

Electrons in Atomically Thin Carbon Sheets Behave like Massless Particles

Traditionally found in particle-physics and cosmology contexts, the relativistic Dirac equation also describes how electrons move in a unique two-dimensional condensed matter system, graphene.

Graphene, a single, one-atom-thick sheet of carbon atoms arranged in a honeycomb lattice, is the two-dimensional building block for carbon materials of every other dimensionality. It can be stacked into 3D graphite, rolled into 1D nanotubes, or wrapped into 0D buckyballs. But for decades scientists presumed that a single 2D graphene sheet could not exist in its free state; they reasoned that its planar structure would be thermodynamically unstable and possibly curl into carbon soot. The University of Manchester's Andre Geim and colleagues there and at the Institute for Microelectronics Technology in Chernogolovka, Russia, put that presumption to rest a few months ago by isolating single graphene sheets.¹

Their method is astonishingly simple: Use adhesive tape to peel off weakly bound layers from a graphite crystal and then gently rub those fresh layers against an oxidized silicon surface. The trick was to find the

relatively rare monolayer flakes among the macroscopic shavings. Although the flakes are transparent under an optical microscope, the different thicknesses leave telltale interference patterns on the SiO₂, much like colored fringes on an oily puddle. The patterns told the researchers where to hunt for single monolayers using atomic force microscopy.

The work confirmed that graphene is remarkable—stable, chemically inert, and crystalline under ambient conditions. Its honeycomb lattice, pictured in figure 1 with each carbon atom connected to its neighbors through strong covalent bonds, explains graphene's strength and rigidity. And it can carry huge current densities—about 10⁸ A/cm², roughly two orders of magnitude greater than copper.

Microelectronics engineers are paying attention. In semiconductor heterostructures used to make FET devices, for instance, it takes million-dollar epitaxy machines and

exquisite care to tie up dangling surface bonds and eliminate impurities in quantum wells. The preparation minimizes the scattering of electrons against interfaces and defects to ensure the largest electron mean-free paths in the device.

But in graphene, just 1 Å thick, scientists have a material that is relatively defect free and whose electrons have a respectable mean-free path naturally, without materials manipulation and processing. Graphene can hardly be more low tech, and yet it still exhibits high conductivities. "It's really counterintuitive and remains to be understood," comments Geim, "but the electron wavefunction appears to localize only parallel to the sheet and does not interact with the outside world, even a few angstroms away."

Experiment meets theory

A calculation of graphene's band structure as early as 1947 captured the dynamics of its electrons in the crystal lattice.² Interest in the material at the time was purely academic. Now, nearly 60 years later, Geim and his collaborators,³ and separately a team from Columbia University led

