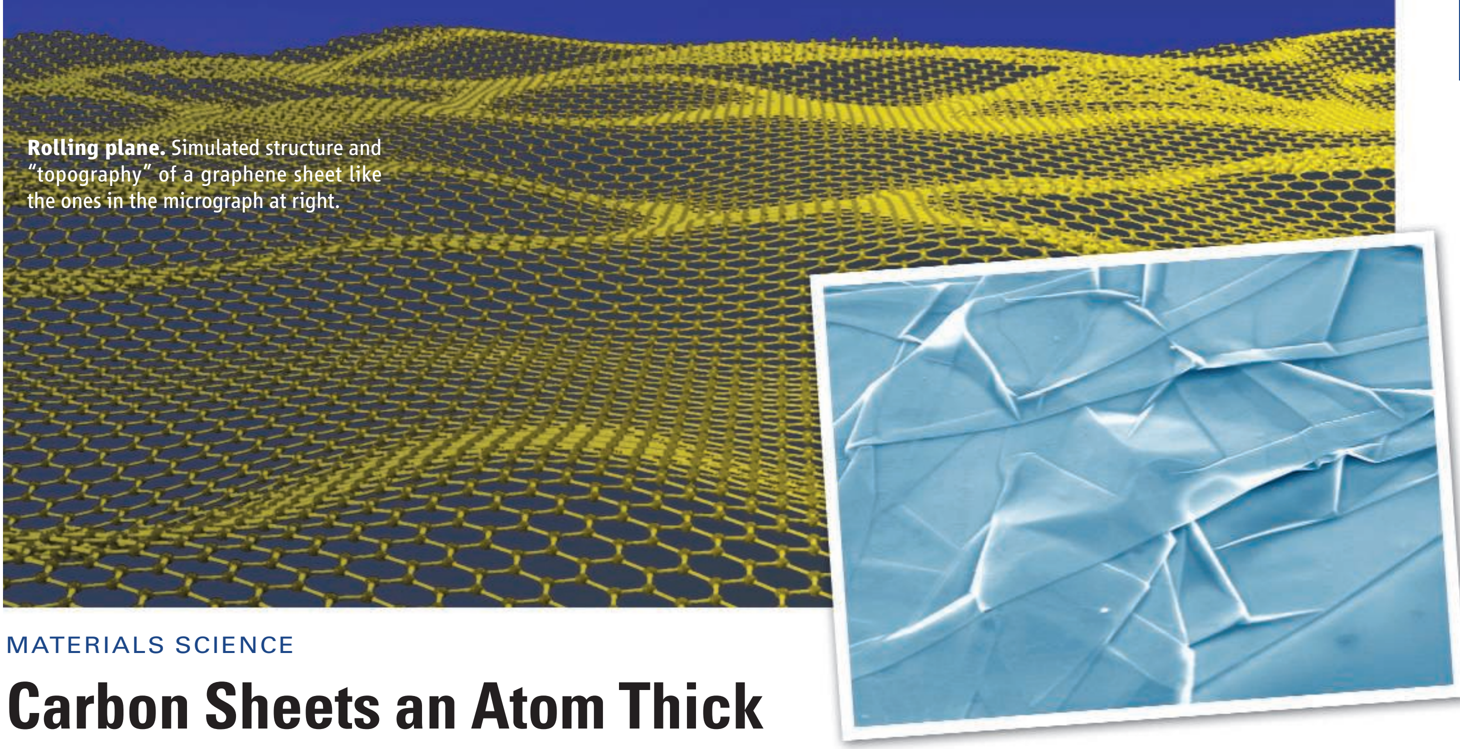


Rolling plane. Simulated structure and "topography" of a graphene sheet like the ones in the micrograph at right.

MATERIALS SCIENCE

Carbon Sheets an Atom Thick Give Rise to Graphene Dreams

Interest in a novel material with amazing properties continues to sweep through physics and chemistry labs worldwide. Will graphene's promise pay off?

The lab-coat realm of science may seem worlds away from the fashion-crazed frenzy of New York City's Garment District. Yet science is not immune to fashion trends. Take the science of new materials: High-temperature superconductors, organic electronic materials, even cold fusion have all been trendy topics—some for longer than others. Scientists flock to new areas that show unique promise and offer knotty riddles, but careers can depend on which fashions have staying power and which are mere fads.

