

its maximum density at 4 °C and then becomes less dense with cooling. The formation of short-lived hydrogen bonds at low temperatures generates transient connections between molecules, thereby increasing the average volume per molecule. By the time water reaches its minimum density, nearly all of the molecules are tetrahedrally coordinated. In the simulations, water's minimum density and the protein refolding occurred synchronously at 195 K. (For more on the unusual behavior of supercooled water, see the article by Pablo Debenedetti and Gene Stanley, *PHYSICS TODAY*, June 2003, page 40.)

It's no accident that the protein's cold refolding coincided with water's evolution to that low-density state. The researchers attribute the compact core's formation to water's increased order. Although the simulated water remained liquid and had no long-range order, on short length and time scales, the molecules were tetrahedrally coordinated. Solvating the protein's core would have disrupted that order, so instead the water was expelled; hence the core's collapse. Water's role in reforming the helix is less clear, but it's likely a factor. "Biology happens in water," points out

Debenedetti. "I would be really surprised if water played no role."

Aqueous oratorio

Accurately capturing water's low-temperature dynamics is a challenge. Many computational models for water exist, and although none are perfect, the TIP4P/2005 model used by Kozuch and coworkers is considered one of the best among classical models. It still has its shortcomings; for example, it places the water's ambient-pressure melting temperature at 252.1 K, more than 20 K below its actual value. That means the researchers' simulations at 200 K are actually only 52 K below freezing, not 73 K. But, importantly, the model has been shown to capture much of water's known behavior—particularly its anomalous dynamics far from ambient conditions—and its complex crystalline phase diagram.

The researchers knew water could influence the protein's behavior, which is why they wanted to capture its dynamics as accurately as possible. In fact, Debenedetti originally wanted to study how Trp-cage's behavior would change around a liquid-liquid phase transition that has been seen in previous simulations of water.⁵ But simulating the protein

at the low temperature and high pressure necessary to reach that transition was unexpectedly difficult because the system took an extraordinarily long time to equilibrate. Luckily for the researchers, decreasing only the temperature was enough to uncover unexpected and intriguing behavior.

Although proteins don't run the risk of becoming supercooled *in vivo*, the simulated temperatures and cooling rates are physically relevant for preparing cryo-electron microscopy and cryopreservation samples. Now that they know where to look, the researchers are repeating their calculations on other proteins to see whether the refolding effect is more general.

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Twisted bilayer graphene enters a new phase

Improved device quality is the key to seeing a whole series of superconducting, correlated, and magnetic states in two layers of graphene assembled at a magic angle.

For years many graphene researchers pursued superconductivity. In 2018 Pablo Jarillo-Herrero of MIT and his colleagues found it in so-called magic-angle bilayer graphene (see *PHYSICS TODAY*, May 2018, page 15). A single layer of graphene, a two-dimensional sheet of carbon atoms, is not superconducting on its own. But two sheets (blue and black in figure 1) vertically stacked at just the right, "magic" angle θ —about 1.1° with respect to each other—have a superconducting transition around 1.7 K.

Now Dmitri Efetov of the Institute of Photonic Sciences in Barcelona, Spain, and his colleagues have replicated Jarillo-Herrero's results and discovered a rich landscape of competing states in magic-angle graphene.¹ By preparing a more homogenous device, Efetov's team could

establish and resolve previously hidden electronic states.

Quest for superconductivity

Researchers long suspected graphene could have correlated states, described by collective rather than individual charge-carrier behavior. Those states, such as superconducting and Mott insulating states, are likely to occur in materials with many electrons sharing the same energy. Such conditions occur in flat regions of the band structure—around a saddle point, for instance. Monolayer graphene has a saddle point in its band structure, but it's several electron volts higher in energy than the Fermi level, the highest occupied state of the material. Raising the Fermi level up to the saddle point isn't feasible with an applied voltage alone. In his grad-

uate work from 2007 to 2014 with Philip Kim, then at Columbia University and now at Harvard University, Efetov tried electrolytic gates, and other groups investigated intercalation to reach higher levels of charge-carrier doping. But none quite reached the saddle point.

A different route to correlated behavior² was proposed by Rafi Bistritzer and Allan MacDonald at the University of Texas at Austin back in 2011. Two layers of graphene at different relative angles form a quasiperiodic structure, or moiré lattice, at a larger length scale than graphene's lattice constant—see the larger hexagons in figure 1, in which the graphene sheets nearly align at their centers and increasingly misalign toward their edges. The periodicity of the moiré lattice tunes the band structure from that of independent monolayers for large angles to that of normal bilayer graphene, which is also not superconducting, when the layers are aligned.

For two layers of graphene mis-

aligned by 1.05° , the largest of a series of magic angles, Bistritzer and MacDonald calculated the emergence of a flat horizontal band, which varies by less than 10 meV as a function of momentum. More importantly, the flat band was at the Fermi level. In effect, the creation of a moiré lattice in bilayer graphene drags the high-energy saddle point from monolayer down to an accessible energy.