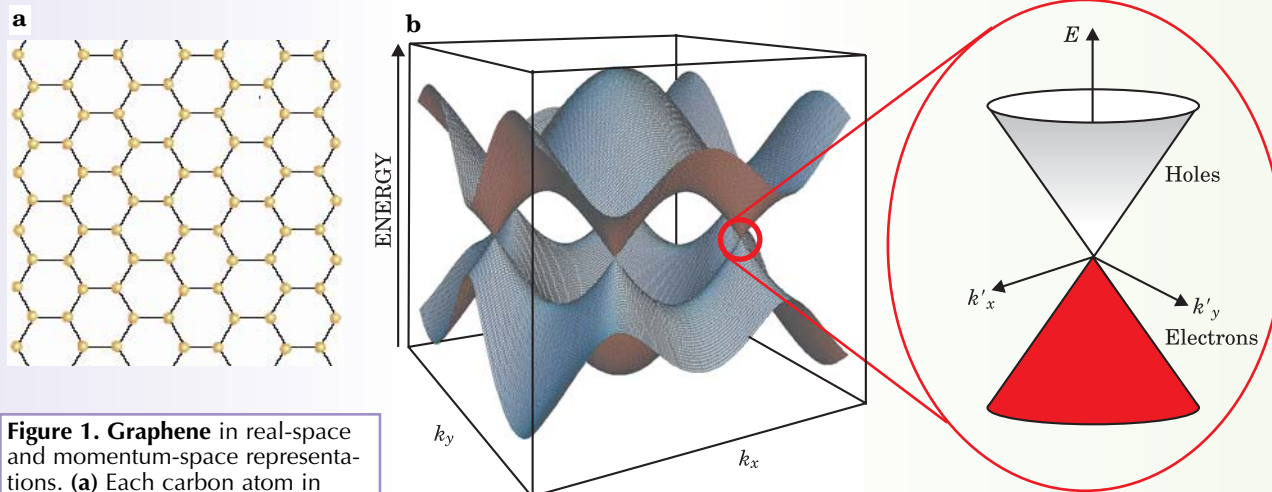


Figure 1. Graphene in real-space and momentum-space representations. **(a)** Each carbon atom in graphene's honeycomb lattice forms strong covalent bonds with its neighbors, with one unbound electron left over to wander across the two-dimensional crystal. **(b)** A band-structure picture of the crystal describes the energy dependence of that electronic motion. A semimetal, graphene has valence and conduction bands that just touch at discrete points in the Brillouin zone. The energy-momentum dispersion relation becomes linear in the vicinity of those points, with the dispersion described by the relativistic energy equation $E = |\hbar\mathbf{k}|v_F$, where v_F is the Fermi velocity and $\hbar\mathbf{k}$ its momentum. Consequently, an electron has an effective mass of zero and behaves more like a photon than a conventional massive particle whose energy-momentum dispersion is parabolic. (Courtesy of Philip Kim.)

by Philip Kim,⁴ have experimentally explored the nature of graphene's conductivity and verified the exotic electrical properties initially predicted so long ago—in particular, that its mobile electrons behave as if they were massless, relativistic fermions.

To appreciate how differently conventional particles and massless ones behave in a crystal lattice, consider their different dispersion relations—how a particle's energy changes with its momentum along valence and conduction bands. In conventional semiconductors, electrons are ascribed an effective mass m^* that accounts for their interaction with the lattice. The energy E depends quadratically on the momentum ($E = \hbar^2 \mathbf{k}^2 / 2m^*$, where $\mathbf{k}$ is the electron wavevector).

Graphite, a semimetal whose bands slightly overlap and allow pockets of electrons and holes to tunnel between staggered layers, bears out such a dispersion relation. But in a single graphene sheet, the overlap shrinks down to a single point, where the bands barely touch (see figure 1b). The result is perfect symmetry between a band filled with holes and a band filled with electrons. More significant, the dispersion of those bands is linear as they approach each other. Consequently, the electron dynamics are best modeled by a relativistic Dirac equation, which describes a linear relation between energy and momentum: $E = \hbar \mathbf{k} v_F$, in which the Fermi velocity v_F of electrons or holes replaces the speed of light. The dispersion curve then implies that the electrons' mass vanishes throughout a large range of momentum values in the crystal lattice.

Electrons are not actually massless, of course; the effective mass is a parameter that describes how an electron at particular wavevectors responds to applied forces. But the vanishing of that parameter indicates that the velocity of the electrons confined on graphene remains constant. Their transport properties become more akin to those of massless particles like photons.

Quantum anomalies

Both Kim's and Geim's groups mapped out this exotic dispersion curve by measuring the response of graphene electrons to electric and magnetic fields. By attaching a gate voltage to the back of the SiO_2 substrate on which graphene sits, the researchers effectively turned their crystals into metallic FETs and could tune the position of the Fermi level, the highest energy level occupied by electrons. Increasing the gate voltage

