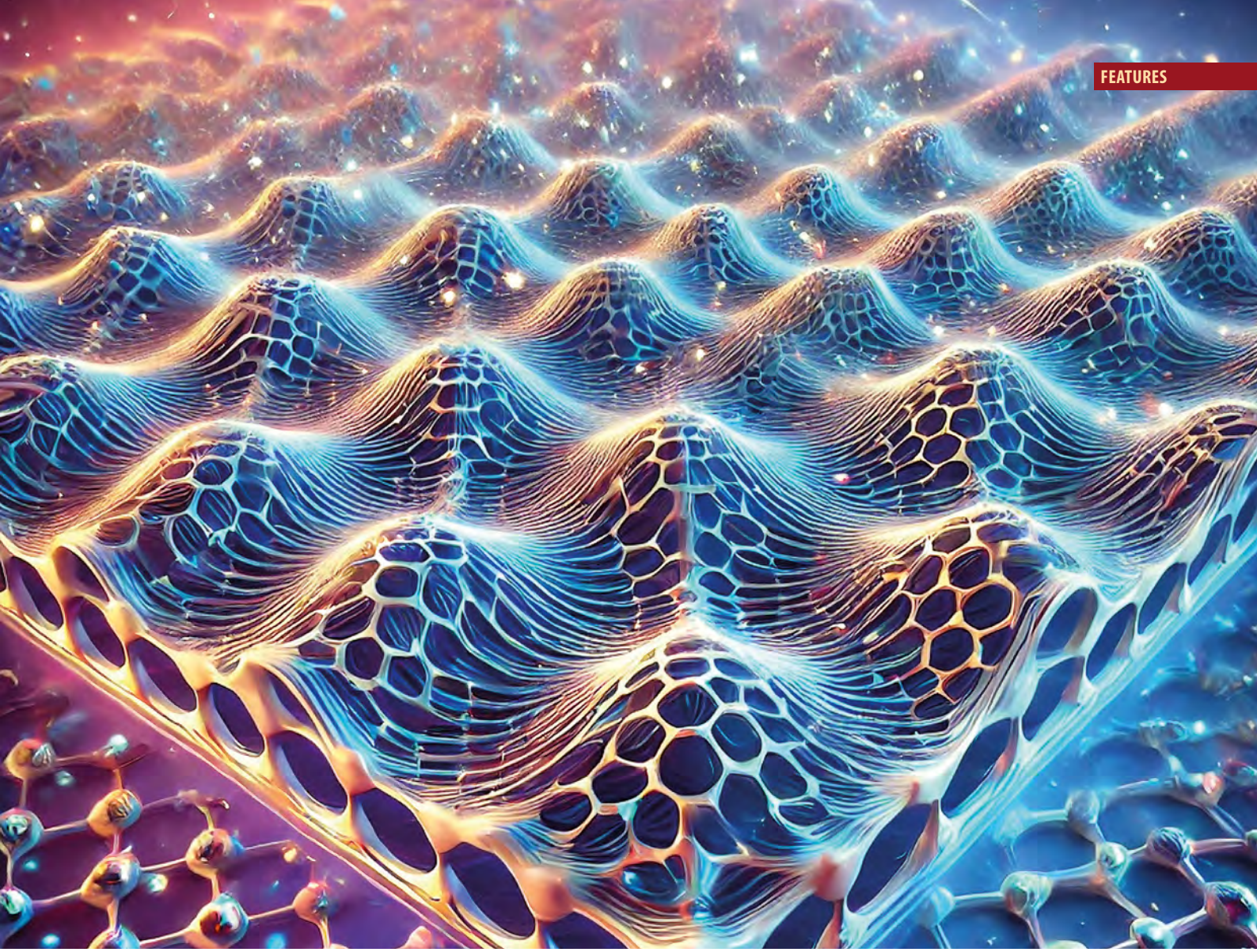

TWISTED 2D MATERIALS – A NEW ERA IN CONDENSED MATTER PHYSICS

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Atomically thin crystals have changed our understanding of materials. With all their atoms exposed at the surface, it has become possible to tune their properties without altering their chemical composition, by means such as strain, electric-fields, or substrate engineering, resulting in new states of matter [1,2].

Starting with the isolation of graphene from graphite by a Manchester University team,[1] the family of 2D materials has grown to include dozens of experimentally viable crystals, with thousands more predicted theoretically. It has given birth to an industry specializing in the manufacture of graphene and other 2D materials. Some advertisers even tout Graphene as the successor to the Stone, Bronze, and Silicon ages (Fig. 1).