When a material called graphene, which consists of single-atom-thick sheets of carbon, came along 5 years ago and caught a spark, it was hard to tell which way it would go. Researchers quickly discovered that these sheets are very strong yet flexible and highly conductive. So interest spiked. But would graphene be a flash in the pan?

Half a decade after its arrival on the scene, graphene is showing staying power. Last year, researchers churned out some 1500 papers on graphene. The number of Google searches on the topic rivals the number for carbon nanotubes, another hot topic with a 20-year head start. "It's gone from zero to infinity," says George Flynn, a chemical physicist at Columbia University. And the torrent shows no sign of abating. "I don't see it saturating anytime soon," says Andre Geim, a physicist at the University of Manchester in the United Kingdom, who led the team that first isolated flecks of graphene back in 2004.

It's easy to see why. Graphene's carbon atoms, which are arranged in a chicken-wire pattern of hexagons, give it a perfect crystalline order. This order makes graphene the strongest material ever made when yanked along the sheets, yet it flexes like plastic wrap. It's also an outstanding heat conductor. Electrons whiz through the sheets at rates far beyond those achieved in other materials. All these characteristics have made graphene a playground for researchers including theoretical and high-energy physicists, chemists, and computer-chip-device makers looking to lend graphene's exceptional properties to tomorrow's ultrasmall gadgetry. "Graphene is amazing in basically every perspective," Vitor Pereira, a physicist at Boston University, told attendees at the recent American Physical Society (APS) meeting in Pittsburgh, Pennsylvania, which featured 23 packed sessions on graphene.

Instigators. Andre Geim (*left*) and Konstantin Novoselov first isolated graphene in 2004.

Uncertain beginnings

It was never obvious that graphene could exist as a freestanding sheet. Throughout the 1980s and 1990s, a variety of research groups worked to extract single layers of graphene from graphite, the "lead" in pencils, which is made up from stacks of graphene sheets. The sheets in graphite are only loosely bound together, which is why scraping a pencil along a piece of paper leaves them behind. Early on, researchers tried to cleave ever-thinner slices from those three-dimensional flecks of graphite. That worked to a point but typically left scientists with thin stacks of about 100 layers of graphene. So groups tried other approaches, such as chemically wedging other atoms between the stacks to exfoliate single sheets or using an atomic-force microscope tip to drag a graphite fleck over a surface in hopes of dislodging a single sheet.

In 2004, Geim and his Manchester colleague Konstantin Novoselov, together with others in Manchester and at the Institute of Microelectronics Technology and High Purity Materials in Chernogolovka, Russia, reported that they had found a simple way to do the job. In a technique that left a lot of people slapping their foreheads and wishing they had thought of it first, Novoselov simply placed a fleck of graphite between two layers of cellophane tape, peeled them apart, and repeated the process multiple times. Eventually, they whittled the graphite down to single layers (*Science*, 22 October 2004, p. 666).

Once graphene was isolated, the race was on to see what it could do. Even in their first *Science* paper, Geim and his colleagues saw some alluring properties. For starters, electrons traveling over microscopic distances raced through graphene with little of

CREDITS (TOP TO BOTTOM): JANNIK MEYER; THE UNIVERSITY OF MANCHESTER the electrical resistance common to other materials, likely because graphene is so atomically pristine that it contains few defects to scatter electrons. The researchers also patterned electrodes atop it to create a transistor. By applying different voltages to their electrodes, they could control the numbers of negatively charged electrons and positively charged electron vacancies (also known as "holes") left behind when a conducting electron surfs from one atom to another. The achievement marked the first time such a "field effect" had been seen in a single-layer conductor.

Those early studies revealed that graphene was a semimetal, a versatile charge carrier that conducts both electrons and holes. The Manchester team's original study found that charges moved through the group's devices at up to 10,000 centimeters squared per volt second (cm^2/vs), the standard unit of current velocity. By contrast, electrons zip through silicon, the workhorse of electronics, at a mere 1500 cm^2/vs and through high-speed gallium arsenide (GaAs) at 8500 cm^2/vs. That initial electron speed record didn't last for long: In 2008, Geim and his colleagues reported that electrons could fly through graphene at an unheard-of 200,000 cm^2/vs. At the recent APS meeting, Columbia University postdoctoral assistant Kirill Bolotin reported that he and colleagues had increased the speed to 250,000 cm^2/vs by chilling a sheet of graphene to 5 kelvin and suspending it between a pair of tiny pillars.

