain a normal metal with the same properties. In contrast, properties of graphene can be altered by simply varying the gate voltage. We can tune graphene from a state close to a normal metal with electrons in concentration $\sim 10^{21} \text{ cm}^{-3}$ to a metal with a similar concentration of holes, all the way through a 'semiconducting' state with few charge carriers.

Even more remarkably, our devices exhibited an astonishing electronic quality. Graphene was completely unprotected from the environment, as it was placed on a microscopically rough substrate and covered from both sides with adsorbates and a polymer residue. Still, electrons could travel submicron distances without scattering, flouting all the elements outside. This level of electronic quality is completely counterintuitive. It contradicts the common wisdom that surface science requires ultra-high vacuum and, even then, thin films become progressively poorer in quality as their thickness

decreases. Even with hindsight, such electronic quality is mystifying and, in fact, not fully understood so far.

In semiconductor physics, electronic quality is described in terms of charge carrier mobility μ . Our *Science* paper reported graphene with room- T $\mu \approx 10,000 \text{ cm}^2/\text{Vs}$ (as of 2010, μ can be 10 and 100 times higher at room and low T , respectively [76,77]). For a general reader, 10,000 may sound like just another number. To explain its significance, let us imagine that in 2004 we made devices from, for example, reduced graphene oxide, which exhibits $\mu \sim 1 \text{ cm}^2/\text{Vs}$ due to its irreversibly damaged crystal lattice [78]. In our second paper on graphene [79], we reported 2D dichalcogenides with equally low μ . Since then, there has been little interest in them. The reported ballistic transport over submicron distances was essential to spark interest in graphene and to allow the observation of many quantum effects reported both in 2004 and later. This would have been impossible if graphene exhibited μ below several $1,000 \text{ cm}^2/\text{Vs}$.

If not for graphene's high quality and tunability, there would be no new physics and, therefore, no graphene boom. In this respect, graphene history has something in common with that of solar planets. Ancient Greeks observed them and called them wandering stars, $\pi\lambda\nu\eta\tau\epsilon\varsigma$. After the physics behind this wandering was discovered, people started perceiving planets quite differently from $\pi\lambda\nu\eta\tau\epsilon\varsigma$. Similarly, during the last six years people discovered what graphene really is, which completely changed the earlier perception. Our *Science* paper offered the first glimpse of graphene in its new avatar as a high quality 2D electronic system and beyond.

MAGIC OF FLAT CARBON

What is this new incarnation? For me, 2004 was only the starting point for the unveiling of many unique properties of graphene. Since then, we have demonstrated that charge carriers in graphene are massless fermions described by a Dirac-like equation rather than by the standard Schrödinger equation [80]. In bilayer graphene, electrons receive yet another makeup as massive Dirac fermions [81]. These properties were unveiled by the observation of two new types of the integer quantum Hall effect, which corresponded to the two types of Dirac fermions [1,65]. We also found that graphene remained metallic in the limit of no charge carriers, even when just a few electrons remained present in a micron-sized device [1,77]. Our experiments have revealed that graphene exhibits a universal optical conductivity of $\pi e^2/2h$, such that its visible opacity is just $\pi\alpha$, where α is the fine structure constant [82]. We suggested that the phenomenon of Klein tunnelling, which was known in relativistic quantum physics for many decades but assumed non-observable, could be probed using graphene devices [83]. Several groups later demonstrated this experimentally. We were lucky to be slightly quicker than others in showing that bilayer graphene was a tuneable-gap semiconductor [84] and that graphene could be carved into devices on a true nm scale [85]. We demonstrated sensors capable of detecting

individual molecules, more sensitive than any sensor before [38]. We suggested that strain in graphene creates pseudo-magnetic fields that alter its electronic properties [86] and later discussed the possibility of creating uniform pseudo-fields and observation of the quantum Hall effect without an external magnetic field [87]. Pseudo-magnetic fields in excess of 400 T were reported experimentally half a year later. We made the first step into graphene chemistry by experimentally introducing its derivatives, graphane and stoichiometric fluorographene [88,89]. This is not even an exhaustive list of the nice phenomena that we and our collaborators found in graphene and, of course, many other researchers reported many other beautiful discoveries that propelled graphene into its new status of a system that can nearly deliver magic.