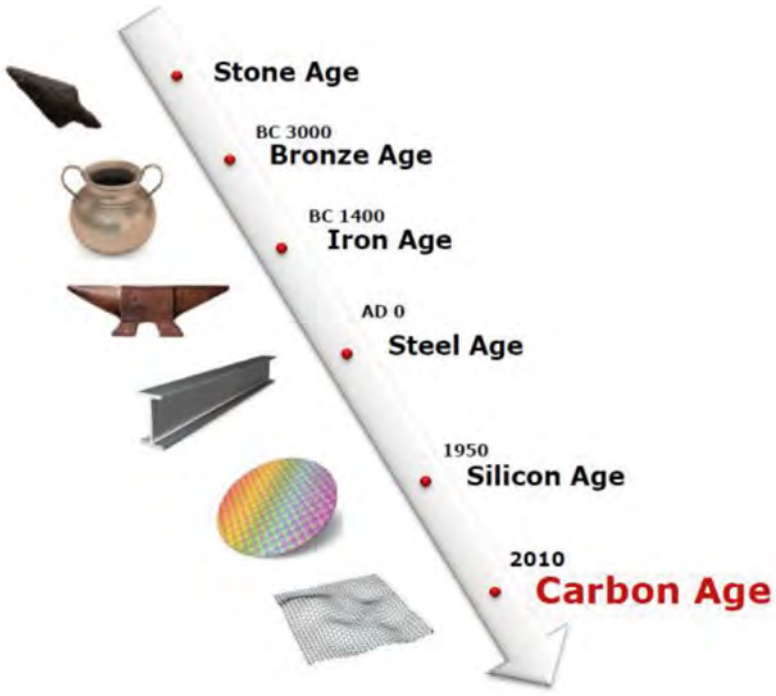
Bilayers offer even more exploration opportunities by using the twist between the layers as a new experimental tuning knob. In 2009, a Rutgers University team using scanning tunneling microscopy (STM) and spectroscopy (STS) discovered the emergence of novel electronic properties induced by moiré patterns in twisted bilayer graphene (TBG).[3] By measuring the twist-angle dependence the team observed the formation of a flat band at a twist-angle of ~1°, later dubbed the "magic" angle. Flat bands, characterized by a divergent density-of-states (DoS), are highly desirable because they are precursors of correlation induced quantum phases such as charge-density waves or superconductivity. They often possess non-trivial topology that is inherited by the correlated phases, protecting them from environmental disturbances. The discovery of a flat band in TBG laid the foundation for the field known as twistronics, or Moiré Materials, sparking a wave of research and innovation that continues to shape our understanding of condensed-matter physics.

Here, I focus on the experimental discoveries and technical breakthroughs that motivated and enabled the research into twisted 2D materials.

2D challenge

Graphene was invented long before it was discovered. First postulated in 1947 by P.R. Wallace as a theoretical construct to calculate the band structure of graphite, this model of a 2D Carbon crystal arranged in a honeycomb lattice revealed the ultra-relativistic Dirac dispersion of the charge-carriers with a V-shaped DoS that vanishes at the Dirac-point. Wallace's graphene model was used in various theoretical contexts, including as a condensed-matter realization of an anomaly, and as a platform for a Quantum Hall Effect (QHE) without a magnetic field also known as the Quantum-Anomalous-Hall effect (QAHE). However, no one imagined that it would be possible one day to create a material realization of this model. This skepticism stemmed from the Mermin–Wagner theorem which was loosely interpreted to mean that long-range-order, and in particular crystals, cannot exist in 2D. Under its influence experimentalists shied away from trying to realize 2D materials, delaying the discovery by decades. Against this backdrop, the isolation of graphene by mechanical-exfoliation from graphite came as a huge surprise. This breakthrough soon led to the observation of the anomalous integer QHE confirming the Dirac nature of charge carriers in graphene.[4,5] However, despite the readily observed QHE, attempts to delve deeper into the Dirac nature of graphene's charge carriers hit a road block.

The challenge to accessing graphene's intrinsic electronic properties was later clarified through the use of STM and single electron transistors. These local probes revealed that graphene, owing to its 2D nature, is extremely sensitive to random potential fluctuations which obscure its intrinsic properties. Therefore, to accurately probe graphene, it became essential to protect it from invasive environmental and substrate-induced disturbances.



