Graphene: Status and Prospects

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Graphene is a wonder material with many superlatives to its name. It is the thinnest known material in the universe and the strongest ever measured. Its charge carriers exhibit giant intrinsic mobility, have zero effective mass, and can travel for micrometers without scattering at room temperature. Graphene can sustain current densities six orders of magnitude higher than that of copper, shows record thermal conductivity and stiffness, is impermeable to gases, and reconciles such conflicting qualities as brittleness and ductility. Electron transport in graphene is described by a Dirac-like equation, which allows the investigation of relativistic quantum phenomena in a one-dimensional (low-D) crystals (3). One-dimensional crystals and nanometer-sized crystallites (Fig. 1) are to be trusted, the amount of literature on graphene will keep rapidly increasing over the next few years. This makes it a real struggle to keep up with the developments. Newcomers are left without a broad perspective and are largely unaware of previous arguments and solved problems, whereas the community’s doyens already show signs of forgetting their earlier papers. To combat this curse of success, many reviews have appeared in the last 2 years [e.g., (2)], and books on graphene are in the making. The electronic properties of graphene were recently discussed in an extensive theory review (3), and this basic information is unlikely to require any revision soon. More specialized papers discussing such topics as the quantum Hall effect in graphene, its Raman properties, and epitaxial growth on SiC are collected in (4). Despite, or perhaps because of, the vast amount of available literature, graphene research has now reached the stage where a strategic update is needed to cover the latest progress, emerging trends, and opening opportunities. This paper is intended to serve this purpose without repeating, whenever possible, the information available in the earlier reviews.

Growing Opportunities

Graphene is a single atomic plane of graphite, which—and this is essential—sufficiently isolated from its environment to be considered free-standing. Atomic planes are, of course, familiar to everyone as constituents of bulk crystals, but one-atom-thick materials such as graphene remained unknown. The basic reason for this is that nature strictly forbids the growth of low-dimensional (low-D) crystals (2). Crystal growth implies high temperatures (7) and, therefore, thermal fluctuations that are detrimental for the stability of macroscopic 1D and 2D objects. One can grow flat molecules and nanometer-sized crystallites, but as their lateral size increases, the phonon density integrated over the 3D space available for thermal vibrations rapidly grows, diverging on a macroscopic scale. This forces 2D crystallites to morph into a variety of stable 3D structures.

The impossibility of growing 2D crystals does not actually mean that they cannot be made artificially. With hindsight, this seems trivial. Indeed, one can grow a monolayer inside or on top of another crystal (as an inherent part of a 3D system) and then remove the bulk at sufficiently low T such that thermal fluctuations are unable to break atomic bonds even in macroscopic 2D crystals and mold them into 3D shapes.

This consideration allows two principal routes for making 2D crystals (Fig. 1). One is to mechanically split strongly layered materials such as graphite into individual atomic planes (Fig. 1A). This is how graphene was first isolated and studied. Although delicate and time-consuming, the handcraft (often referred to as a Scotch-tape technique) provides crystals of high structural and electronic quality, which can currently reach millimeter size. It is likely to remain the technique of choice for basic research and for making proof-of-concept devices in the foreseeable future. Instead of cleaving graphene manually, it is also possible to automate the process by using, for example, ultrasonic cleavage (5). This leads to stable suspensions of submicrometer graphene crystallites (Fig. 1B), which can then be used to make polycrystalline films and composite materials (5, 6). Conceptually similar is the ultrasonic cleavage of chemically “loosened” graphite, in which atomic planes are partially detached first by intercalation, making the sonification more efficient (6). The sonification allows graphene production on an industrial scale.