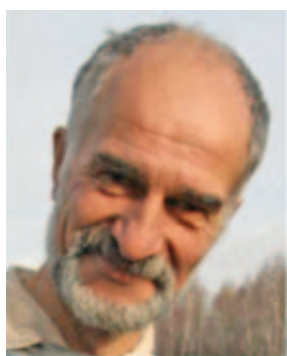
ODE TO ONE

After reading about the beautiful properties of graphene, the reader may wonder why many atomic layers stacked on top of each other, as in graphite, do not exhibit similar properties. Of course, any graphitic derivative has something in common with its parent, but in the case of graphene, differences between the parent and descendants are fundamental. To appreciate this, let us simplify the task and compare graphene with its bilayer. The crucial distinctions are already there.

First, graphene exhibits record stiffness and mechanical strength [90]. As for its bilayer, this strength is jeopardised by the possibility that the two layers will slide relative to each other. This leads to a principal difference if, for example, graphene or any thicker platelets are used in composite materials. Second, graphene chemistry is different depending on whether one or both surfaces of a monolayer are exposed. For example, atomic hydrogen cannot bind to graphene from one side but makes a stoichiometric compound (graphane) if both surfaces are exposed. This makes graphene much more reactive than its bilayer. Third, an electric field is screened in graphite at distances of about the interlayer separation, and the electric screening becomes important even for a bilayer. For multilayer graphene, the electric field can dope no more than a couple of near-surface atomic planes, leaving the bulk unaffected. This makes it naïve to speculate about the use of graphitic multilayers in active electronics. Fourth, charge carriers in a monolayer are massless Dirac fermions whereas they are massive in a graphene bilayer. This leads to essential differences in many electronic properties including Shubnikov-de Haas oscillations, quantum Hall effect, Klein tunnelling and so on. The Sorites paradox refers to a moment when a heap is no longer a heap if the grains are removed one by one. For graphene, even its bilayer is so different that two already make a heap.

TO COLLEAGUES AND FRIENDS

Our *Science* report was a collective effort, and I would again – on behalf of Kostya and myself – like to thank all the other contributors. Serge Morozov was and remains our ‘multitasking measurement machine’ working 24x7 when in Manchester. His electrical measurement skills are unmatched, and I know that any curve he brings in is completely reliable and no questions are ever asked whether this and that was checked and crosschecked. Da Jiang was around from the very start, and it is unfortunate that I had to take the project away from him because it was beyond the scope of a single new PhD student. Sergey Dubonos and Yuan Zhang were the ones who made all the devices without which our work would obviously have been impossible. I utterly regret that our life trajectories have later diverged and, especially, that Sergey has switched from microfabrication technology to goat farming. I also acknowledge help of Anatoly Firsov in making those devices. Irina Grigorieva helped with scanning electron microscopy but, more importantly, with writing up the 2004 manuscript.



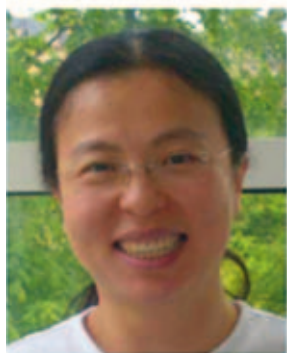
Sergey Dubonos



Serge Morozov



Irina Grigorieva



Yuan Zhang



Da Jiang



Anatoly Firsov

Figure 4. Those who made our first graphene paper possible but did not get the Prize.