▾ FIG. 1: Graphene Platform Corporation's advertisement of their graphene products.

Graphene on Graphite

A minimally invasive substrate must be atomically flat with a uniform surface potential. Graphite meets these criteria and, as an electrical conductor, screens potential fluctuations while remaining accessible to STM/STS studies. However, since graphene is a layer of graphite, its electronic-properties would match those of the parent graphite crystal, unless it is electronically decoupled from it. To overcome this challenge Rutgers researchers partially exfoliated graphite leaving an electronically decoupled graphene layer on the surface, thus providing the cleanest laboratory for accessing its properties by STM/STS. Using this technique, they demonstrated the V-shaped DoS of graphene's Dirac electrons, and its vanishing at the Dirac-point (Figure 2 top-left). Additionally, by applying a magnetic field, they observed the Landau level sequence which followed the square-root dependence on field, characteristic of Dirac-electrons (Figure 2 top-right). The direct observation of a Landau-level sequence was made possible by graphene's 2D nature providing direct STM/STS access to its charge carriers. Prior to these experiments, the existence of Landau-levels could only be inferred indirectly from measurements of the QHE or optical transitions observed in semiconductor heterostructures where the 2D electrons are buried deep beneath the surface.

Suspended graphene

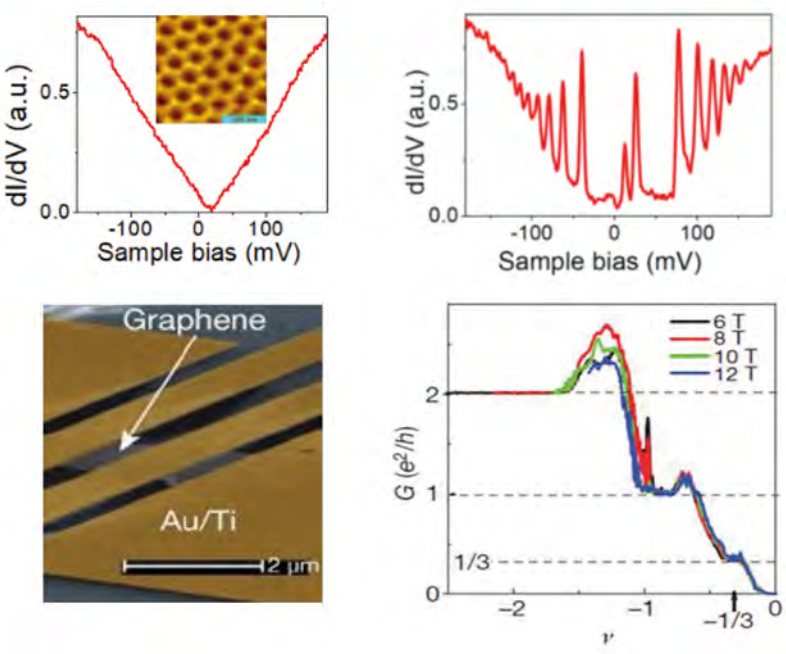
Although graphite serves as an excellent substrate for STM/STS studies, its conductive nature interferes with transport measurements, and also prevents tuning the Fermi-level by gating. To address this challenge, groups from Rutgers and Columbia developed techniques to isolate mechanically exfoliated graphene samples from their substrate by suspending them from electrical leads. This resulted in dramatically improved transport properties, achieving record-high mobility and the observation of ballistic transport.

The high mobility of suspended graphene devices suggested that they might exhibit the fractional QHE (FQHE), a crucial test for establishing the presence and strength of correlations in 2D electron-systems. However, skeptics questioned this hypothesis, as it was widely believed that interactions in graphene would be negligibly small. Indeed, despite the high mobility, efforts to observe the FQHE using the standard Hall bar geometry were unsuccessful, validating the skeptics' concerns. Surprisingly, these devices even failed to exhibit precise integer QHE plateaus.

As it turned out, the absence of the FQHE did not stem from weak interactions, but rather from the use of a Hall bar measurement configuration. The Rutgers team found that the very small size of the suspended samples, which was necessary for ensuring mechanical and structural integrity, caused the leads to short out the Hall voltage. They further demonstrated that this problem could be circumvented in a two-terminal lead geometry (Figure 2 middle-left). This enabled the observation of both precise integer QHE and FQHE plateaus in suspended graphene devices (Figure 2 middle-right).[6] By using the two-terminal technique other groups were soon able to report FQHE in suspended devices.[7] Contrary to expectations, they found that the FQHE in graphene is much more robust than in semiconductor heterojunctions. This showed that, far from following trivial single-particle physics, electrons in graphene are strongly interacting signaling their potential to form intriguing quantum-phases.