Lending a hand

Graphene's high speed for electrons and other remarkable properties are promising practical payoffs in applications as diverse as energy-storing capacitors and sensors. Most of the excitement right now focuses on using graphene to improve silicon-based computer chips, which form the backbone of a $260-billion-a-year industry. Chipmakers have thrived over the past 4 decades by continually shrinking the dimensions of transistors and other devices and packing more of them into a tighter area, thereby steadily increasing computing power. But researchers are nearing the limits of conventional transistors, which rely on silicon as the semiconductor to ferry electrical charges in a channel between electrodes. One strategy for further boosting the performance of transistors is to replace the silicon channel with a better conductor.

For use in conventional transistors, however, graphene is too good a conductor. A key property of a semiconductor is that its conductivity can be switched on and off: Digital circuits differentiate between binary "0s" and "1s" by whether a semiconductor transmits an electrical current. But graphene's conductivity never turns off.

That shortcoming doesn't automatically count graphene out for use in chips. It could prove handy in mobile phones, for example. Cell phones use analog-based radiofrequency

RELATIVISTIC PHYSICS IN THE LAB

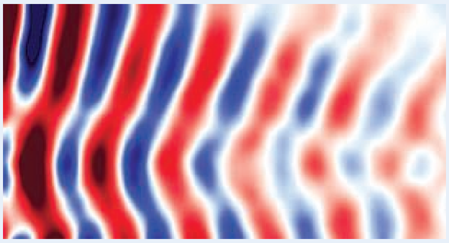
Graphene holds enormous promise for transistors and other electronic devices. But it is already making an impact in the arcane world of high-energy physics.

That's because electrons in graphene don't behave like electrons in a standard metal. In the lattice of a typical metal, electrons feel the push and pull of surrounding charges as they move. As a result, moving electrons behave as if they have a different mass from their less mobile partners. When electrons move through graphene, however, they act as if their mass is zero—behavior that makes them look more like neutrinos streaking through space near the speed of light.

At such "relativistic" speeds, particles don't follow the usual rules of quantum mechanics. Instead, physicists must invoke the mathematical language of quantum electrodynamics, which combines quantum mechanics with Albert Einstein's relativity theory. Even though electrons course through graphene at only 1/300 the speed of neutrinos, physicists realized several years ago that the novel material might provide a test bed for studying relativistic physics in the lab.

Andre Geim and his team at the University of Manchester in the United Kingdom pounced on the idea. In the September 2006 issue of *Nature Physics*, they suggested that by tracking the way charges move in graphene, scientists might be able to demonstrate a 90-year-old quantum mechanical oddity called the Klein paradox. In 1929, Swedish physicist Oskar Klein came up with a thought experiment: What would happen if a relativistic particle—one traveling near the speed of light—tried to cross a high-energy barrier? Quantum mechanics states that subatomic particles behave not like tiny billiard balls, which exist in one definite place at a given time, but like waves in which the probability of their being in any one place is spread out. Such ephemeral behavior suggests that a low-speed particle has a small chance of "tunneling" through a modest energetic barrier, because the particle's wavelike nature gives it some probability of appearing on the other side. Electron tunneling is commonly seen in modern materials and even vexes computer-chip designers by enabling electrons to stray to where they are not wanted. To keep the electrons on course, computer makers raise energy barriers around electrical conductors by surrounding them with strong insulators.

Klein realized that when electrons travel at relativistic speeds, the likelihood that they will tunnel through a barrier can skyrocket. That's because in the spooky world of quantum mechanics, within which particles can wink in and out of existence, a relativistic particle that hits a barrier can generate its own antiparticle, in this case a positron. The electron and positron can then pair up and travel through the barrier as if it weren't even there.



Klein's fingerprint. Wiggles in this interference pattern verified a 90-year-old paradox.