The end of my timeline was only a start for further hard work involving many collaborators. Our rapid progress would be impossible without Misha Katsnelson who provided us with all the theoretical help an experimentalist can only dream of. Since 2006, I have been enjoying collaboration with other great theory guys including Antonio Castro Neto, Paco Guinea, Nuno Peres, Volodya Fal'ko, Leonid Levitov, Allan MacDonald, Dima Abanin, Tim Wehling and their co-workers. In particular, I want to acknowledge many illuminating discussions and banter over dinners with Antonio and Paco. As for experimentalists, the list is longer and includes Philip Kim, Ernie Hill, Andrea Ferrari, Eva Andrei, Alexey Kuzmenko, Uschi Bangert, Sasha Grigorenko, Uli Zeitler, Jannik Meyer, Marek Potemskii and many of their colleagues.

Philip deserves special praise. In August 2004, before our *Science* paper was published, his group submitted another important paper [91]. His report described electronic properties of ultra-thin graphite platelets (down to ~35 layers). Except for the thicker devices, Philip's group followed the same route as our now-celebrated paper. How close he was can be judged from the fact that, after adopting the Scotch tape technique, Philip started studying monolayers in early 2005. This allowed him to catch up quickly and, in mid-2005, our two groups submitted independent reports that appeared back-to-back in *Nature*, both describing the all-important observation of Dirac fermions in monolayer graphene [80,92]. Later, I had the pleasure of closely working with Philip on two joint papers, for *Science* and *Scientific American*. For me personally, those back-to-back *Nature* papers signified a watershed. People within the large semiconducting community no longer rumoured that 'the results were as difficult to reproduce as those by Hendrik Schön', and friends no longer stopped me in corridors with 'be more careful; you know ...' I owe Philip a great deal for this, and many people heard me saying – before and after the Nobel Prize – that I would be honoured to share it with him.

Last but not least, let me acknowledge many bright young, and not so young, colleagues: Peter Blake, Rahul Nair, Roman Gorbachev, Leonid Ponomarenko, Fred Schedin, Daniel Elias, Sasha Mayorov, Rui Yang, Vasyl Kravets, Zhenhua Ni, Wencai Ren, Rashid Jalil, Ibtisam Riaz, Soeren Neubeck, Tariq Mohiuddin and Tim Booth. They were PhD students and postdocs here in Manchester over the last six years and, as always, I avoid using the feudal word 'my'.

Finally, I acknowledge the financial support of EPSRC in its best, that is, the responsive mode. This Nobel Prize would be absolutely impossible without this mode. Let me also thank the Royal Society and the Leverhulme Trust for reducing my teaching loads, which allowed me to focus on the project. I have also received funding from the Office of Naval Research and the Air Force Office of Scientific Research, which helped us to run even faster. The Körber Foundation is gratefully acknowledged for its 2009 award. However, I can offer no nice words for the EU Framework programmes which, except for the European Research Council, can be praised only by Europhobes for discrediting the whole idea of an effectively working Europe.