Jarillo-Herrero and colleagues assembled twisted bilayer graphene devices with relative angles near 1.1° . They first observed insulating behavior below 4 K. Although the density of states doesn't have a gap, the strong interaction between charge carriers keeps them from moving. At even lower temperatures, increasing or decreasing the number of charge carriers leads to superconducting states. Those states can be summoned in and out of existence by changing either the angle between the graphene sheets during assembly or the charge-carrier density with an applied voltage.

Beyond that tunability, magic-angle graphene's superconductivity is interesting because the transition temperature's relationship with the carrier density—the so-called superconducting dome indicated by orange dashed lines in figure 2—resembles that of high- T_c cuprates. Magic-angle graphene could serve as a convenient platform for studying unconventional superconductivity.

Since Jarillo-Herrero's paper came out, other groups have tried their hands at making twisted graphene devices. Four groups performed scanning tunneling spectroscopy on magic-angle graphene to visualize the moiré lattice and measure the density of states in the flat band.³ Cory Dean of Columbia University and his colleagues applied more than 1 GPa of hydrostatic pressure to induce superconductivity in a twisted bilayer device with a larger twist angle of 1.27° that did not otherwise show any correlated behavior.⁴ Feng Wang of the University of California, Berkeley, and his colleagues found superconductivity in twisted trilayer graphene.⁵ In the bustling field of twisted bilayer graphene research, Efetov has produced the most uniform magic-angle graphene to date and thus measured many previously unobserved correlated states with diverse properties.

Improving the device

The group's thorough electrical phase di-

agram of magic-angle graphene was largely possible through the development of improved devices, which were fabricated by Efetov's postdoc Xiaobo Lu. In a normal layer of graphene, the electrical mobility is limited by impurities. In twisted bilayer graphene, an additional impediment comes from local variations in the angle, which broaden the features in electrical measurements and obscure small energy gaps. A sample with a more uniform angle will reveal behaviors not distinguishable in measurements on other devices.

To realize the magic angle, Lu uses the established tear-and-stack technique: He tears one sheet of graphene in two. He then rotates one piece just past the magic angle, by about 1.2° , to account for the small decrease in the angle when the layers settle. He then stacks the rotated layer on top of the other. In most electrical devices, the final step is annealing to clean the sample and get rid of any air bubbles between the layers. But in magic-angle graphene, with the layers misaligned by such a small angle, heating the sample snaps the layers back into alignment. So instead of annealing, Lu rolls the top layer down gradually, starting from one edge, rather than dropping the second layer directly down onto the first. That method, called mechanical cleaning, squeezes out any air bubbles as they form.

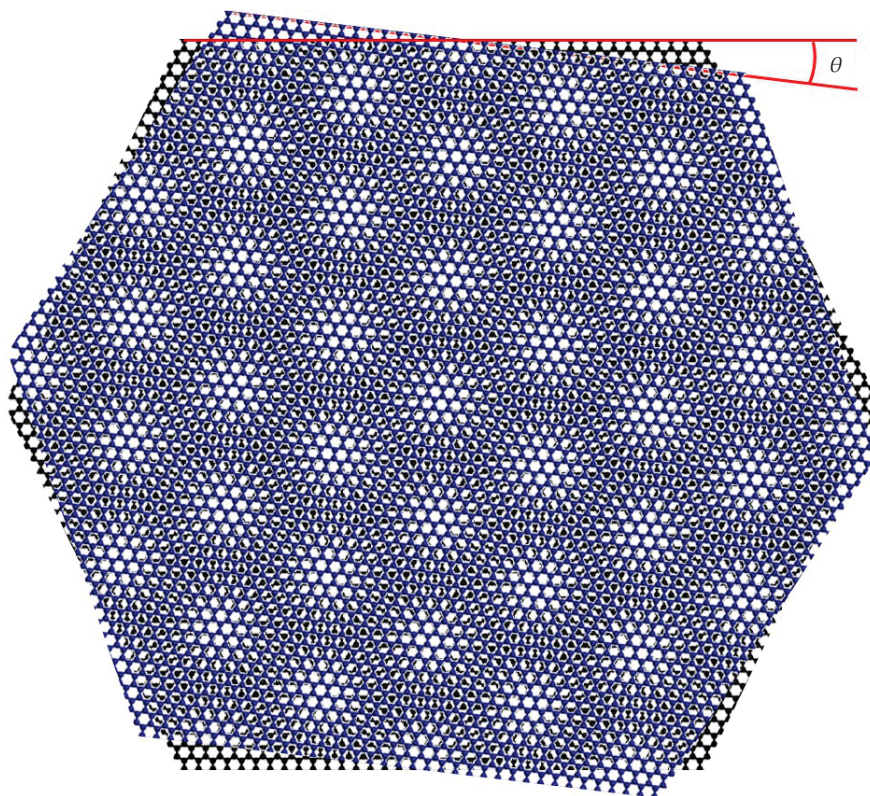


FIGURE 1. THE MOIRÉ LATTICE from two layers of graphene (blue and black hexagonal patterns) is the larger quasi-periodic hexagonal pattern formed by regions where the graphene lattices nearly align. The relative angle θ between the layers determines the periodicity of the moiré lattice. (Courtesy of ICFO/Xiaobo Lu.)