Twisted bilayer graphene

While suspended mechanically-exfoliated graphene devices enabled the discovery of the FQHE, they were too small and fragile for STM probes. Further progress required larger and more robust suspended samples. This was achieved in 2009 by using CVD (chemical-vapor-deposition) graphene suspended on transmission-electron microscope (TEM) grid. The CVD graphene sample. grown at MIT, was transferred onto the TEM grid at Manchester, and subsequently probed by STM/STS at Rutgers.



▲ **FIG. 2:** Probing electronic properties of graphene and TBG.
Top: STM/STS of graphene on graphite Left - STS shows the "V shaped" DoS. Inset: - Atomic resolution topography (scale bar 500pm). Right - STS at 4.2K and 4T shows Landau level sequence (G. Li *et al.*, PRL 102, 176804, 2009).
Bottom: FQHE in suspended graphene. Left: SEM micrograph of 2-terminal device. Right: Conductance versus filling factor measured at 1.2K, shows a FQHE plateau at v=1/3 and integer QHE plateaus at v=1, 2. (X. Du *et al.*, Nature 462, 192,2009).

This sample, comprising large 50μm diameter suspended regions accessible by STM, revealed the moiré patterns of TBG regions spanning a wide range of twist-angles. A systematic STM/STS study of the twist-angle dependence of both the topography and the DoS, showed that the twist not only generated intricate moiré patterns but that, surprisingly, it also had a dramatic effect on the electronic-properties. They showed that the twist introduced saddle points in the band structure resulting in two van Hove singularities (VHS) observed as peaks in the DoS. The gap between the two peaks decreased with decreasing twist-angle until, at an angle of ~1.1°, they merged to form a flat band (Figure 3 bottom-left). The appearance of a gap at the Fermi level within the flat band, together with the concomitant formation of a charge density wave, gave a first indication of an emergent correlated state in TBG (Figure 3 bottom-right).

In these early experiments the TBG samples were suspended on a metallic grid in a cryostat with base temperature of 4.2K. This precluded tuning the Fermi level by gating as well as reaching lower temperatures. To make further progress it was necessary to support samples on a non-invasive insulating substrate, to devise ways to precisely control the twist-angle, and to attain lower temperatures. These were tall orders at the time, but researchers soon rose to the challenge.

The hBN substrates thus made it possible to access graphene's electronic properties in gateable non-suspended device configurations, that were fabricated using well-tried techniques developed for semiconductor research. These devices could be mounted and probed in standard transport cryostats providing access to ultra-low temperatures and high magnetic-fields.

