

Thomas Heine

Two-dimensional materials – A ROMANCE in four dimensions

What is a two-dimensional (2D) material in a three (or higher) dimensional universe? In abstract mathematics, the definition of a dimensionality of 2 is obvious, but what about nature? Things are different in 2D. 2D objects in a 3D world are different. This has been known for a long time (except for members of the flat earth society – yes, it does exist indeed!) and even impacts on a possible 2D society entered belletristic literature [1]. But how about the hard sciences, chemistry, physics? Landau and Peierls doubted the existence of 2D crystals at temperatures above 0K [2, 3]. The statement “A very similar argument rules out the existence of long-range crystalline ordering in one or two dimensions, without making the harmonic approximation.” also known as the Mermin-Wagner theorem, was published in 1966 [4, 5]. Obviously, chemical bond stretching typically is taking less energy than bond compression. Hence, in a thermal motion, it costs less energy if the atoms of a compressed bond escape to the third dimension. Nonetheless, atom/molecule-thick crystals have been reported, first “dünnste Kohlenstoff-Folien” by Boehm and colleagues [6], later MoS₂ by Frindt [7, 8]. How does this compare with the theoretical predictions of Landau, Peierls, Mermin and Wagner? In fact, these 2D crystals are not really 2D. They ripple at finite temperature, as evidenced for graphene [9, 10] and also for MoS₂ [11], thus keeping theoretical physics considerations and materials science in harmony.

Those early works did not attract much attention, as despite the beautiful demonstration that atom/molecule-thick materials can be prepared in the laboratory, there was little reason to research or to apply them in a purposeful manner. The breakthrough of 2D crystals was in 2004, when Novoselov, Geim and others published their famous “pencil science” paper [12] that eventually led to the Nobel prize in 2010. The attention was well-deserved, as despite making atomically-thin carbon layers that are stable in ambient environment, the authors also showed that the electronic properties of a crystalline monolayer exfoliated from graphite significantly differs from those of the layered bulk. This so-called proximity effect was entirely unexpected – why should the weak London dispersion interaction between two saturated layers make a difference in electronic structure? The surprise was not restricted to graphene, also MoS₂ monolayers (and most other transition-metal dichalcogenides (TMDCs)) show strong differences between single layer and bulk: An indirect-to-direct band

gap transition gives a strongly enhanced photoluminescence signal for single-layer MoS₂ [13], and the electronic mobility is significantly higher than in the bulk, allowing for the construction of field-effect transistors [14]. Besides, TMDC monolayers lack inversion symmetry, contrary to bilayers or their 2H bulk counterparts, which results in a giant spin-orbit splitting in these materials [15]. There are numerous other examples that demonstrate that 2D crystal properties can significantly differ from their bulk structure [16]. Today, comprehensive libraries of stable 2D crystals have been established using high-throughput modelling and are readily available in online data repositories [17, 18].

Simulation and experiment of these 2D crystals base on flat layers. They typically are made flat – experimentalists use a substrate for this purpose, which makes them, strictly speaking, surfaces, where the arguments of Lifshitz, Peierls, Mermin and Wagner opposing the existence of 2D crystals do not apply. Yet, albeit being a surface heterostructure, apparently the electronic properties of surface-supported monolayers are in most cases indeed close to those of the atomically flat 2D crystals [19]. This is appreciated by the theorists, who can put the 2D systems in small periodic cells, much smaller than the rippling lengths of the free-standing natural material.

In 3D space, two-dimensionality is difficult to define. When is a material to be considered 2D? Is it the thickness? Then when should we consider it to be truly two-dimensional? If it is atomically thin as graphene or hexagonal boron nitride? What if the atoms are somewhat corrugated, as in phosphorene or silicene? Are covalently bound 2D crystals, where a monolayer is made of several atomic planes, as for example TMDCs or any other exfoliated monolayer of a van der Waals crystal, truly two-dimensional? In a discussion with Hans-Peter Steinrück and Xinliang Feng an interesting suggestion for a definition came up: 2D crystals have translational symmetry in two-dimensions, but not in the 3rd one. This definition was adopted to TU Dresden’s collaborative research center “Chemistry of synthetic 2D materials”, CRC 1415 funded by Deutsche Forschungsgemeinschaft. The definition nicely works for free-standing and deposited monolayers, but also for few layers and for stacks of materials where the material does not crystallize in the third dimension. This is the case for 2D polymers and covalent-organic frameworks, where molecular building blocks are stitched together to form strong covalent bonds [20–22]. Here, even in the layered bulk, translational invariance in the stacking direction is broken, limiting the sharpness of the powder X-ray diffractograms [23]. These 2D materials can be realized in virtually any 2D lattice symmetry. While early 2D COFs and 2D polymers did not have conjugated molecular orbitals and hence pronounced semiconductor properties with dispersed electronic

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bands, the introduction of conjugation by suitable coupling reactions changed this picture [24]. Indeed, also for these materials, based on well-defined molecular building blocks, the crystal symmetry determines the electronic properties [25], which has been recently demonstrated on honeycomb-kagome lattices, where the honeycomb-imposed Dirac cone has been experimentally demonstrated using angle-resolved photoelectron spectroscopy [26], confirming earlier theoretical predictions [27].