Mechanical cleaning hadn't been used for magic-angle graphene before because it frequently causes the twist angle to deviate from the intended angle. But Efetov regards the higher failure rate as worth the better device quality. The result is a relative angle that varies by only 0.02° over a $10\text{ }\mu\text{m}$ device, a record for magic-angle graphene. The fabrication overall is tricky; in the first three months, just 2 of the 30 devices worked. Now their success rate is closer to 20%.

Counting the states

Efetov and his group measured the electrical resistance over a wide range of charge-carrier densities and were surprised to find a host of states, shown in figure 2. When the device had a carrier density of about $-2 \times 10^{12}\text{ cm}^{-2}$, below the charge neutral point, they saw the same superconducting state as Jarillo-Herrero, plus three new superconducting states at carrier densities as low as $0.5 \times 10^{12}\text{ cm}^{-2}$, a record low absolute value for a super-

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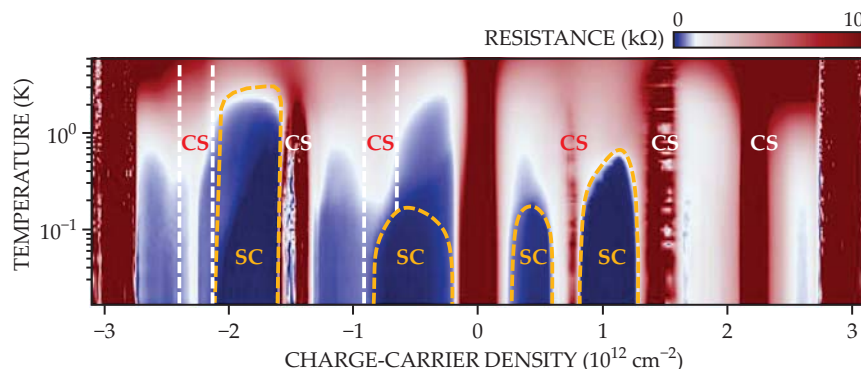


FIGURE 2. IN THIS ELECTRICAL PHASE DIAGRAM of magic-angle graphene, the orange dashed lines indicate the 50% resistance value of the phase transition to a superconductor (SC) with the highest transition temperature of 3 K. Between the SC states, the magic-angle graphene is in a correlated state (CS). (Courtesy of ICFO/Xiaobo Lu.)

conducting state. For the original superconducting state, Efetov and his colleagues found a nearly two times higher transition temperature, 3 K, than previously reported—perhaps due to their improved sample quality. The three new superconducting states had much lower transition temperatures in the hundreds of millikelvin.

At charge-carrier densities between all superconducting regimes, magic-angle graphene showed resistance peaks from correlated states, such as the insulating behavior Jarillo-Herrero saw. Three of the correlated states were insulating, and three seemed semimetallic. Two of the noninsulating states were also topologically nontrivial: A charge carrier that traveled in a closed loop in the band structure wouldn't return to its original state. The topological states were characterized by invariants, known as Chern numbers, of 1 and 2. (For more on Chern numbers, see the article by Joseph Avron, Daniel Osadchy, and Ruedi Seiler, *PHYSICS TODAY*, August 2003, page 38.) The correlated states occurred whenever the carrier density supplied an integer number of carriers, from one to four, for each moiré unit cell (the larger hexagons in figure 1). Those densities correspond to filling each of the four valence and four conduction bands; the eight bands arise from lifting the valley and spin degeneracies.

Efetov and Lu also found a ferromagnetic state, similar to one observed previously by David Goldhaber-Gordon of Stanford University.⁶ With the application of an external magnetic field, monolayer graphene and magic-angle bilayer graphene exhibit the Hall effect. The conventional Hall resistance varies linearly with the magnetic field, but some materi-

als show a hysteresis loop from the anomalous quantum Hall effect, which indicates magnetization of the material. After the application of a large enough field—3.6 T—magic-angle graphene shows a combination of conventional and anomalous Hall effects and thus has an induced magnetic state. Most magnetic states arise from the spin of the charge carriers, but twisted bilayer graphene's magnetism is from the orbital angular momentum.

The outstanding question is, what are the mechanisms behind all the superconducting and correlated states? Electron-electron interactions can't account for all of them. Electron-phonon interactions could explain magic-angle graphene's superconductivity, but its proximity to correlated insulating states suggests a more exotic pairing mechanism. Efetov plans to shed light on the correlation mechanisms by investigating how the varied states' behaviors change due to the dielectric environment around magic-angle graphene. If a change in the surrounding dielectric function kills the superconducting state but not the correlated insulating states, they arise from different mechanisms. Says Efetov, "There will be a lot of surprises in the next year."

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