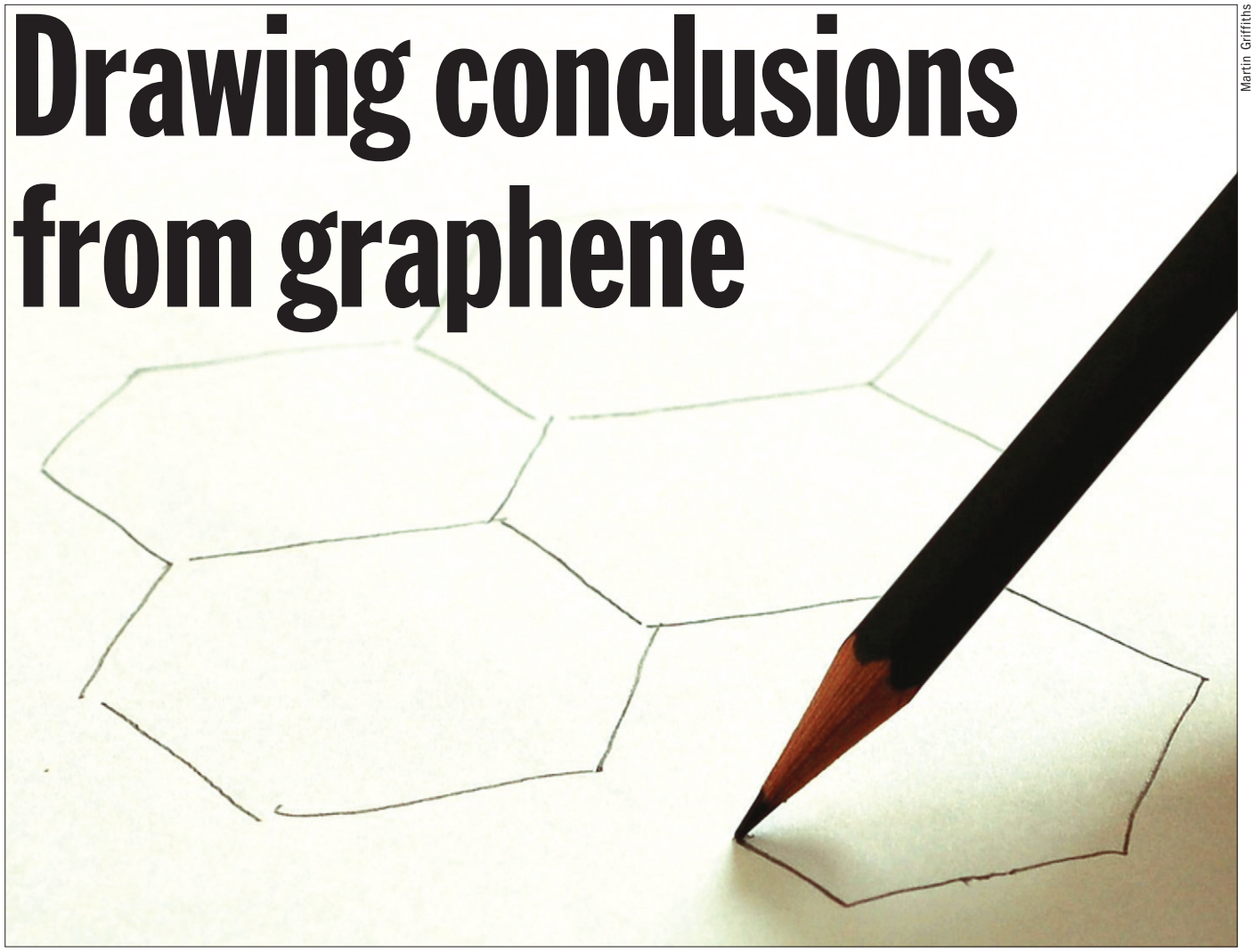
Drawing conclusions from graphene



Martin Griffiths

The unique electronic properties of graphene – a one-atom-thick sheet of carbon that was produced for the first time just two years ago – make it an ideal testing ground for fundamental physics, describe **Antonio Castro Neto, Francisco Guinea** and **Nuno Miguel Peres**

In a time when cutting-edge scientific research is expensive and complex, it seems absurd that a breakthrough in physics could be achieved with simple adhesive tape. But in 2004, Andre Geim, Kostya Novoselov and co-workers at the University of Manchester in the UK did just that. By delicately cleaving a sample of graphite with sticky tape, they produced something that was long considered impossible: a sheet of crystalline carbon just one atom thick, known as graphene. Many physicists believed that a 2D crystal like graphene would always roll up rather than stand free in a planar form; but Geim's group brought to an end years of unsuccessful attempts to isolate graphene, and was able to visualize the new crystal using a simple optical microscope (figure 1).