Experimental physicists love a good challenge, and several groups sought to use graphene to turn Klein's thought experiment into reality. After some initial progress by others, Columbia University physicist Philip Kim and his graduate student Andrea Young recently confirmed that Klein tunneling occurs in graphene. Young and Kim patterned a trio of electrodes atop a graphene sheet, allowing them to raise a narrow energetic barrier to charges moving through the graphene. The quantum mechanical waves of charges moving through this barrier create an interference pattern. In the March 2009 issue of *Nature Physics*, the pair reported that when they turned a magnetic field on these charges, it shifted their interference pattern—the expected signature of Klein tunneling (see figure).

"It's the first step in realizing quantum field effects in graphene," Young says. Kim adds that the insights that can be gleaned using graphene are just beginning. Most materials, he notes, are complex, dirty mixtures of atoms, impurities, and defects, which make calculating their expected behavior nearly impossible. But that problem goes away with graphene. "For the theorists, it's one of the simplest systems. But it has very rich physics," Kim says. **–R.F.S.**

CREDIT: A. YOUNG AND P. KIM, *NATURE PHYSICS*, MARCH 2009

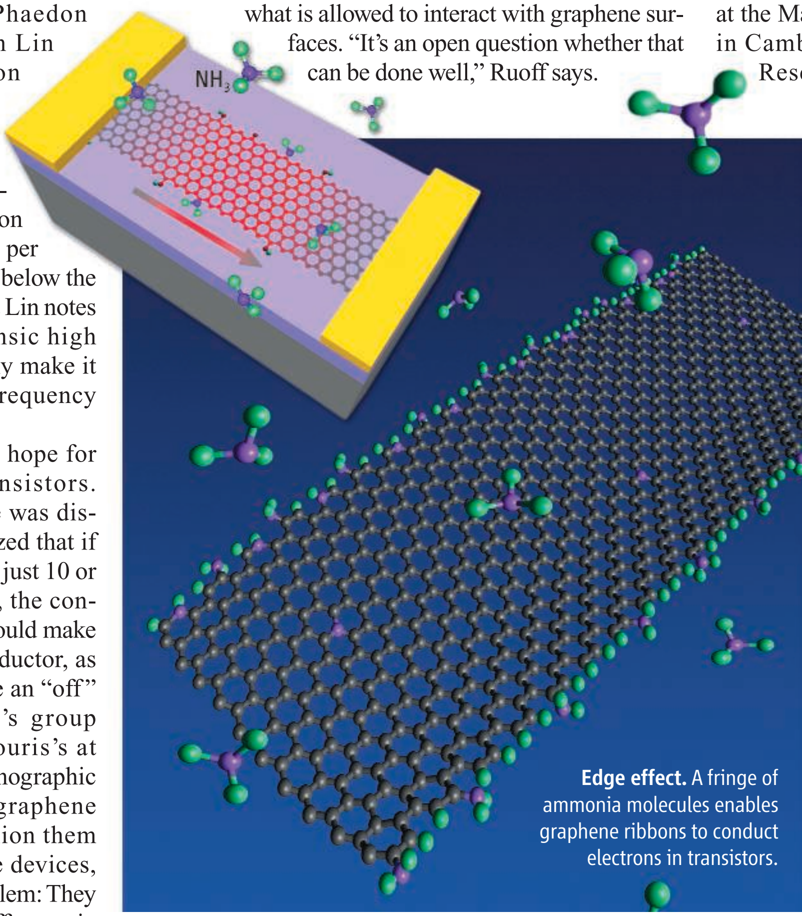
(RF) circuitry. Instead of digital circuitry's simple on/off states, RF devices differentiate signals by their relative strength. RF circuits are traditionally made from high-priced semiconductors such as GaAs and indium phosphide (InP). Because charges move more quickly in graphene, it has a shot at beating out conventional devices.

Progress is already beginning. In the 14 January issue of *Nano Letters*, for example, researchers led by Phaedon Avouris and Yu-Min Lin at IBM's T. J. Watson Research Center in Yorktown Heights, New York, reported making graphene transistors that can switch on and off 26 billion times per second. That's still well below the performance of InP. But Lin notes that graphene's intrinsic high speed should eventually make it possible to push the frequency much higher.