The alternative route is to start with graphite layers grown epitaxially on top of other crystals (7) (Fig. 1C). This is the 3D growth during which epitaxial layers remain bound to the underlying substrate and the bond-breaking fluctuations are suppressed. After the epitaxial structure is cooled down, one can remove the substrate by chemical etching. Technically, this is similar to making, for example, SiN membranes; however, the survival of one-atom-thick crystals was deemed impossible, and no one tried this route until recently (8–10). The isolation of epitaxial monolayers and their transfer onto weakly binding substrates (2) may

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Fig. 1. Making graphene. (A) Large graphene crystal prepared on an oxidized Si wafer by the Scotch-tape technique. [Courtesy of Graphene Industries Ltd.] (B) Left panel: Suspension of microcrystals obtained by ultrasonic cleavage of graphite in chloroform. Right panel: Such suspensions can be printed on various substrates. The resulting films are robust and remain highly conductive even if folded. [Courtesy of R. Nair, University of Manchester] (C) The first graphene wafers are now available as polycrystalline one- to five-layer films grown on Ni and transferred onto a Si wafer, [Courtesy of A. Reina and J. Kong, MIT] (D) State-of-the-art SiC wafer with atomic terraces covered by a graphitic monolayer (indicated by “1”). Double and triple layers (“2” and “3”) grow at the steps (12).
now seem obvious, but it was realized only last year (9, 10).

With progress continuing apace, the production of graphene wafers looks like a done deal. Imagine the following technology: Let us start with a tungsten (011) wafer of many inches in diameter and epitaxially grow a thin Ni (111) film on top (11). This is to be followed by chemical vapor deposition of a carbon monolayer (the growth of graphene on Ni can be self-terminating with little lattice mismatch) (7, 11). In this manner, wafer-scale single crystals of graphene (chemically bound to Ni) have been grown on Ni (11). A polymer or another film can then be deposited on top, and Ni is etched away as a sacrificial layer, leaving a graphene monolayer on an insulating substrate and the expensive W wafer ready for another round. The full cycle has not yet been demonstrated and will probably differ from the gedanken one outlined above (e.g., Cu can be used instead of Ni). Nonetheless, wafers of continuous few-layer graphene have already been grown on polycrystalline Ni films and transferred onto plastic and Si wafers (9, 10) (Fig. 1C). These films exhibit carrier mobility $\mu$ of up to 4000 cm$^2$ V$^{-1}$ s$^{-1}$ (10)—close to that of cleaved graphene—even before the substrate material, growth, and transfer procedures have been optimized.

Where does this leave graphitic layers grown on SiC (4, 12) (Fig. 1D)? These have been considered as a champion route to graphene wafers for electronics applications, mostly because SiC automatically provides an insulating substrate. First of all, one must distinguish between two principally different types of “graphene on SiC.” One consists of single and double layers grown on the Si-terminated face, and the other is “multilayer epitaxial graphene” that rapidly grows on the carbon face (4, 12). In the former case, carbon layers are bound to the substrate sufficiently weakly to retain graphene’s linear spectrum away ($\approx 0.2$ eV) from the charge neutrality point (NP) (13). However, interaction with the substrate induces strong doping ($\approx 10^{13}$ cm$^{-2}$) and spectral disorder at low energies (13, 14) for a possible model for the complex graphene-SiC interface. The crystal quality and coverage homogeneity for the Si-face films have recently improved (12), and $\mu$ values start approaching those for graphene transferred from Ni. As for the carbon face, its epitaxial multilayers probably should be referred to as turbostratic graphene because they are rotationally disordered (no Bernal stacking) and separated by a distance slightly larger than that in graphite (4, 15). Turbostratic graphene exhibits the Dirac-like spectrum of free-standing graphene, little doping, and exceptionally high electronic quality ($\mu \approx 250,000$ cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature) (15). These features can be attributed to weak electronic coupling between inner layers; their protection from the environment by a few outer layers; and the absence of microscopic corrugations (2, 8).

Because an external electric field is screened within just a couple of near-surface layers, turbostratic graphene probably offers limited potential for electronics but is interesting from other perspectives, especially for fundamental studies close to NP. Whichever way one now looks at the prospects for graphene production in bulk and wafer-scale quantities, those challenges that looked so daunting just 2 years ago have suddenly shrunk, if not evaporated, thanks to the recent advances in growth, transfer, and cleavage techniques.

