

TEN YEARS OF NATURE PHYSICS

The ABC of 2D materials

When do structures comprising a few crystalline sheets become truly two dimensional? The number of layers certainly plays a role, but in trilayer graphene, the way they're stacked matters too — as shown in a series of *Nature Physics* papers from 2011.

Alberto F. Morpurgo

Two-dimensional (2D) materials, consisting of a limited number of crystalline layers of atomic thickness, display electronic properties that differ drastically from those of their bulk parent compounds. Research on 2D materials, which took off just over a decade ago with the isolation of graphene, has resulted in remarkable discoveries. Yet many important questions remain to be answered. One such question is: below what thickness can we consider a thin crystal to be a 2D material? In 2011, a trio of *Nature Physics* papers^{1–3} touched on this issue by exploring the behaviour of trilayer graphene and showing that not only the thickness, but also the way the layers are stacked, is crucial in determining the stack's electronic properties.

Generally, whether a crystal of a given thickness can be considered a 2D material may depend on the specific compound and on the physical phenomenon considered. As different compounds are thinned down, significant qualitative changes in their electronic properties can occur at thicknesses of tens of monolayers. Although exploring the evolution of the electronic properties of materials with decreasing thickness has certainly resulted in unexpected findings, when exactly a thin crystal should be considered a 2D material may be a matter of debate — or of definition. The case of graphene illustrates this very well.

It has long been known that graphene monolayers are zero-gap semiconductors with low-energy electrons behaving as linearly dispersing massless Dirac fermions. They are chiral, because their wave function has two components — a property known as pseudospin — and the direction of the pseudospin is pinned to the electron momentum⁴. From the very beginning, however, graphene bilayers were classed as physically distinct 2D systems⁵: zero-gap semiconductors with low-energy chiral electrons, but with quadratic rather than linear low-energy dispersion. This difference has important consequences in different contexts⁴. Additionally, the band structure of a bilayer can be tuned electrostatically, meaning that the application