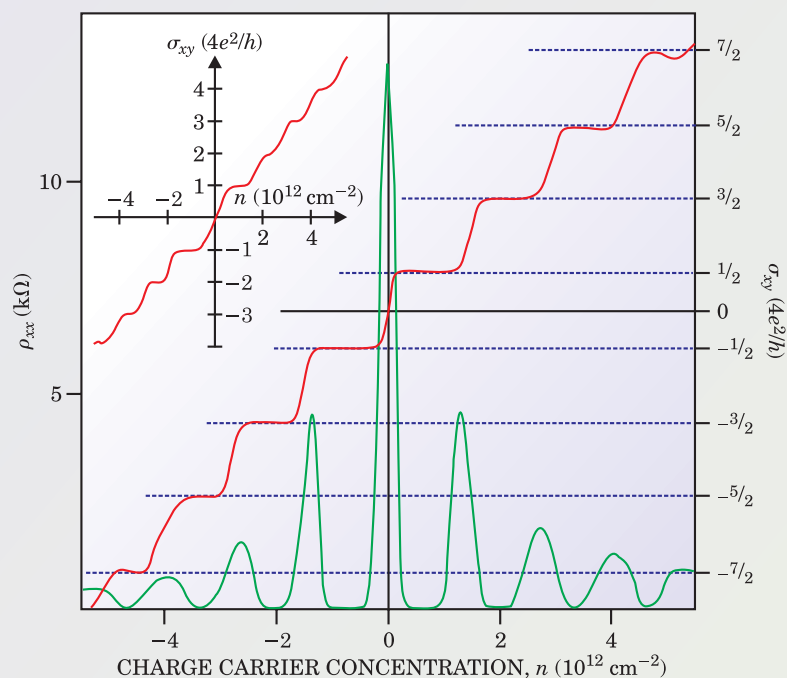


Figure 2. Quantum Hall effect in graphene. The hallmark of the integer QHE is that the longitudinal resistivity ρ_{xx} (shown in green) of a two-dimensional electron gas in a high magnetic field vanishes at precisely those discrete values where the transverse conductivity σ_{xy} (red) is quantized in units of e^2/h , where h is Planck's constant and e the charge on an electron or hole. An extra factor of 4 accounts for the spin and band-structure degeneracy in graphene. At 4 K and 14 T, σ_{xy} increases in quantized steps as researchers sweep the gate voltage applied to the crystal to vary the electron density n . But those steps come at integer values shifted by one-half of a unit because electrons mimic the relativistic behavior of Dirac fermions. Adding even one additional sheet to the system alters the band symmetry and removes the 1/2-integer phase shift, as the inset plot shows. (Adapted from ref. 3.)

injected additional electrons into the crystal and thereby increased its carrier concentration and Fermi level. Depositing gold electrodes on the surface turned the graphene crystals into Hall bars, devices the researchers could use to measure transverse and longitudinal resistances.

In a magnetic field perpendicular to the plane, electrons travel in closed circular orbits. In a 2D electron gas, those orbits occur only at discrete, quantized values—so-called Landau levels—of the electron energies. Both groups found that graphene, when sufficiently cold and exposed to a high magnetic field, exhibits a distinctive quantum Hall effect. Typically, the Hall conductivity—the conductivity measured perpendicular to the applied current—is quantized in a series of plateaus having values of ve^2/h , where v is the filling factor, or ratio of the number of electrons to the number of magnetic flux lines.

The actual sequence of quantized steps observed in graphene, though, deviates from what one would expect

in an ordinary quantum Hall system (see figure 2). The first plateau in the Hall conductivity occurs at an electron density that corresponds to a half-filled Landau level— $2e^2/h$, half of what is expected. (Graphene's degenerate spin states and bands contribute a factor of 4 to the value at each conductivity plateau.) All other plateaus then follow in integer steps. The half-integer shift is a subtle consequence of graphene's symmetric topology, which prompts its electrons to obey equations of motion derived from the relativistic Dirac Hamiltonian.

In addition to having two spin configurations, graphene electrons also appear to come endowed with a so-called pseudospin, essentially the spinors from Dirac theory. University of Pennsylvania theorist Charles Kane explains that as a graphene electron completes an orbit in a magnetic field, its pseudospin rotates, introducing a 180° phase shift in the electron wavefunction. That half-wavelength shift, or Berry's phase, changes the pattern of allowed energy

levels and quantized steps in Hall conductivity by just the observed amount.

Both in the quantum Hall regime and in the absence of a magnetic field, the longitudinal resistance rises markedly when the gate voltage is turned off so that the Fermi level lies at the intersection between the two bands. The density of states should be extremely small there, effectively zero where the bands meet. That makes it exceedingly sensitive to fluctuations. But, contrary to their expectations, both research teams find that the electrical conductivity of graphene never falls below a certain minimum value, even when there are no mobile electrons in the graphene sheet.

Geim's graphene devices differ from Kim's in only one respect. Both groups peel away graphite layers and follow similar protocols to locate their monolayer flakes, which come in various sizes. To make devices, though, Geim's group etched away the edges of each flake to create Hall-bar geometries with well-defined lengths and widths. In an experiment that measured the resistivity of 15 such samples with widely varying electron mobilities, Geim and colleagues found that the maximum resistivity averaged, to within 10%, a distinct value, $h/4e^2$. A quarter century ago Nevill Mott argued that the mean-free path for electrons in a metal can never be shorter than their Fermi wavelengths. Geim says his experimental result makes sense in that context, at least for 2D Dirac fermions, and demonstrates a fundamental quantized limit to the metallic system's minimum conductivity. But not everyone agrees, and the actual value for such a limit remains unclear. Boston University's Antonio Castro Neto comments, "We'll have to rewrite the theory of metals for this problem."