The single-layered honeycomb structure of graphene makes it the "mother" of all carbon-based systems: the graphite we find in our pencils is simply a stack of graphene layers; carbon nanotubes are made of rolled-up sheets of graphene; and buckminsterfullerene molecules, or "buckyballs", are nanometre-size spheres of wrapped-up graphene (figure 2). These forms of carbon were isolated long before graphene and have been used in many applications, but their electric, magnetic and elastic properties all originate in the properties of graphene.

Just months after the initial discovery, Geim's group improved its method for producing graphene. Rather than ripping sheets of carbon from graphite with adhesive tape, the team produced higher-quality graphene by gently pushing small graphite crystals along a hard surface – using a technique akin to drawing with a pencil. Soon after, a group headed by Philip Kim at Columbia University in the US confirmed the existence of graphene using the same drawing technique, while Walt de Heer and Claire Berger at Georgia Tech developed an epitaxial growth process that may be suitable for mass-producing graphene for industrial applications.

Despite only being isolated two years ago, graphene has already appeared in hundreds of papers. The reason is that the material has unique properties arising from its honeycomb-lattice structure that could allow us to observe strange relativistic effects at speeds much slower than the speed of light. In addition, our ability

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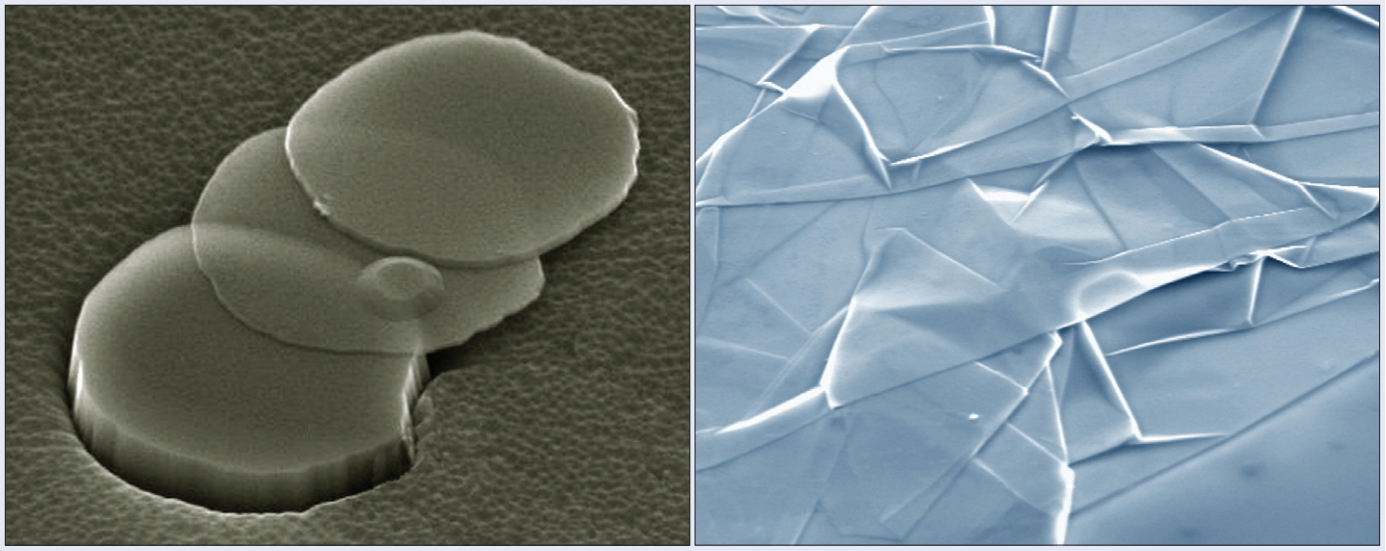
1 A sticky success



Graphene was first isolated by Andre Geim's team at the University of Manchester just two years ago using the surprisingly simple technique of ripping layers from a graphite surface using adhesive tape. By repeatedly peeling away thinner layers (left), single-atom-thick sheets were obtained (right), as shown in these scanning electron micrographs.

to manipulate the motion of the electrons in graphene paves the way to virtually lossless and ultrafast transistors with atomic dimensions.

