Consider the humble pencil. It may come as a surprise to learn that the now common writing instrument at one time topped the list of must-have, high-tech gadgets. In fact, the simple pencil was once even banned from export as a strategic military asset. But what is probably more unexpected is the news that every time someone scribes a line with a pencil, the resulting mark includes bits of the hottest new material in physics and nanotechnology: graphene.

Graphene comes from graphite, the “lead” in a pencil: a kind of pure carbon formed from flat, stacked layers of atoms. The tiered structure of graphite was discerned centuries ago, and so it was natural for physicists and materials scientists to try splitting the mineral into its constituent sheets—if only to study a substance whose geometry might turn out to be so elegantly simple. Graphene is the name given to one such sheet. It is made up entirely of carbon atoms bound together in a network of repeating hexagons within a single plane just one atom thick.

For years, however, all attempts to make graphene ended in failure. The most popular early approach was to insert various molecules between the atomic planes of graphite to wedge the planes apart—a technique called chemical exfoliation. Although graphene layers almost certainly detached from the graphite at some transient stage of the process, they were never identified as such. Instead the final product usually emerged as a slurry of graphitic particles—not much different from wet soot. The early interest in chemical exfoliation faded away.

Soon thereafter experimenters attempted a more direct approach. They split graphite crystals into progressively thinner wafers by scraping or rubbing them against another surface. In spite of its crudeness, the technique, known as...
micromechanical cleavage, worked surprisingly well. Investigators managed to peel off graphite films made up of fewer than 100 atomic planes. By 1990, for example, German physicists at RWTH Aachen University had isolated graphite films thin enough to be optically transparent.

A decade later one of us (Kim), working with Yuanbo Zhang, then a graduate student at Columbia University, refined the micromechanical cleavage method to create a high-tech version of the pencil—a “nanopencil,” of course. “Writing” with the nanopencil yielded slices of graphite just a few tens of atomic layers thick [see box on page 93]. Still, the resulting material was thin graphite, not graphene. No one really expected that such a material could exist in nature.

That pessimistic assumption was put to rest in 2004. One of us (Geim), in collaboration with then postdoctoral associate Kostya S. Novoselov and his co-workers at the University of Manchester in England, was studying a variety of approaches to making even thinner samples of graphite. At that time, most laboratories began such attempts with soot, but Geim and his colleagues serendipitously started with bits of debris left over after splitting graphite by brute force. They simply stuck a flake of graphite debris onto plastic adhesive tape, folded the sticky side of the tape over the flake and then pulled the tape apart, cleaving the flake in two. As the experimenters repeated the process, the resulting fragments grew thinner [see box on page 95]. Once the investigators had many thin fragments, they meticulously examined the pieces—and were astonished to find that some were only one atom thick. Even more unexpectedly, the newly identified bits of graphene turned out to have high crystal quality and to be chemically stable even at room temperature.

The experimental discovery of graphene led to a deluge of international research interest. Not only is it the thinnest of all possible materials, it is also extremely strong and stiff. Moreover, in its pure form it conducts electrons faster at room temperature than any other substance. Engineers at laboratories worldwide are currently scrutinizing the stuff to determine whether it can be fabricated into products such as supertough composites, smart displays, ultrafast transistors and quantum-dot computers.

In the meantime, the peculiar nature of graphene at the atomic scale is enabling physicists to delve into phenomena that must be described by relativistic quantum physics. Investigating such

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**EVERYDAY PENCIL MARKS** include minute quantities of graphene, one of the hottest “new” materials in science and engineering.

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**KEY CONCEPTS**

- Graphene is a one-atom-thick sheet of carbon that stacks with other such sheets to form graphite—pencil “lead.” Physicists have only recently isolated the material.

- The pure, flawless crystal conducts electricity faster at room temperature than any other substance.

- Engineers envision a range of products made of graphene, such as ultrahigh-speed transistors. Physicists are finding the material enables them to test a theory of exotic phenomena previously thought to be observable only in black holes and high-energy particle accelerators.

— The Editors
phenomena, some of the most exotic in nature, has heretofore been the exclusive preserve of astrophysicists and high-energy particle physicists working with multimillion-dollar telescopes or multibillion-dollar particle accelerators. Graphene makes it possible for experimenters to test the predictions of relativistic quantum mechanics with laboratory benchtop apparatus.