Thus, with graphene, hexagonal boron nitride, inorganic 2D crystals, including TMDCs and others, and synthetic 2D materials, such as 2D COFs and 2D polymers, an immense variety of 2D crystals are available and ready for our use. They include semiconductors, 2D metals, Dirac semimetals, superconductors, trivial and topological insulators. Chemical functionality can be incorporated using defects or functional groups. As if this is not interesting enough, a new world of 2D materials is just starting to thrill us. A bilayer 2D crystal already can have significantly different properties compared to the respective monolayer. In bilayers, a band gap opens in graphene, group 6 TMDCs become indirect band gap semiconductors without spin-orbit gap [28], and some noble-metal dichalcogenides can become metallic [29]. It really gets interesting if the layers are twisted with respect to each other, forming a Moiré superlattice [30]. First, these investigations were mainly of theoretical interest, as the Moiré patterns create minibands which can form, for example, Hofstadter's butterfly [31]. The breakthrough was achieved when the emergence of a flat band has been discovered for twisted bilayer graphene at a specific twist angle of 1.05° , first theoretically [32] and later in experiment, where the half-filled flat band gave rise to superconductivity [33]. An interesting special case of twisted bilayer graphene appears at a twist angle of exactly 30° , as it gives a 2D quasi crystal [34]. Moiré patterns also emerge in other bilayer 2D crystals, e.g., in MoS_2 . Here, for small twist angles, a strong lattice reconstruction leads to the formation of large low-energy domains, which form a hexagonal pattern with alternating symmetries between adjacent domains. The resulting superlattice is predicted to give a Dirac band at the top of the valence band [35] (see Figure 1). Thus, in twisted bilayers, without the breaking or formation of a chemical bond, materials characteristics can change drastically. Controlling the electronic structure using a superlattice can be a new way of controlling material's properties, which can also work in the 4th dimension – time: in a smart setup, the twist angle of graphene bilayers can be controlled dynamically using the tip of an atomic force microscopy [36].

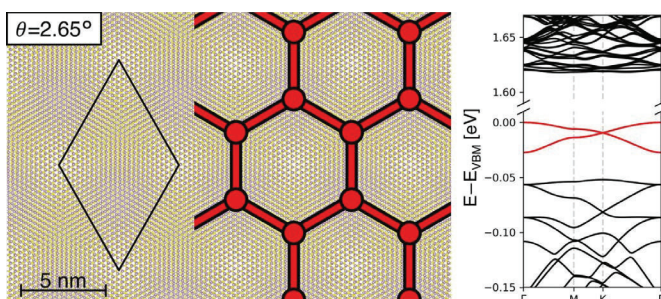


Fig. 1: Representation of a superlattice (red) in a twisted bilayer MoS_2 structure. The twist angle is 2.65° . The moiré cell, shown in black, comprises 2814 atoms. In the resulting band structure (right), the honeycomb super lattice imposes a Dirac cone at about 15 meV below the Fermi level. Idea taken from ref. [35]. Copyright: Florian Arnold, TUD.

Superlattices are not restricted to bilayers of the same crystal. Due to the lattice mismatch, heterostructures of different 2D crystals show Moiré patterns even without twist. These structures are currently being explored world-wide, including in Germany, where more than 30 groups investigate their properties in Priority Program “2D materials: the physics of 2D van der Waals [hetero]structures”, supported by Deutsche Forschungsgemeinschaft (DFG SPP 2244).

This short survey did not discuss many application-oriented aspects of 2D materials, such as nanoelectronics beyond silicon, transistors operating with very low power by using interlayer excitons as charge carriers, atom-thin membranes to transfer protons or filter hydrogen isotopes, and many others. The number of potential applications of 2D crystals increases day by day, and first consumer products made with them are currently entering the market. But besides, 2D crystals offer a huge scientific playground for the implementation of new quasiparticles, magnetism, multiferroics, topological properties, and exotic states of matter.

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Thomas Heine was undecided what to study – in 1989 computers came up and he was fascinated by the possibility to predict structure and properties of molecules theoretically. For that time he made the right choice – and studied physics (TU Clausthal), did his PhD in physics (1999, TU Dresden), but in the meantime worked in Theoretical Chemistry workgroups (Montréal, Canada, 1997, Exeter, UK, 1998-1999). His *venia legendi* in Physical Chemistry he obtained in 2006 at TU Dresden, after postdoctoral stages in Bologna and Geneva. In 2008, he started his research group as Associate Professor at Jacobs University Bremen, where he was promoted to Full Professor in 2011. After being the Chair of Theoretical Chemistry at Leipzig University from 2015-2018 he moved to his current position at TU Dresden. His research interest is located at the interface of chemistry and physics and focuses on the computational science of nanostructured materials, in particular of two-dimensional crystals and molecular framework materials. Prof. Heine is a highly cited author with more than 300 peer-reviewed articles, an h-index of 87 (ISI)/96 (Google Scholar). He gave more than 100 invited talks at international workshops and conferences. He is elected member of the Review Board of Deutsche Forschungsgemeinschaft (DFG) and fellow of the Royal Society of Chemistry and the Academia Europaea. He coordinates the DFG Priority Program PP 2244 “2D Materials: Physics of van der Waals [hetero]structures”, is deputy speaker of DFG CRC 1415 “Chemistry of Synthetic 2D Materials” at TU Dresden and coordinates the Marie S. Curie European Training Network “2Exciting”.