Massless electrons

Graphene's unique properties arise from the collective behaviour of electrons. That in itself is nothing new: as summarized in Philip Anderson's famous dictum "more is different", we know that when a large number of particles interact strongly with each other, unexpected collective motions can emerge. In the case of graphene, however, the interaction between electrons and the honeycomb lattice causes the electrons to behave as if they have absolutely no mass (see box on page 35). Because of this, the electrons in graphene are governed by the Dirac equation – the quantum-mechanical description of electrons moving relativistically – and are therefore called Dirac fermions.

The relativistic behaviour of electrons in graphene was first predicted in 1947 by the Canadian theorist Philip Russell Wallace. At the time, however, nobody believed that a one-atom-thin solid could exist, so Wallace instead used the graphene model as his starting point to study graphite. Building on his work, the thermodynamic and transport properties of graphite were studied extensively in the 1960s, and the remarkable agreement between the theoretical predictions of properties such as the heat capacity and the experimental data is regarded as one of the greatest successes of condensed-matter physics.

We are already familiar with massless Dirac fermions in high-energy particle physics: neutrinos. But neutrinos have no electric charge and therefore do not interact strongly with any kind of matter. The Dirac fermions in graphene, in contrast, carry one unit of electric charge and so can be manipulated using electromagnetic fields. Since the manipulation of electrons within materials is at the heart of modern electronics, the radically different behaviour of electrons in graphene may allow us to go beyond the limits of silicon-based semiconductor technology.

The trademark behaviour that distinguishes a graphene sheet from an ordinary metal, for example, is the unusual form of the Hall effect. In the original Hall effect, discovered in 1879, a current flowing along the surface of a metal in the presence of a transverse magnetic field causes a drop in potential at right angles to both the current and the magnetic field. As the ratio of the potential drop to the current flowing (called the Hall resistivity) is directly proportional to the applied magnetic field, the Hall effect is used to measure magnetic fields.

A century later, Klaus von Klitzing discovered that in a 2D electron gas at a temperature close to absolute zero the Hall resistivity becomes quantized, taking only discrete values of h/ne^2 (where h is Planck's constant, n is a positive integer and e is the electric charge). The quantization is so precise that this "quantum Hall effect" (QHE) is used as the standard for the measurement of resistivity.

During a discussion about the discovery of graphene at a tea party in Boston in early 2005, the present authors started to wonder whether the QHE would be different in graphene. We realized that due to a quantum-mechanical effect called a Berry's phase, the

At a Glance: Graphene

- Graphene is a one-atom-thick sheet of carbon that was isolated for the first time in 2004 – a feat long thought to be impossible
- Graphene's 2D nature and honeycomb atomic structure cause electrons moving in the material to behave as if they have no mass
- Electrons in graphene move at an effective speed of light 300 times less than the speed of light in a vacuum, allowing relativistic effects to be observed without using particle accelerators
- A key experimental signature of graphene is the way it modifies the quantum Hall effect seen in metals and semiconductors
- The electrons in graphene can travel large distances without being scattered, making it a promising material for very fast electronic components

Hall resistivity should be quantized in terms of odd integers only. Graphene has a Berry's phase of π, meaning that if you "rotate" the quantum-mechanical wavefunction of the Dirac fermions in graphene through a full 360°, the system does not end up in the state that it started in; instead the wavefunction changes sign. A similar prediction to ours was made independently in 2005 by Valery Gusynin at the Bogolyubov Institute for Theoretical Physics in Kiev, Ukraine, and Sergei Sharapov at McMaster University in Canada.