Making devices

Advocates of carbon nanotubes have long argued that their remarkable electronic properties—ballistic transport observable up to room temperature, for instance—make the material an ideal replacement for silicon electronics. The hurdle in achieving that vision has always been what to do about the 1D nature of the tubes. Making a circuit always involves attaching the nanotubes to other metals, which creates large contact resistances.

The availability of graphene layers provides a way around the problem. Electronically, graphene sheets should be identical to nanotubes. But its 2D structure—effectively an unrolled tube—allows the material to be engineered to suit different device applications. Graphene is a semimetal at the micron scale or larger. But when it is trimmed down to less than 100 nm, electron confinement opens its bandgap, an effect that can be used to tune the crystal's electronics for different purposes. Georgia Tech's Walter de Heer envisions graphene sheets sliced wider or narrower and in different patterns depending on whether it's a wire, ribbon, or some other component needed to make up a circuit. To avoid the contact-resistance problem, for instance, one could pattern the graphene sheet into an array of thin parallel strips or wires.

Interest in the micromanipulation of graphitic crystals has been intense, even before researchers could isolate graphene. Paul McEuen's group at Cornell University recently wired up 5-nm-thick graphitic quantum dots on SiO_2 and measured conductance properties.⁵ And prior to their *Nature* report, Kim's group measured the transport in crystals made using a "nano-pencil," which rubs off thin layers from a force microscope's cantilever whose tip is a graphite crystal.⁶ De Heer and his colleagues take a dif-

ferent approach, growing ultrathin graphite on silicon carbide, which provides an epitaxial orientation.⁷ "We peeled layers [too]," de Heer said, "but that reminded me too much of the nanotube track," which involves the labor-intensive process of harvesting the nanotubes and then manually laying them on some surface. Growing single sheets of graphene remains a problem—the monolayer crystal flakes are most vulnerable to damage while being cooked up in the ovens.

Still, de Heer's group has achieved mobilities up to 10 000 cm^2/Vs in their graphite crystals. In comparison, graphene has shown mobilities as high as 50 000 cm^2/Vs . The 10⁷ cm^2/Vs now achievable in quantum-well heterostructures like gallium aluminum arsenide seems a long way off. But the tough, resilient nature of carbon may allow some chance of getting clean and nearly perfect crystals at some future stage, argues Columbia's Horst Stormer. "In all the research in 2D, higher mobility was always what led you to new horizons."

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References

1. K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, A. K. Geim, *Proc. Natl. Acad. Sci. USA* **102**, 10451 (2005); 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).
2. P. R. Wallace, *Phys. Rev.* **71**, 622 (1947).
3. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov, *Nature* **438**, 197 (2005).
4. Y. Zhang, Y.-W. Tan, H. Stormer, P. Kim, *Nature* **438**, 201 (2005).
5. J. S. Bunch et al., *Nano Lett.* **5**, 287 (2005).
6. Y. Zhang et al., *Phys. Rev. Lett.* **94**, 176803 (2005).
7. C. Berger et al., *J. Phys. Chem. B* **108**, 19912 (2004).

Densely Packed Positronium Atoms Interact Chemically

Nature's simplest atom does not appear in the periodic table. Positronium (Ps), the short-lived bound system of an electron and its antiparticle, the positron, was independently predicted by Arthur Ruark and John Wheeler after the positron was discovered in 1932. Four years before positronium itself was discovered in 1951, Egil Hylleraas and Aadne Ore had performed a variational calculation¹ and concluded that Ps atoms could combine to form the diatomic

For the first time, experimenters have seen atoms made from an electron and a positron exchange spins and perhaps form diatomic molecules.

molecule Ps_2 . Two Ps atoms can also interact by swapping the spins of their two electrons or positrons.

Interactions of Ps atoms with each other are much more difficult to observe than to envision. To create Ps, researchers shoot positrons at a suitable target. If the Ps atoms are to be close enough to react, a large number of positrons must be accumulated and

then quickly dumped onto a small-diameter spot. That's a challenge, because the positrons are available only at low currents; to be accumulated, they must be drastically cooled and also must be isolated from ordinary matter to prevent their rapid annihilation with electrons. In addition, the Ps formed in the target quickly decays into annihilation photons, so experimenters need