Quantum Update

The most explored aspect of graphene physics is its electronic properties. Despite being recently reviewed (2–4), this subarea is so important that it necessitates a short update. From the most general perspective, several features make graphene’s electronic properties unique and different from those of any other known condensed matter system. The first and most discussed is, of course, graphene’s electronic spectrum. Electrons propagating through the honeycomb lattice completely lose their effective mass, which results in quasi-particles that are described by a Dirac-like equation rather than the Schrödinger equation (2–4). The latter—so successful for the understanding of quantum properties of other materials—does not work for graphene’s charge carriers with zero rest mass. Figure 2 provides a visual summary of how much our quantum playgrounds have expanded since the experimental discovery of graphene. Second, electron waves in graphene propagate within a layer that is only one atom thick, which makes them accessible and amenable to various scanning probes, as well as sensitive to the proximity of other materials such as high-$\kappa$ dielectrics, superconductors, ferromagnetics, etc. This feature offers many enticing possibilities in comparison with the conventional 2D electronic systems (2DES).

Third, graphene exhibits an astonishing electronic quality. Its electrons can cover submicrometer distances without scattering, even in samples placed on an atomically rough substrate, covered with adsorbates and at room temperature. Fourth, as a result of the massless carriers and little scattering, quantum effects in graphene are robust and can survive even at room temperature. The initial studies of graphene’s electronic properties were focused on the analysis of what new physics could be gained by using the Dirac equation within the standard condensed matter formalism (2–4). This “recycling” of quantum electrodynamics for the case of graphene has quickly led to the understanding of the half-integer quantum Hall effect and the predictions of such phenomena as Klein tunneling, zitterbewegung, the Schwinger production (16), supercritical atomic collapse (3, 17), and Casimir-like interactions between adsorbates on graphene (18). As for experiment, only the Klein tunneling has been verified in sufficient detail (19, 20). Furthermore, transport properties of real graphene devices have turned out to be much more complicated than theoretical quantum electrodynamics, and some basic questions about graphene’s electronic properties still remain to be answered. For example, there is no consensus about the scattering mechanism that currently limits $\mu$, little understanding of transport properties near NP (especially on zero Landau level (21)), and no evidence for many predicted interaction effects.
In the near term, much of this research will continue being driven by our knowledge of other low-D systems and by the “recycling” of the known issues and phenomena. Graphene-based quantum dots (22, 23), p-n junctions (19, 20), nanoribbons (23–25), quantum point contacts (22), and, especially, magnetotransport near NP have not received even a fraction of the attention they deserve. Also, it is easy to foresee the revisiting of lateral superlattices, magnetic focusing, electron optics, and many interference and ballistic effects studied previously in the conventional 2DES (26), which hopefully can either be more spectacular in graphene or clarify its physics. Among other usual suspects are electro- and magneto-optics, where graphene offers many unexplored opportunities.

Graphene is structurally malleable, and its electronic, optical, and phonon properties can be strongly modified by strain and deformation (27). For example, strain allows one to create local gauge fields (3) and even alter graphene’s band structure. Research on bended, folded, and scrolled graphene is also gearing up. Furthermore, graphene and turbostratic graphene offer a dream playground for scanning probe microscopy, and many experiments can be constructed for observing supercritical screening, detecting local magnetic moments, mapping wave functions in quantizing fields, etc. Further down the line are interaction effects in split bilayers; observing such effects would be experimentally challenging but may bring up physics even more spectacular than that in the other 2DES (28). On the frontier of exploration is the fractional quantum Hall effect, whose possibility has already been tormenting graphene researchers who occasionally observe plateau-like features at fractional fillings, only to find them irreproducible for different devices.

The above sketchy agenda may take many years to complete, and the speed of developments will crucially depend on progress in growing wafers and improvements in sample quality. Inch-size wafers with μ values in the range of 1 million can no longer be dismissed as “graphene dreams,” and when this happens, many-body phenomena and new physics that cannot even be envisaged at this stage are likely to emerge.