Soon after its prediction, this "anomalous integer QHE" was observed experimentally by both Geim and Kim, laying to rest any lingering doubts that graphene had really been isolated. Interestingly, Geim's group observed the QHE in graphene at room temperature, while it is only observed in ordinary metals at very low temperatures. This is because the magnetic energy of the electrons, called the cyclotron energy, in graphene is 1000 times greater than it is in other materials. The researchers also found that the anomalous integer QHE is extremely sensitive to the thickness of the sample. For instance, a sample with two layers of graphene displays a different effect again – meaning that the anomalous integer QHE can be used to distinguish between single-layer graphene and multilayer samples.

While the anomalous integer QHE is a theoretical curiosity, another odd property of graphene may have major practical implications. Unlike an ordinary metal, in which any impurities in the crystal scatter electrons and so lead to energy loss, the electrical resistance in graphene is independent of the number of impurities. This means that electrons can travel for many microns without colliding with any impurities, making graphene a promising material for a potential high-speed electronic switching device called a "ballistic transistor".

The universal resistance of graphene was predicted in 1986 by Eduardo Fradkin at the University of Illinois at Urbana-Champaign and finally observed experimentally by Geim and collaborators in 2005. However, the value of the resistivity was about 20% less than the theoretical prediction. This result remains a mystery, although Geim has suggested that it may be due to electrons being scattered by ripples in the surface of the graphene sheet itself.

Fundamentally weird

Graphene could allow us to see strange relativistic effects that have never been observed before. This is because the massless Dirac fermions in graphene behave as though the speed of light is just $10^6\,\mathrm{m\,s^{-1}}$, rather than the vacuum value of $3\times10^8\,\mathrm{m\,s^{-1}}$. Thus, graphene could effectively be used as a bench-top particle-physics laboratory, allowing us to investigate the quantum field theories that describe the fundamental interactions of matter.

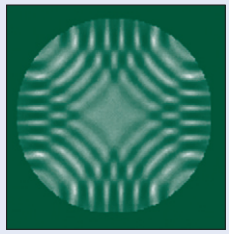
For example, in quantum electrodynamics (QED), the strength of electromagnetic interactions between charged particles is described by the fine-structure constant, $\alpha = e^2/\hbar c$, where $\hbar$ is Planck's constant divided by 2π and c is the speed of light. With a value of 1 divided by $137.03599911 \pm 0.00000046$, this is one of the most precisely measured physical quantities in nature. Unfortunately, we have no idea *why* the fine-structure constant has this value. Since the effective speed of light for the Dirac fermions in graphene is 300 times less, graphene's fine-structure constant should have a much larger value of about two, though it has not yet been measured precisely.

This example shows that physical constants like α can be modified by the presence of a complex environment, in this case graphene's honeycomb lattice. So perhaps we should not be mystified by the seemingly arbitrary value of the QED fine-structure constant after all. Maybe, as proposed recently by Xiao-Gang Wen at the Massachusetts Institute of Technology, the electron is not as elementary as one would think, but is instead a consequence of interactions between more complex degrees of freedom not yet experimentally accessible.

Graphene may give us a new insight into another phenomenon from particle physics called zitterbe-

Graphene could be used as a bench-top particle-physics laboratory, allowing us to investigate the fundamental interactions of matter