REFERENCES

1. A. K. Geim, K. S. Novoselov. *Nature Mater.* **6**, 183 (2007).
2. A. K. Geim, P. Kim. *Sci. Am.* **298**, 90 (2008).
3. A. K. Geim. *Science* **324**, 1530 (2009).
4. A. K. Geim. *JETP Lett.* **50**, 389 (1989).
5. S. J. Bending, K. von Klitzing, K. Ploog. *Phys. Rev. Lett.* **65**, 1060 (1990).
6. A. K. Geim, P. C. Main, P. H. Beton, P. Streda, L. Eaves, C. D. Wilkinson, S. P. Beaumont. *Phys. Rev. Lett.* **67**, 3014 (1991).
7. A. K. Geim, P. C. Main, P. H. Beton, L. Eaves, C. D. W. Wilkinson, S. P. Beaumont. *Phys. Rev. Lett.* **69**, 1248 (1992).
8. A. K. Geim, S. V. Dubonos, J. G. S. Lok, I. V. Grigorieva, J. C. Maan, L. T. Hansen, P. E. Lindelof. *Appl. Phys. Lett.* **71**, 2379 (1997).
9. I. V. Grigorieva. *Supercond. Sci. Technol.* **7**, 161 (1994).
10. J. S. Baker, S. J. Judd. *Water Research* **30**, 247 (1996).
11. A. Geim. *Phys. Today* **51**, No. 9, 36 (1998).
12. K. Autumn, Y. A. Lang, S. T. Ksieh, W. Zesch, W. P. Chan, T. W. Kenny, R. Fearing, R. J. Full. *Nature* **405**, 681 (2000).
13. A. K. Geim, S. V. Dubonos, I. V. Grigorieva, K. S. Novoselov, A. A. Zhukov, S. Y. Shapoval. *Nature Mater.* **2**, 461 (2003).
14. G. Lamarche, F. Lamarche, A. M. Lamarche, *Europhys. Lett.* **53**, 378 (2001).
15. I. I. Barbolina, K. S. Novoselov, S. V. Morozov, S. V. Dubonos, M. Missous, A. O. Volkov, D. A. Christian, I. V. Grigorieva, A. K. Geim. *Appl. Phys. Lett.* **88**, 013901 (2006).
16. T. Cohen-Karni, Q. Qing, Q. Li, Y. Fang, C. M. Lieber. *Nano Lett.* **10**, 1098 (2010).
17. Nevill Mott, *A Life in Science*, Taylor & Francis, 1986.
18. E. Bose, *Phys. Z.* **7**, 373 (1906).
19. A. V. Butenko, Dm. Shvarts, V. Sandomirsky, Y. Schlesinger, R. Rosenbaum. *J. Appl. Phys.* **88**, 2634 (2000).
20. V. T. Petrashov, V. N. Antonov, B. Nilsson. *J. Phys. – Cond. Mat.* **3**, 9705 (1991).
21. R. E. Glover, M. D. Sherrill. *Phys. Rev. Lett.* **5**, 248 (1960).
22. C. H. Ahn *et al.* *Rev. Mod. Phys.* **78**, 1185 (2006).
23. M. S. Dresselhaus, G. Dresselhaus. *Adv. Phys.* **30**, 139 (1981).
24. Y. Kopelevich, P. Esquinazi, J. H. S. Torres, S. Moehlecke. *J. Low Temp. Phys.* **119**, 691 (2000).
25. H. Kempa, P. Esquinazi, Y. Kopelevich. *Phys. Rev. B* **65**, 241101 (2002).
26. K. S. Novoselov, A. K. Geim, S. V. Dubonos, E. W. Hill, I. V. Grigorieva. *Nature* **426**, 812 (2003).
27. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov. *Science* **306**, 666 (2004).
28. J. A. Venables, G. D. T. Spiller, M. Hanbucken. *Rep. Prog. Phys.* **47**, 399 (1984).
29. J. W. Evans, P. A. Thiel, M. C. Bartelt. *Sur. Sci. Rep.* **61**, 1 (2006).
30. O. A. Shenderova, V. V. Zhirnov, D. W. Brenner, *Crit. Rev. Solid State Mater. Sci.* **27** 227 (2002).
31. D. Tománek, W. Zhong, E. Krastev. *Phys. Rev. B* **48**, 15461 (1993).
32. R. Seton. *Carbon* **34**, 69 (1996).
33. S. Braga, V. R. Coluci, S. B. Legoas, R. Giro, D. S. Galvão, R. H. Baughman. *Nano Lett.* **4**, 881 (2004).
34. C. D. Simpson, J. D. Brand, A. J. Berresheim, L. Przybilla, H. J. Rader, K. Mullen. *Chem. Eur. J.* **8**, 1424 (2002).
35. A. Affoune, B. Prasad, H. Sato, T. Enoki, Y. Kaburagi, Y. Hishiyama, *Chem. Phys. Lett.* **348**, 17 (2001).
36. T. J. Booth, P. Blake, R. R. Nair, D. Jiang, E. W. Hill, U. Bangert, A. Bleloch, M. Gass, K. S. Novoselov, M. I. Katsnelson, A. K. Geim. *Nano Lett.* **8**, 2442 (2008).