Meet the Graphene Family
Given how widespread the pencil is today, it seems remarkable that what became known as graphite did not play a role in ancient literate civilizations such as those of China or Greece. Not until the 16th century did the English discover a large deposit of pure graphite, then called *plumbago* (Latin for “lead ore”). Its utility as a marker was immediately apparent, though, and the English wasted no time in making it into an easy-to-use substitute for quill and ink. The pencil soon became all the rage among the European intelligentsia.

But it was not until 1779 that Swedish chemist Carl Scheele showed that *plumbago* is carbon, not lead. A decade later German geologist Abraham Gottlob Werner suggested that the substance could more appropriately be called graphite, from the Greek word meaning “to write.” Meanwhile munitions makers had discovered another use for the crumbly mineral: they found it made an ideal lining in casting molds for cannonballs. That use became a tightly guarded military secret. During the Napoleonic Wars, for instance, the English Crown embargoed the sale to France of both graphite and pencils.

In recent decades graphite has reclaimed some of its once lofty technological status, as investigators have explored the properties and potential applications of several previously unrecognized molecular forms of carbon that occur in ordinary graphitic materials. The first of them, a soccer ball–shaped molecule dubbed the buckyball, was discovered in 1985 by American chemists Robert Curl and Richard E. Smalley, along with their English colleague Harry Kroto. Six years later Sumio Iijima, a Japanese physicist, identified the honeycombed, cylindrical assemblies of carbon atoms known as carbon nanotubes. Although nanotubes had been reported by many investigators in earlier decades, their importance had not been appreciated. Both the new molecular forms were classified as fullerenes. (That name and the term “buckyball” were coined in honor of the visionary U.S. architect and engineer Buckminster Fuller, who investigated those shapes before the carbon forms themselves were discovered.)
Molecular Chicken Wire

Graphite, the fullerenes and graphene share the same basic structural arrangement of their constituent atoms. Each structure begins with six carbon atoms, tightly bound together chemically in the shape of a regular hexagon—what chemists call a benzene ring.

At the next level of organization is graphene itself, a large assembly of benzene rings linked in a sheet of hexagons that resembles chicken wire [see box on opposite page]. The other graphitic forms are built up out of graphene. Buckyballs and the many other nontubular fullerenes can be thought of as graphene sheets wrapped up into atomic-scale spheres, elongated spheroids, and the like. Carbon nanotubes are essentially graphene sheets rolled into minute cylinders. And as we mentioned earlier, graphite is a thick, three-dimensional stack of graphene sheets; the sheets are held together by weak, attractive intermolecular forces called van der Waals forces. The feeble coupling between neighboring graphene sheets is what enables graphite to be broken so easily into minuscule wafers that make up the mark left on paper when someone writes with a pencil.

With the benefit of hindsight, it is clear that fullerenes, despite going unnoticed until recently, have been close at hand all along. They occur, for instance, in the soot that coats every barbecue grill, albeit in minute quantities. Just so, bits of graphene are undoubtedly present in every pencil mark—even though they, too, long went undetected. But since their discovery, the scientific community has paid all these molecules a great deal of attention.

Buckyballs are notable mainly as an example of a fundamentally new kind of molecule, although they may also have important applications, notably in drug delivery. Carbon nanotubes combine a suite of unusual properties—chemical, electronic, mechanical, optical and thermal—that have inspired a wide variety of innovative potential applications. Those innovations include materials that might replace silicon in microchips and fibers that might be woven into lightweight, ultrastrong cables. Although graphene itself—the mother of all graphitic forms—became part of such visions just a few years ago, it seems likely that the material will offer even more insights into basic physics and more intriguing technological applications than its carbonaceous cousins.

Exceptional Exception

Two features of graphene make it an exceptional material. First, despite the relatively crude ways it is still being made, graphene exhibits remarkably high quality—resulting from a combination of the purity of its carbon content and the orderliness of the lattice into which its carbon atoms are arranged. Investigators have so far failed to find a single atomic defect in graphene—say, a vacancy at some atomic position in the lattice or an atom out of place. That perfect crystalline order seems to stem from the strong yet highly flexible interatomic bonds, which create a substance harder than diamond yet allow the planes to bend when mechanical force is applied. The flexibility enables the structure to accommodate a good deal of deformation before its atoms must reshuffle to adjust to the strain.