There may even be hope for digital graphene transistors. Even before graphene was discovered, theorists realized that if it were cut into ribbons just 10 or 20 nanometers across, the confinement of electrons could make the material a semiconductor, as crowding would enable an "off" state. In 2007, Kim's group at Columbia and Avouris's at IBM reported using lithographic patterning to create graphene nanoribbons and fashion them into transistors. Those devices, however, still had a problem: They didn't show as large a difference in the conductivity between the off and on states as chipmakers would like for reliable circuits.

A team led by Hongjie Dai, a chemist at Stanford University in Palo Alto, California, improved matters with a scheme for making nanoribbons chemically, which produced much larger on/off ratios (*Science*, 29 February 2008, p. 1229). Those devices turned out to be good at ferrying positive charges, making them positive, or p-type, transistors. To make modern circuitry, however, chipmakers need negative-charge-conducting, or n-type, transistors as well. In the 8 May issue of *Science* (p. 768), Dai's group reported that by adding ammonia groups to the edges of the graphene nanoribbons, they can "dope" the material and use it to make n-type transistors. Rodney Ruoff, a chemical engineer at the University of Texas (UT), Austin, calls the progress "encouraging."

Even so, graphene transistors remain a long way from finding their way into your next computer. Numerous groups have recently shown that atoms and surfaces that sit next to graphene can dramatically influence its conductivity, among other properties. So making millions of devices that all work the same way—an essential property for computer chips—will require controlling exactly what is allowed to interact with graphene surfaces. "It's an open question whether that can be done well," Ruoff says.



Edge effect. A fringe of ammonia molecules enables graphene ribbons to conduct electrons in transistors.

CREDITS: LI ZHANG, LIYING JIAO, XINRAN WANG, AND HONGJIE DAI; INSET: XINRAN WANG ET AL.

Growing prospects

Up to this point, an even bigger hurdle has been manufacturing large-area graphene films, say Ruoff, Geim, and others. Geim acknowledges that his team's original cellophane-tape approach to making graphene flakes has little chance of being scaled up into an industrial operation capable of covering the 300-millimeter-wide silicon wafers that are the industry's standard substrate. So researchers around the globe have been racing to come up with other ways to grow large-area graphene films at low cost.

Several groups have made steady progress in growing graphene atop wafers made from silicon carbide. The technique uses high temperatures to boil off silicon from the outer surface of the wafer, leaving graphene behind. Researchers have created large graphene sheets with this approach. But because there is no easy way to peel those graphene layers off the expensive silicon carbide wafer, many groups are looking for answers elsewhere.

They've been finding them. "There has been spectacular progress in the last 2 or 3 months," Geim says. In 2008, for example, a team led by Jing Kong, an electrical engineer at the Massachusetts Institute of Technology in Cambridge, reported at the Materials Research Society meeting in Boston that they had used a technique known as chemical-vapor deposition to grow large graphene sheets atop thin nickel films sitting on silicon wafers (*Science*, 19 December 2008, p. 1785). They also showed that they could pattern the graphene films using a simple stamping procedure. In the 5 February issue of *Nature*, researchers at Sungkyunkwan University and the Samsung Advanced Institute of Technology, both in South Korea, reported that they had extended the technique to transfer high-quality nickel-grown films onto sheets of transparent plastics for use as transparent electrodes in light-emitting diodes and other devices.

Researchers are growing large graphene sheets on other metals as well. In a paper posted online in *Science* on 7 May (www.sciencemag.org/cgi/content/abstract/1171245), Ruoff's team at UT, working with researchers at Texas Instruments in Dallas, reports using a similar technique to grow large-area graphene films on thin copper foils. Both the nickel and the copper growth techniques form highly pure graphene. But because copper normally forms larger grains that network themselves together in sheets, it makes larger regions of pristine graphene, Ruoff says.

Will larger area graphene sheets ensure that the ultrathin carbon membrane will be a scientific or commercial success? Not necessarily, Ruoff and others say. But materials science, physics, and chemistry are crowded, highly competitive fields. "People are desperately looking for a new idea," Avouris says. So far, graphene is offering them in bunches. As long as that continues, graphene will remain firmly in fashion.

–ROBERT F. SERVICE