37. S. Ryu, L. Liu, S. Berciaud, Y. J. Yu, H. Liu, P. Kim, G. W. Flynn, L. E. Brus. *Nano Lett.* **10**, 4944 (2010).
38. F. Schedin, A. K. Geim, S. V. Morozov, E.W. Hill, P. Blake, M. I. Katsnelson, K. S. Novoselov. *Nature Mater.* **6**, 652 (2007).
39. *Letter to the Editor. "October 22, 2004: Discovery of Graphene"* www.aps.org/publications/apnews/201001/letters.cfm
40. B. C. Brodie. *Philos. Trans. R. Soc. London* **149**, 249 (1859).
41. D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff. *Chem. Soc. Rev.* **39**, 228 (2010).
42. G. Ruess, F. Vogt. *Monatshfte Chem.* **78**, 222 (1948).
43. H. P. Boehm, A. Clauss, G. O. Fischer, U. Hofmann. *Z. anorg. allgem. Chem.* **316**, 119 (1962).
44. J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, D. Obergfell, S. Roth, C. Girit, A. Zettl. *Solid State Commun.* **143**, 101 (2007).
45. H. Shioyama. *J. Mat. Sci. Lett.* **20**, 499 (2001).
46. L. M. Viculis, J. J. Mack, R. B. Kaner. *Science* **299**, 1361 (2003).
47. S. Horiuchi, T. Gotou, M. Fujiwara, T. Asaka, T. Yokosawa, Y. Matsui. *Appl. Phys. Lett.* **84**, 2403 (2004).
48. H. P. Boehm, R. Setton, E. Stumpp. *Carbon* **24**, 241 (1986).
49. J. T. Grant, T. W. Haas. *Surf. Sci.* **21**, 76 (1970).
50. J. M. Blakely, J. S. Kim, H. C. Potter. *J. Appl. Phys.* **41**, 2693 (1970).
51. R. Rosei, M. De Crescenzi, F. Sette, C. Quaresima, A. Savoio, P. Perfetti. *Phys. Rev. B* **28**, 1161 (1983).
52. C. F. McConville, D. P. Woodruff, S. D. Kevan, M. Weinert, J. W. Davenport. *Phys. Rev. B* **34**, 2199 (1986).
53. T. A. Land, T. Michely, R. J. Behm, J. C. Hemminger, G. Comsa. *Surf. Sci.* **264**, 261 (1992).
54. A. J. van Bommel, J. E. Crombeen, A. van Tooren. *Surf. Sci.* **48**, 463 (1975).
55. A. Nagashima, K. Nuka, K. Satoh, H. Itoh, T. Ichinokawa, C. Oshima, S. Otani. *Surf. Sci.* **287**, 609 (1993).
56. M. Terai, N. Hasegawa, M. Okusawa, S. Otani, C. Oshima. *Appl. Surf. Sci.* **130**, 876 (1998).
57. I. Forbeaux, J. M. Themlin, J. M. Debever. *Phys. Rev. B* **58**, 16396 (1998).
58. K. Seibert, G. C. Cho, W. Kütt, H. Kurz, D. H. Reitze, J. I. Dadap, H. Ahn, M. C. Downer, A. M. Malvezzi. *Phys. Rev. B* **42**, 2842 (1990).
59. T. W. Ebbesen, H. Hiura, *Adv. Mater.* **7**, 582 (1995).
60. X. Lu, M. Yu, H. Huang, R. S. Ruoff. *Nanotechnology* **10**, 269 (1999).
61. Y. Gan, W. Chu, L. Qiao, *Surf. Sci.* **539**, 120 (2003).
62. Y. Ohashi, T. Koizumi, T. Yoshikawa, T. Hironaka, K. Shiiki. *TANSO* **180**, 235 (1997).
63. Y. Ohashi, T. Hironaka, T. Kubo, K. Shiiki. *TANSO* **195**, 410 (2000).
64. E. Dujardin, T. Thio, H. Lezec, T. W. Ebbesen. *Appl. Phys. Lett.* **79**, 2474 (2001).
65. A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, A. K. Geim. *Rev. Mod. Phys.* **81**, 109 (2009).
66. P. R. Wallace. *Phys. Rev.* **71**, 622 (1947).
67. G. W. Semenoff. *Phys. Rev. Lett.* **53**, 2449 (1984).
68. F. D. M. Haldane. *Phys. Rev. Lett.* **61**, 2015 (1988).
69. J. Gonzales, F. Guinea, M. A. H. Vozmediano. *Phys. Rev. B* **59**, 2474 (1999).
70. E. V. Gorbar, V. P. Gusynin, V. A. Miransky, I. A. Shovkovy. *Phys. Rev. B* **66**, 045108 (2002).
71. T. Ando, T. Nakanishi, R. Saito. *J. Phys. Soc. Jpn.* **67**, 2857 (1998).
72. Y. Zheng, T. Ando. *Phys. Rev. B* **65**, 245420 (2002).
73. R. Saito, M. Fujita, G. Dresselhaus, M. S Dresselhaus. *Appl. Phys. Lett.* **60**, 2204 (1992).
74. H. J. Teuschler. *Method of producing isolated field effect transistors employing pyrolytic graphite*. US Patent 3,522,649.
75. R. B. Little. *J. Cluster Sci.* **14**, 135 (2003).