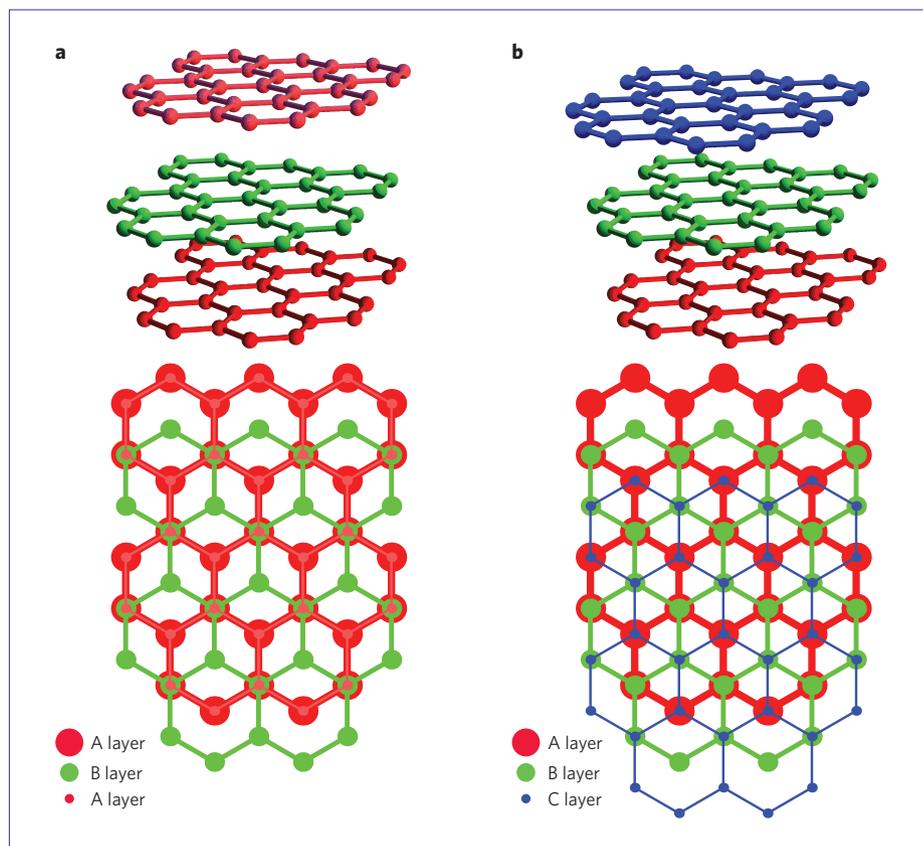


Figure 1 | Different ways of stacking three graphene layers. **a,b**, In a single graphene layer, carbon atoms are arranged on a honeycomb lattice. The most energetically stable stack of two graphene layers (AB) has the second layer shifted over the length of one carbon–carbon bond with respect to the first layer. When adding a third layer, this shift can be ‘undone’, resulting in ABA trilayer graphene (**a**), or ‘repeated’ to yield ABC trilayer graphene (**b**). The electronic properties of these two variants are qualitatively different, as demonstrated experimentally in 2011 (refs 1–3).

of a perpendicular electric field opens a gap between valence and conduction bands, and transforms charge-neutral bilayers into insulators⁶.

What about thicker graphene multilayers: are there new phenomena emerging that justify considering these systems as distinct 2D materials? Research on thicker well-characterized multilayers has been limited, and most of the work has focused on trilayer structures. Trilayers are the thinnest graphene multilayers for which different

crystalline stackings are found in nature. The most common stacking — also found in natural graphite crystals — is the so-called Bernal, or ABA configuration (Fig. 1a). In certain graphite crystals, however, domains with ABC stacking (Fig. 1b) are often present as structural defects. Exfoliation of these crystals therefore enables ABC-stacked trilayers to be isolated and used to design electronic devices.

In 2011, three groups^{1–3} reported experiments demonstrating that

ABC-stacked trilayers are distinct from all other graphene multilayers. Low-energy electrons in ABC-trilayers had been predicted to be chiral and to exhibit a dispersion that is neither linear (like in monolayers) nor quadratic (like in bilayers), but cubic. This prediction was confirmed by measurements of the quantization sequence of the Hall conductance¹. Whereas in ABA-stacked trilayers the application of a perpendicular electric field increases the overlap between valence and conduction bands, and enhances the conductivity⁷, in ABC trilayers it opens a bandgap at charge neutrality, similar to the case of bilayers. A field-induced gap was indeed observed experimentally, the measured magnitude of which matched theoretical expectations². Finally, whereas electron–electron interactions do not affect the electronic properties of ABA-stacked trilayers, in ABC-stacked trilayers they generate a gapped insulating state near charge neutrality, detectable in suspended devices. This gapped state is similar to that observed in bilayer graphene, but the phenomenon is much more pronounced and seems to be more robust, because the larger density of states associated with the cubically dispersing band enhances interaction effects³.

Besides demonstrating that ABC-stacked trilayer graphene is a unique 2D material, these experiments indicate that thicker multilayers (or even bulk crystals) with ABC-like stacking are interesting systems for all thicknesses. According to theory, they have an even larger density of states at the charge neutrality point, making the occurrence of new broken-symmetry states very likely, and they have different symmetry

properties compared with ABA-stacked trilayers. Unfortunately, however, graphite crystals with ABC-like stacking have never been grown, which prevents the experimental study of thicker ABC multilayers.