Technical breakthroughs

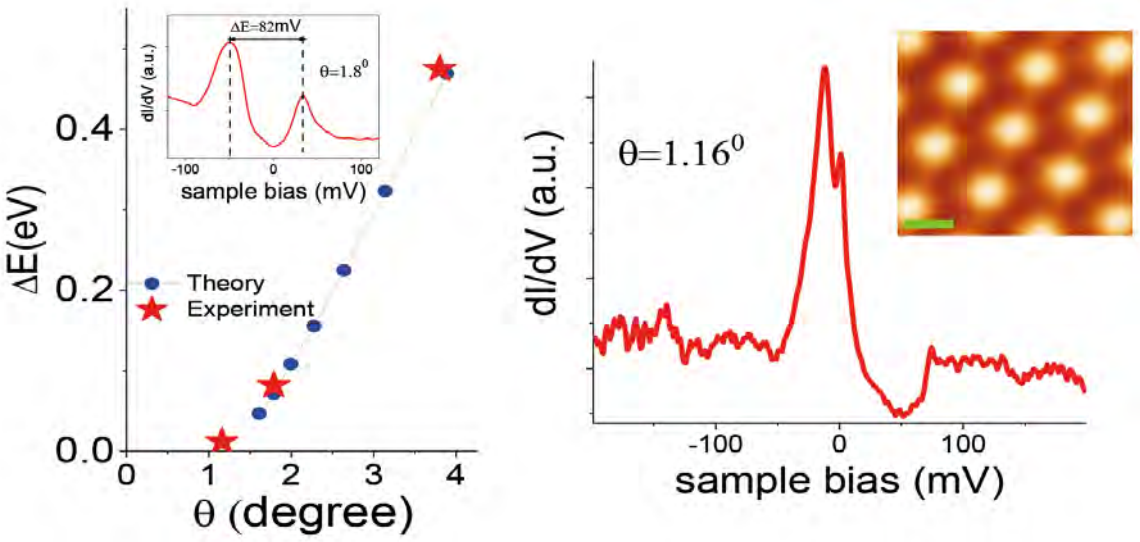
In 2010 a Columbia-University team used a hexagonal Boron Nitride (hBN) crystal, grown by researchers from NIMS Japan, as a substrate to support graphene in a Hall bar device [8]. They found that these atomically-smooth electrically-insulating and cleavable hBN crystals reduced random potential fluctuations, leading to a 3-fold increased mobility compared to the prevalent SiO_2 substrates. By encapsulating graphene in hBN and employing a non-invasive edge-contact method to fabricate a Hall bar measurement-configuration, they observed the FQHE. The hBN substrates thus made it possible to access graphene's electronic properties in gateable non-suspended device configurations, that were fabricated using well-tried techniques developed for semiconductor research. These devices could be mounted and probed in standard transport cryostats providing access to ultra-low temperatures and high magnetic-fields. The ability to tune the Fermi level and displacement-fields by gating in these devices, enabled the search for long-sought correlation induced phase-transitions. Following this technical breakthrough, hBN has become the substrate of choice for most 2D devices.

While the use of hBN substrates gave a tremendous boost to graphene research, it did not extend to TBG. Although TBG obtained from CVD graphene showed a flat band and intriguing evidence of correlated behavior, the inability to control the twist-angle, hindered further progress. This changed in 2016 when researchers from UT Austin and University of Arizona invented the tear-and-stack technique for precise twist-angle control.[9] This advance completed the creation of a twistronics toolbox, popularizing 2D materials research by opening it up to standard techniques including optics, transport and local probes.

TBG superconductivity

A significant breakthrough came in 2018, when researchers at MIT used hBN encapsulation and the tear-and-stack method to fabricate a magic-angle TBG field-effect transistor. [10,11] Upon cooling the sample to ultralow temperatures they observed the onset of superconductivity and correlated insulating phases. Surprisingly, they found that even though superconductivity in TBG only sets in at very low temperatures, its electronic properties closely mimicked those of high-temperature superconductors, raising hopes of gaining new insights into this decades-old mystery. These findings highlighted the potential of twisted 2D materials as a platform for exploring strongly correlated-electron-systems, unleashing a wave of intense research.

▼ **FIG. 3: Twist angle dependence, Van Hove singularities , and Flat band in TBG. Left: Energy separation between vHS. Inset: STS spectrum at θ=1.80. Right: STS spectrum at θ=1.160 shows the flat band . Insert: Topography at θ=1.160 shows moiré period of 13nm. (Scale bar 8nm). (G. Li *et al.*, *Nature Physics* 6, 109 (2010).**



Recent developments

The ability to utilize the twist degree-of-freedom for creating flat-bands and inducing quantum phases inspired many researchers to join the field, bringing a diverse range of expertise. This influx of talent led to the discovery of superconductivity in other twisted 2D materials, including WSe_2, rhombohedral graphene, and trilayer graphene.

The recognition that twist-induced flat bands are not accidental, but rather stem from the inherent quantum-geometry of the wave-functions, has unveiled intriguing connections between quantum-phases and the wave-function topology of twisted 2D materials.[12] These connections have resurfaced in the recent discoveries of the integer and fractional QAHE in twisted $MoTe_2$ and in pentalayer graphene.[13,14]

The rapid pace of discoveries in twisted 2D materials suggests that we are only beginning to explore their vast potential. To unlock their deeper secrets, much work lies ahead, starting with the development of methods to identify the most promising materials and techniques to precisely engineer flat bands with tunable bandwidths and Chern numbers. Considering their rich history, we can expect more discoveries and surprises from moiré materials research. ■

About the author

Eva Y. Andrei is a Board of Governors professor in the department of Physics at Rutgers University. Andrei, the recipient of the 2023 Dresselhaus prize in Nanoscience and Nanomaterials, is recognized for her experimental work on low-dimensional electron systems and the discovery of twisted bilayer graphene.

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