76. C. R. Dean *et al.* *Nature Nano* **5**, 722 (2010).
77. E. V. Castro, H. Ochoa, M. I. Katsnelson, R. V. Gorbachev, D. C. Elias, K. S. Novoselov, A. K. Geim, F. Guinea. *Phys. Rev. Lett.* **105**, 266601 (2010).
78. K. Erickson, R. Erni, Z. Lee, N. Alem, W. Gannett, A. Zettl. *Adv. Mat.* **22**, 4467 (2010).
79. K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim. *Proc. Natl. Acad. Sci. U.S.A.* **102**, 10451 (2005).
80. K. S. Novoselov, A. K. Geim, S. M. Morozov, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov. *Nature* **438**, 197 (2005).
81. K. S. Novoselov, E. McCann, S. V. Morozov, V. I. Fal'ko, M. I. Katsnelson, U. Zeitler, D. Jiang, F. Schedin, A. K. Geim. *Nature Phys.* **2**, 177 (2006).
82. R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, A. K. Geim. *Science* **320**, 1308 (2008).
83. M. I. Katsnelson, K. S. Novoselov, A. K. Geim. *Nature Phys.* **2**, 620 (2006).
84. E.V. Castro, K. S. Novoselov, S. V. Morozov, N. M. R. Peres, J. M. B. Lopes dos Santos, J. Nilsson, F. Guinea, A. K. Geim, A. H. Castro Neto. *Phys. Rev. Lett.* **99**, 216802 (2007).
85. L. A. Ponomarenko, F. Schedin, M. I. Katsnelson, R. Yang, E. W. Hill, K. S. Novoselov, A. K. Geim. *Science* **320**, 356 (2008).
86. S. V. Morozov, K. S. Novoselov, M. I. Katsnelson, F. Schedin, L. A. Ponomarenko, D. Jiang, A. K. Geim. *Phys. Rev. Lett.* **97**, 016801 (2006).
87. F. Guinea, M. I. Katsnelson, A. K. Geim. *Nature Phys.* **6**, 30 (2010).
88. D. C. Elias *et al.* *Science* **323**, 610 (2009).
89. R. R. Nair *et al.* *Small* **6**, 2877 (2010).
90. C. Lee, X. Wei, J. W. Kysar, J. Hone. *Science* **321**, 385 (2008).
91. Y. Zhang, J. P. Small, M. E. S. Amori, P. Kim. *Phys. Rev. Lett.* **94**, 176803 (2005).
92. Y. B. Zhang, Y. W. Tan, H. L. Stormer, P. Kim. *Nature* **438**, 201 (2005).

Portrait photo of Professor Geim by photographer Ulla Montan.