Chemistry Matters

Graphene is an ultimate incarnation of the surface: It has two faces with no bulk in between. Although this surface’s physics is currently at the center of attention, its chemistry has remained largely unexplored. What we have so far learned about graphene chemistry is that, similar to the surface of graphite, graphene can adsorb and desorb various atoms and molecules (for example, NO2, NH3, K, and OH). Weakly attached adsorbates often act as donors or acceptors and lead to changes mostly in the carrier concentration, so that graphene remains highly conducting (29). Other adsorbates such as H+ or OH- give rise to localized (“mid-gap”) states close to NP, which results in poorly conductive derivatives such as graphene oxide (6) and “single-sided graphene” (30). Despite the new names, these are not new chemical compounds but are the same graphene randomly decorated with adsorbates. Thermal annealing or chemical treatment allows the reduction of graphene to its original state with relatively few defects left behind (30). This reversible dressing up and down is possible because of the robust atomic scaffold that remains intact during chemical reactions.

Within this surface science perspective, graphene chemistry looks similar to that of graphite, and the latter can be used for guidance. There are principal differences too. First, chemically induced changes in graphene’s properties are much more pronounced because of the absence of an obscuring contribution from the bulk (29). Second, unlike graphite’s sur-

Similar to the case of graphite, which is well known for its surface superstructures. Instead of doping with atomic hydrogen (as in graphene), F-, OH-, and many functional groups appear to be viable candidates in the search for novel graphene-based 2D crystals.

Graphene chemistry is likely to play an increasingly important role in future developments. For example, stoichiometric derivatives offer a way to control the electronic structure, which is of interest for many applications including electronics. Chemical changes can probably be induced even locally. Imagine, then, an all-graphene circuitry in which interconnects are made from pristine graphene, whereas other areas are modified to become semiconducting and allow transistors. Disordered graphene-based derivatives should not be overlooked either. They can probably be referred to as functionalized graphene, suitable for specific applications. “Graphene paper” is a spectacular example of how important such functionalization could be (Fig. 3). If it is made starting with a suspension of nonfunctionalized flakes (5), the resulting material is porous and extremely fragile. However, the same paper made of graphene oxide is dense, stiff, and strong (6, 32). In the latter case, the functional groups bind individual sheets together, which results in a microscopic structure not dissimilar to that of nacre, known for its strength. Instead of aragonite bound in nacre by biopolymer glue, graphene oxide laminate, in particular its reduced version (32), makes use of atomic-scale stitching of the strongest known nanomaterial.

Despite a cornucopia of possible findings and applications, graphene chemistry has so far attracted little interest from professional chemists. One reason is that graphene is neither a standard surface nor a standard molecule. However, the main obstacle has probably been the lack of samples suitable for traditional chemistry. The recent progress in making graphene suspensions (5, 6) has opened up a way to liquid-phase chemistry, and hopefully, the professional help that graphene researchers have long been waiting for is now coming.

Sleeping Beauty

It is customary these days to start reports on graphene by referring to it as a “unique electronic system.” This statement belittles what graphene is actually about. 2DES and even Dirac-like quasi-particles were known before, but one-atom-thick materials were not. In this respect, graphene has founded a league of its own, but little is known about its non-electronic properties. The situation is now rapidly changing, and this brings beautiful new dimensions into graphene research.

Last year, the first measurements of graphene’s mechanical and thermal properties were reported. It exhibits a breaking strength of ~40 N/m, reaching the theoretical limit (33). Record values for room-temperature thermal conductivity (~5000 W m⁻¹ K⁻¹) (34) and Young’s modulus (~1.0 TPa) (33) were also reported. Graphene can be stretched elastically
by as much as 20%, more than any other crystal (27, 33). These observations were partially expected on the basis of previous studies of carbon nanotubes and graphite, which are structurally made of graphene sheets. Somewhat higher values observed in graphene can be attributed to the virtual absence of crystal defects in samples obtained by micromechanical cleavage. Even more intriguing are those findings that have no analogs. For example, unlike any other material, graphene shrinks with increasing $T$ at all values of $T$ because membrane phonons dominate in 2D (35). Also, graphene exhibits simultaneously high pliability (folds and pleats are commonly observed) and brittleness [it fractures like glass at high strains (36)]. The notions constitute an oxymoron, but graphene combines both properties. Equally unprecedented is the observation that the one-atom-thick film is impermeable to gases, including helium (37). When wafers become available, there should be an explosion of interest in (bio)molecular and ion transport through graphene and its membranes with designer pores.