The quality of its crystal lattice is also represen-

[THE AUTHORS]

Andre K. Geim (left) and Philip Kim (right) are condensed matter physicists who in recent years have investigated the nanoscale properties of one-atom-thick, "two-dimensional" crystalline materials. Geim is a fellow of the Royal Society and Langworthy Professor of Physics at the University of Manchester in England. He also directs the Manchester Center for Mesoscience and Nanotechnology. Geim received his Ph.D. from the Institute of Solid State Physics in Chernogolovka, Russia. Kim, a fellow of the American Physical Society who received his doctoral degree from Harvard University, is associate professor of physics at Columbia University. His research focuses on quantum thermal and electrical transport processes in nanoscale materials.
Interpreting quantum electrodynamics never comes without a good deal of wrestling with ordinary intuition.

Quantum Electrodynamics Enters the Lab

Electrons move virtually unimpeded through the highly regular atomic structure of graphene, reaching such great speeds that their behavior cannot be described by “ordinary” quantum mechanics. The theory that applies instead is known as relativistic quantum mechanics, or quantum electrodynamics (QED), a theory whose distinctive (and weird) predictions were thought, until now, to be observable only in black holes or high-energy particle accelerators. With graphene, though, physicists can test one of the weirdest predictions of QED in the laboratory: “perfect quantum tunneling.”

In classical, or Newtonian, physics, a low-energy electron (green ball in 1a) acts like an ordinary particle. If its energy is not enough to carry it over the top of a potential-energy barrier, it remains trapped on one side of the barrier (1b) as surely as a truck out of gas in a valley remains stranded on one side of a hill.

In the ordinary quantum-mechanical picture, an electron acts in some contexts like a wave that spreads out in space. The wave represents, roughly, the probability of finding the electron at a particular point in space and time. When this “slow-moving” wave approaches a potential-energy barrier (blue wave in 2a), it penetrates the barrier in such a way that there is some probability, neither 0 nor 100 percent, that the electron will be found on the far side of the barrier (2b). In effect, the electron tunnels through the barrier.

When a high-speed electron wave in graphene (orange wave in 3a) comes to a potential-energy barrier, QED makes an even more startling prediction: the electron wave will subsequently be found on the far side of an energy barrier with 100 percent probability (3b). The observation that graphene conducts electricity so well seems to confirm that prediction.
tron at all. In fact, its closest analogue is another elementary particle, the nearly massless neutrino. Of course, the neutrino, in accord with its name, is electrically neutral (in Italian, neutrino means “little neutral one”), whereas the quasiparticle in graphene carries the same electric charge as the electron. But because the neutrino travels at nearly the speed of light, no matter what its energy or momentum, it must be described in terms of the theory of relativity. Similarly, a quasiparticle in graphene always moves at a high constant speed, albeit about 300 times slower than the speed of light. In spite of its scaled-down speed, its behavior closely parallels the relativistic behavior of the neutrino.

The relativistic nature of the quasiparticles in graphene renders ordinary, nonrelativistic quantum mechanics useless in describing how they act. Physicists must reach for a more complex framework in their arsenal of theories: relativistic quantum mechanics, which is now known as quantum electrodynamics. That theory has its own language, and central to that language is the probabilistic equation named after English physicist Paul A. M. Dirac, who first wrote his equation down in the 1920s. Accordingly, theorists sometimes describe electrons moving within graphene as massless Dirac quasiparticles.

Particles from “Nothing”
Unfortunately, interpreting quantum electrodynamics never comes without a good deal of wrestling with ordinary intuition. One must become familiar, if never quite comfortable, with phenomena that seem paradoxical. The paradoxes of quantum electrodynamics often arise from the fact that relativistic particles are always accompanied by their Bizarro-world alter egos: antiparticles. The electron, for instance, pairs with an antiparticle called the positron. Its mass is exactly the same as that of the electron, but its electric charge is positive. A particle-antiparticle pair can appear under relativistic conditions because it costs little energy for an extremely fast-moving, high-energy object to create a pair of “virtual particles.” Oddly, the pair emerges directly from nothing—from the vacuum.

Why that happens is a consequence of one of the many versions of Heisenberg’s uncertainty principle in quantum mechanics: roughly speaking, the more precisely an event is specified in time, the less precise is the amount of energy associated with that event. Consequently, on extremely short timescales, energy can take on almost any value. Because energy is equivalent to mass, according to Einstein’s famous formula \( E = mc^2 \), the energy equivalent to the mass of a particle and its antiparticle can appear out of nothing. For example, a virtual electron and a virtual positron can suddenly pop into existence by “borrowing” energy from the vacuum, provided the lifetimes of the virtual particles are so short that the energy deficit is paid back before it can be detected.