Electrons lose their mass

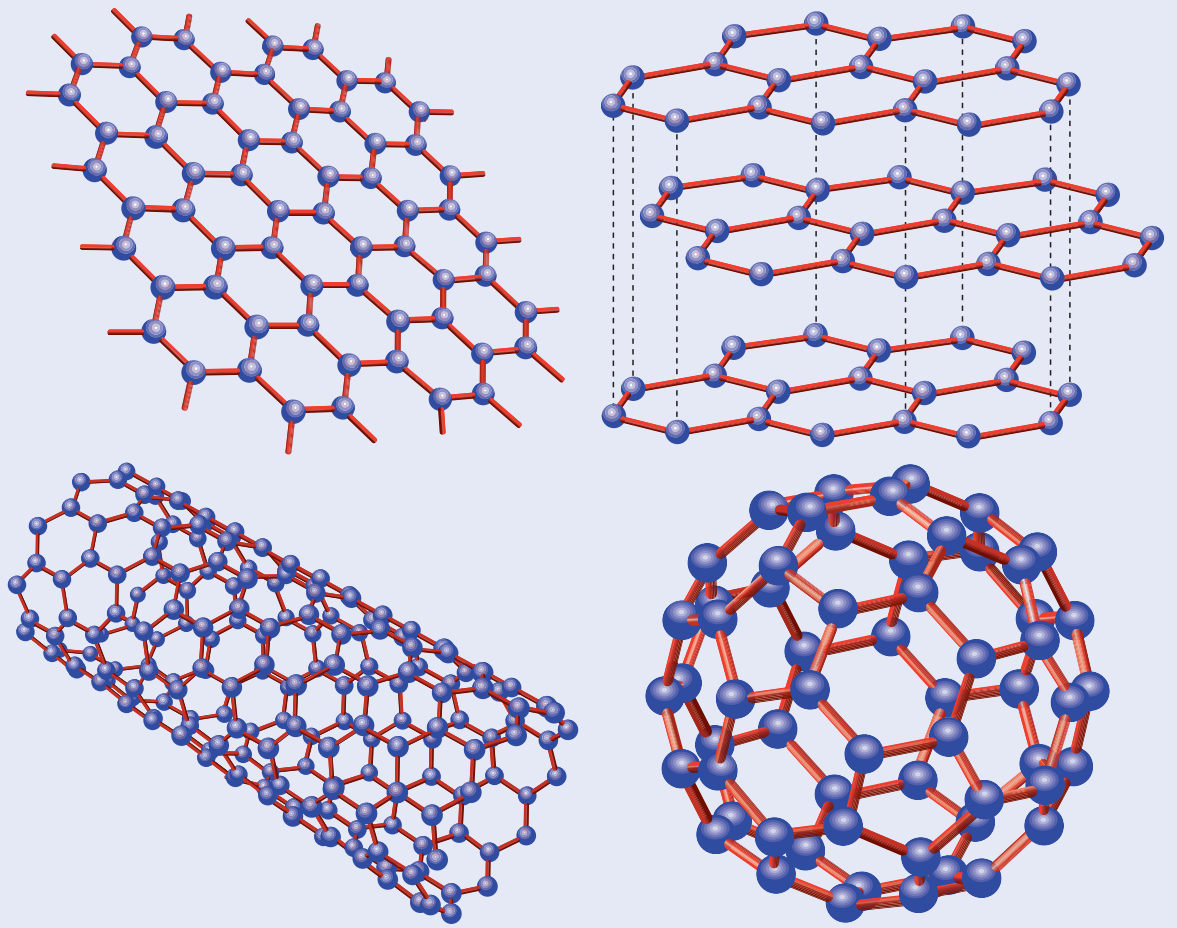


The interactions between electrons and the honeycomb structure of carbon atoms in graphene causes them to behave as if they have no mass. In any crystal, the ordered arrangement of atoms creates a periodic potential, which causes electrons to move in waves called Bloch waves. Just as we associate photons with light waves, we can associate each Bloch wave with a "quasiparticle" that has an energy $E = \hbar\omega$ (where $\hbar$ is Planck's constant divided by 2π and ω is the frequency of the wave). Strictly speaking, these quasiparticles are not electrons, but condensed-matter physicists often give them this name. Special relativity tells us that the energy of a particle, E, is related to its momentum, P, by the equation $E = \sqrt{(M^2c^4 + P^2c^2)}$, where M is the mass of the particle and c is the speed of light.

In an ordinary solid, electrons travel much slower than the speed of light and so this equation can be approximated by $E \approx Mc^2 + P^2/(2M)$, where the first term, Mc^2, is Einstein's famous rest energy and the second term is the non-relativistic kinetic energy of the particle. For the "electrons" corresponding to Bloch waves in a solid, the mass, M, is called the "band mass", and it is not necessarily equal to the mass of an electron moving in free space. The band mass determines almost all the electrical properties of metals and semiconductors, in particular their ability to carry electrical current.

Graphene, however, behaves in a strikingly different way. Strong interactions between the electrons and the honeycomb lattice of carbon atoms mean that the relationship between energy and momentum is instead given by $E = \nu P$, where ν is called the "Fermi–Dirac velocity". This is exactly the same energy–momentum relationship as for a massless relativistic particle like a photon – the earlier equation reduces to $E = cP$ when $M = 0$. However, the Fermi–Dirac velocity in graphene is only about 300 times less than the speed of light. Strangely, only a honeycomb lattice produces this peculiar energy–momentum relationship; atoms arranged in other periodic structures, such as square or triangular lattices, always generate electrons with a finite band mass.