Luckily, we are not limited to fantasizing about hypothetical systems: apart from graphene, many other layered compounds that have been (re-)discovered in the context of 2D materials provide a seemingly unlimited playground. For some of these compounds, crystals with stacking equivalent to both ABA and ABC can be grown, and the comparison with graphene can be instructive. An example is MoS₂. Like graphene, MoS₂ monolayers feature a honeycomb lattice — formed by Mo atoms and S₂ units rather than carbon atoms — and possess two valleys (regions in momentum space hosting the low-energy electronic states related by time-reversal symmetry). In the bulk, two of the existing MoS₂ crystalline structures, 2H and 3R, correspond to stacked monolayers following, respectively, the ABA and ABC patterns observed in graphene. 2H- and 3R-MoS₂ multilayers have similar band structure; however, because of their different symmetry upon spatial inversion, their response under illumination is drastically different. In 3R-MoS₂, but not in 2H-MoS₂, multilayers of all thicknesses exhibit a valley-selective coupling to circularly polarized light, which enables electrons in different valleys to be addressed separately⁸. Interestingly, analogies between different 2D materials work both ways and — as 3R-MoS₂ crystals can be grown — we should think again whether ‘ABC-graphite’ crystals are really impossible to grow.

In principle, thicker multilayers are also likely to lead to new surprises and there is no reason to stop at trilayers. But in practice, extremely high device quality is often essential to reveal experimentally new phenomena in ‘thick 2D materials’. A recent study of tetralayer graphene based on ultraclean suspended devices, for example, has given strong indications for the existence of an unexpected effect of electron–electron interactions pertaining to the parity of the number of layers. Close to charge neutrality, this effect can turn even-numbered Bernal-stacked multilayers into insulators⁹. What is surprising is that the insulating state is more pronounced in tetralayers than in bilayers, indicating that the effect does not die out with increasing thickness, and prompting again the old question of how the properties of bulk graphite emerge from those of graphene upon increasing thickness. □

Alberto F. Morpurgo is in the Department of Quantum Matter Physics and the Group of Applied Physics at the University of Geneva, CH-1211 Geneva, Switzerland.
e-mail: Alberto.Morpurgo@unige.ch

References

- Zhang, L., Zhang, Y., Camacho, J., Khodas, M. & Zaliznyak, I. *Nature Phys.* **7**, 953–957 (2011).
- Lui, C. H., Li, Z., Mak, K. F., Cappelluti, E. & Heinz, T. F. *Nature Phys.* **7**, 944–947 (2011).
- Bao, W. *et al.* *Nature Phys.* **7**, 948–952 (2011).
- Castro Neto, A. H., Guinea, F., Peres, N. M. R., Novoselov, K. S. & Geim, A. K. *Rev. Mod. Phys.* **81**, 109–162 (2009).
- Novoselov, K. S. *et al.* *Nature Phys.* **2**, 177–180 (2006).
- Oostinga, J. B., Heersche, H. B., Liu, X., Morpurgo, A. F. & Vandersypen, L. M. K. *Nature Mater.* **7**, 151–157 (2008).
- Craciun, M. F. *et al.* *Nature Nanotech.* **4**, 383–388 (2009).
- Suzuki, R. *et al.* *Nature Nanotech.* **9**, 611–617 (2014).
- Grushina, A. L. *et al.* *Nature Commun.* **6**, 6419 (2015).

GRAVITY

Wanna be quantum

Superpositions of massive objects would be hard to spot on Earth even in well-isolated environments because of the decoherence induced by gravitational time dilation.

Angelo Bassi

Who wouldn't like to experience a quantum life? We could do many things in parallel: working, playing, doing sports, having a meal and sleeping. All at the same time — at least as long as no one is watching us. We could instantly teleport ourselves far away when annoyed with a situation. Many childhood dreams would come true. However, it seems we are bound to be classical; not a boring life, but less exciting than a quantum one. A

much-debated question among physicists is: why so? In the end, we are made of atoms, which are quantum. But their most amazing quantum properties do not survive when they combine to form macroscopic objects. Why so?

Writing in *Nature Physics* Igor Pikovski and colleagues¹ argue that Earth's gravitational field causes any delocalized state of a quantum system to decohere and lose its quantum properties — even if the system is

isolated from the rest of the world. And this effect seems strong enough to be significant for objects on human scales. The new element is that this decoherence is triggered by time dilation — one of the striking predictions of general relativity. Here is how it goes.

Every experimentalist trying to measure quantum delocalization of material systems (the situation in which a quantum system is in a superposition of two different locations at the same time) faces the same