The intriguing dynamism of the vacuum in quantum electrodynamics leads to many peculiar effects. The Klein paradox is a good example. It describes circumstances in which a relativistic object can pass through any potential-energy barrier, no matter how high or how wide [see box on opposite page]. A familiar kind of potential-energy barrier is an ordinary rise in the landscape that surrounds a valley. A truck leaving the valley gains potential energy as it

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**D.I.Y. Graphene**

1. Work in a clean environment; stray dirt or hair plays havoc with graphene samples.
2. Prepare a wafer of oxidized silicon, which helps you see graphene layers under a microscope. To smooth out the surface to accept the graphene and to clean it thoroughly, apply a mix of hydrochloric acid and hydrogen peroxide.
3. Attach a graphite flake to about six inches of plastic sticky tape with tweezers. Fold the tape at a 45-degree angle right next to the flake, so that you sandwich it between the sticky sides. Press it down gingerly and peel the tape apart slowly enough so that you can watch the graphite cleaving smoothly in two.
4. Repeat the third step about 10 times. This procedure gets harder to do the more folds you make.
5. Carefully lay the cleaved graphite sample that remains stuck to the tape onto the silicon. Using plastic tongs, gently press out any air between the tape and sample. Pass the tongs lightly but firmly over the sample for 10 minutes. With the tongs, keep the wafer planted on the surface while slowly peeling off the tape. This step should take 30 to 60 seconds to minimize shredding of any graphene you have created.
6. Place the wafer under a microscope fitted with a 50× or 100× objective lens. You should see plenty of graphite debris: large, shiny chunks of all kinds of shapes and colors (upper image) and, if you’re lucky, graphene: highly transparent, crystalline shapes having little color compared with the rest of the wafer (lower image). The upper sample is magnified 115×; the lower 200×.

—JR Minkel, online news reporter
Graphene has been available for too short a time for engineers to have developed any products that use it, but the list of prospective graphene-based technologies is long. Two examples include:

**GRAPHENE-BASED TECHNOLOGY**

A nanoscale graphene plane can be formed into a single-electron (or quantum-dot) transistor. The diagram (upper left) shows schematically how two electrodes, a "source" and a "drain," are connected by an "island" of conducting material, or quantum dot, that is only 100 nanometers across. The island, which appears in the center of an electron micrograph of such a device (lower left)—shown here magnified 40,000×—is too small to accommodate more than one new electron at a time; any second electron is kept away by electrostatic repulsion. An electron from the source tunnels quantum mechanically to the island, then leaves by tunneling on to the drain. The voltage applied to a third electrode called the gate (not shown in the electron micrograph) controls whether a single electron can enter or exit the island, thereby registering either a 1 or a 0.

**SINGLE-ELECTRON TRANSISTORS**

In the long run, one can envision entire integrated circuits carved out of a single graphene sheet.

**COMPOSITE MATERIALS**

Two or more complementary materials can often be combined to obtain the desirable properties of both. Typically a bulk matrix and a reinforcement are used: think of a fiberglass boat hull made of plastic infused with strong glass fibers. Investigators are testing the physical properties of composites fabricated from polymers reinforced with graphene-based materials such as graphene oxide, a chemically modified version of graphene that is stiff and strong. Unlike graphene, graphene oxide "paper" (right, inset) is relatively easy to make and may soon find its own useful applications in laminated composites (right, background). The scale bar is one micron long.

**Testing the Bizarre**

Particles, too, can readily move “downhill” on their own, from relatively high regions of potential energy to relatively low ones. If a “hillside” of high potential energy surrounds a particle in an energy “valley,” however, the particle is no less stuck than a truck out of gas in a real valley. There is one big caveat to that conclusion, which occurs in ordinary, nonrelativistic quantum mechanics. A second version of Heisenberg’s uncertainty principle states that it is impossible to know the exact position of a particle. Accordingly, physicists describe the position of a particle probabilistically. A strange consequence is that even though a low-energy particle might seem to be “trapped” by a high barrier, there is some probability that the particle will later be found outside that barrier. If it is, its ghostly passage through the energy barrier is called quantum tunneling.