2 Graphene: mother of them all



Graphene (top left) consists of a 2D hexagonal lattice of carbon atoms. Each atom is covalently bonded to three others; but since carbon has four valence electrons, one is left free – allowing graphene to conduct electricity. Other well-known forms of carbon all derive from graphene: graphite is a stack of graphene layers (top right); carbon nanotubes are rolled-up cylinders of graphene (bottom left); and a buckminsterfullerene (C_{60}) molecule consists of graphene balled into a sphere by introducing some pentagons as well as hexagons into the lattice (bottom right).

wegung. Translated literally as "jittery motion", this arises because it is not possible to localize the wavefunction of a relativistic particle in a distance smaller than its Compton wavelength – the characteristic scale at which QED effects become important. To explain this, Dirac had to invent the concept of negative energy states, which were later interpreted as antiparticles. An electron moving at relativistic speeds can spawn its own antiparticle, and the interaction between the two causes the path of the electron to jitter.

Normally this motion occurs too rapidly to be observed. In a solid, however, the equivalent of an antiparticle is a "hole": that is the absence of an electron. Thus, when Dirac fermions are confined in graphene samples, zitterbewegung can be interpreted in terms of the mixing of electron and hole states. Since the Compton wavelength of the Dirac fermions is of the order of a nanometre, it may be possible to spot the jitter in graphene using a high-resolution microscope.

Another as-yet unobserved quantum-mechanical effect is the "Klein paradox", whereby a very large potential barrier becomes completely transparent to relativistic electrons. But the probability that an electron "tunnels" through drops exponentially with the height of the barrier. However, calculations show that for relativistic particles the tunnelling probability *increases* with the barrier height, since a potential barrier that repels electrons will also attract their antiparticles.

This effect has never been observed experimentally because a large enough barrier can only be found close to a super-heavy nucleus or, even more exotically, a black hole. But recently Geim and co-workers have shown that the effect could be displayed much more easily with the massless Dirac fermions in graphene. They suggest a way to test the effect using a simple graphene circuit that is broken by a semiconductor barrier with an adjustable voltage: as the voltage is raised, electrons should begin to tunnel through the barrier.

Sticking with the theme of fundamental physics, graphene may also help address the puzzle of "chiral symmetry breaking". The chirality of a particle tells us whether it differs from its own mirror image, like a right-handed and left-handed screw, for example. In graphene there are "left-handed" and "right-handed" Dirac fermions, but they behave in the same way as each other. This is in stark contrast to neutrinos, which only appear in their left-handed form. Whether or not the symmetry between the left-handed and right-handed particles in graphene can be broken may help us to understand how the same symmetry is broken in particle physics.

Gary Meek, Georgia Tech

Commercializing graphene Walt de Heer of Georgia Tech believes that graphene will usher in a new era of nanoelectronics.

It is spellbinding to think that so many profound implications could come from a pencil and an adhesive tape

Graphene dreams

For many years it was believed that carbon nanotubes would create a revolution in nano-electronics because of their microscopic dimensions and very low electrical resistance. These hopes, however, have not yet come to fruition because of various difficulties. These include producing nanotubes with well-defined sizes, the high resistance at the connections between nanotubes and the metal contacts that connect them to circuits, and the difficulty of integrating nanotubes into electronic devices on a mass-production scale.

Walt de Heer argues that with graphene we will be able to avoid all of these problems. Using electron-beam lithography it is possible to pattern graphene into electron waveguides, and to control its electronic properties by applying external voltages using electronic gates. Furthermore, unlike 1D nanotubes, graphene is a continuous medium and hence the heating associated with high resistance at electrical contacts is minimized. This kind of heating is essentially the limiting factor for the miniaturization of silicon microchips, so graphene is especially interesting for the electronics industry. Perhaps even more remarkably, graphene offers the prospect of carving whole processors out of a single sheet.

Graphene research is still in its infancy and we wait to see what marvels it will produce in both fundamental science and technological applications. It is spellbinding to think that so many profound implications could come from a pencil and an adhesive tape. Indeed, the new field of graphene science illustrates well the remark of Ludwig Wittgenstein: "The aspects of things that are most important to us are hidden because of their simplicity and familiarity."

More about: Graphene

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