In nonrelativistic quantum tunneling, the probability that a low-energy particle will tunnel through a high potential-energy barrier varies, but it can never be 100 percent. The probability of quantum tunneling shrinks as the barrier gets higher and thicker. The Klein paradox completely changes the character of quantum tunneling, however. It states that relativistic particles should tunnel through barrier regions of high energy and broad expanse with 100 percent probability. At a barrier the particles just pair up with their antiparticle twins, which experience the world in an upside-down, topsy-turvy fashion whereby real-world hills are seen as antiparticle valleys. After traveling readily through the odd, antiworld valley of the barrier, the antiparticles convert back into particles at the other side and emerge unimpeded. Even to many physicists, this prediction of quantum electrodynamics seems deeply counterintuitive.

Such an outlandish prediction cries out for testing, yet it has long remained unclear whether the Klein paradox could be tested at all, even in principle. The massless Dirac quasiparticles in graphene have now come to the rescue. In graphene, the Klein paradox becomes a routine effect with readily observable consequences. As charge-carrying, massless Dirac quasiparticles move within a graphene crystal across which a voltage, or potential-energy difference, has been applied, experimenters can measure the material’s electrical conductivity. Perfect (100 percent probability) tunneling accounts for the lack of additional resistance that one would expect from the extra barriers and boundaries. Investigators are now measuring the flow of such tunneling particles through potential barriers of varying heights. Physicists expect that graphene will also
help demonstrate many of the other oddball effects predicted by quantum electrodynamics.

2-D or Not 2-D
It is too early to fully assess the many possible technological applications of graphene. But more than a decade of research on carbon nanotubes—rolled-up graphene—gives graphene a huge head start. It is not unreasonable to think that nearly every useful role envisaged for nanotubes is also open to their flat cousin. High-tech industries are penciling in some commercial applications, and some are already placing bets on its promise. Meeting the demand for such applications will call for graphene output on an industrial scale, and many technology research teams are hard at work developing improved production techniques. Although graphene powder can already be made in industrial quantities, sheet graphene is still difficult to make and currently ranks as probably the most expensive material on the planet. Today a micromechanically cleaved graphene crystallite smaller than the thickness of a human hair can cost more than $1,000. Groups in Europe and at several U.S. institutions—the Georgia Institute of Technology, the University of California, Berkeley, and Northwestern University among them—have grown graphene films on silicon carbide wafers similar to the ones common in the semiconductor industry.

In the meantime, engineers worldwide are striving to exploit the highly desirable physical and electronic properties unique to graphene [see box on opposite page and at left]. Its high surface-to-volume ratio, for instance, should make it handy in manufacturing tough composite materials. The extreme thinness of graphene could also lead to more efficient field emitters—needle-like devices that release electrons in the presence of strong electric fields.

The properties of graphene can be finely tuned by applying electric fields, which could make it possible to build improved superconducting and so-called spin-valve transistors, as well as ultra-sensitive chemical detectors. Finally, thin films fabricated from overlapping patches of graphene show great promise in serving as transparent and conducting coatings for liquid-crystal displays and solar cells. The list is far from exhaustive, but we expect that some niche applications could reach the market in only a few years.

Reprieve for Moore’s Law?
One engineering direction deserves special mention: graphene-based electronics. We have emphasized that the charge carriers in graphene move at high speed and lose relatively little energy to scattering, or colliding, with atoms in its crystal lattice. That property should make it possible to build so-called ballistic transistors, ultra-high-frequency devices that would respond much more quickly than existing transistors do.

Even more tantalizing is the possibility that graphene could help the microelectronics industry prolong the life of Moore’s law. Gordon Moore, a pioneer of the electronics industry, pointed out some 40 years ago that the number of transistors that can be squeezed onto a given area doubles roughly every 18 months. The inevitable end of that continuing miniaturization has been prematurely announced many times. The remarkable stability and electrical conductivity of graphene even at nanometer scales could enable the manufacture of individual transistors substantially less than 10 nanometers across and perhaps even as small as a single benzene ring. In the long run, one can envision entire integrated circuits carved out of a single graphene sheet.

Whatever the future brings, the one-atom-thick wonderland will almost certainly remain in the limelight for decades to come. Engineers will continue to work to bring its innovative by-products to market, and physicists will continue to test its exotic quantum properties. But what is truly astonishing is the realization that all this richness and complexity had for centuries lain hidden in nearly every ordinary pencil mark.