Speaking of non-electronic properties, we do not even know such basic things about graphene as how it melts. Neither the melting temperature nor the order of the phase transition is known. Ultrathin films are known to exhibit melting temperatures that rapidly decrease with decreasing thickness. The thermodynamics of 2D crystals in a 3D space could be very different from that of thin films and may more closely resemble the physics of soft membranes. For example, melting can occur through generation of defect pairs and be dependent on the lateral size, similar to the Kosterlitz-Thouless transition. Experimental progress in studying graphene’s thermodynamic properties has been hindered by the small sizes of available crystals, but the situation may change soon. On the other hand, theoretical progress is likely to remain slow because small sizes have also proven to be a problem in molecular dynamics and other numerical approaches, which struggle to grasp the underlying physics when studying crystals of only a few nanometers in size.

**Grandeur and Plainness**

Potential applications of graphene were discussed in (2) and, during the past 2 years, substantial progress has been made along many lines. The major difference between now and then is the advent of mass production technologies for graphene. This has changed the whole landscape by making the subject of applications less speculative and allowing the development of new concepts unimaginable earlier.

Most of the current buzz surrounds graphene’s long-term prospects in computer electronics. Immediate, but often mundane, applications are least discussed and remain unnoticed even within parts of the graphene community. An extreme example of popular speculations is an idea about graphene becoming the base electronic material “beyond the Si age.” Although this possibility cannot be ruled out, it is so far beyond the horizon that it cannot be assessed accurately. At the very least, graphene-based integrated circuits require the conducting channel to be completely closed in the off state. Several schemes have been proposed to deal with graphene’s gapless spectrum and, recently, nanoribbon transistors with large on-off current ratios at room temperature were demonstrated (22, 25) (Fig. 4A). Nonetheless, the prospect of “graphenium inside” remains as distant as ever. This is not because of graphene shortfalls, but rather because experimental tools to define structures with atomic precision are lacking. More efforts in this direction are needed, but the progress is expected to be painstakingly slow and to depend on technological developments outside the research area.

An example to the contrary is the use of graphene in transmission electron microscopy (TEM). It is a tiny niche application, but it is real. Single-crystal membranes, one atom thick and with low atomic mass, provide the best imaginable support for atomic-resolution TEM. With micrometer-sized crystallites now available in solution (5) for their cheap and easy deposition on standard grids and with films transferable from metals (9, 10) onto such grids, graphene membranes are destined to become a routine TEM accessory (Fig. 4D).

The space between graphene dreams and immediate reality is packed with applications. One such application is neither grand nor mundane: individual ultrahigh-frequency analog transistors (Fig. 4B). This area is currently dominated by GaAs-based devices known as high-electron-mobility transistors (HEMTs), which are widely used in communication technologies. graphene offers a possibility to extend HEMTs’ operational range into terahertz frequencies. The fundamentals allowing this are well known: graphene exhibits room-temperature ballistic transport such that the charge transit between source and drain contacts takes only 0.1 ps for a typical channel length of 100 nm. Gate electrodes can be placed as close as several nanometers above graphene, which allows shorter channels and even quicker transit. Although graphene’s gapless spectrum leads to low on-off ratios of 10 to 100, they are...
considered sufficient for the analog electronics. The progress toward graphene HEMTs is hindered by experimental difficulties in accessing the microwave range. The first frequency tests of graphene transistors were reported only recently (38). Long channels and low mobility in these experiments limited the cutoff frequencies to less than 30 GHz (38), well below the operational range of GaAs-based HEMTs. However, the observed scaling of the operational frequency as a function of the channel length and μ indicates that the terahertz range is accessible (38). With graphene wafers in sight, these efforts are going to intensify, and HEMTs and other ultrahigh-frequency devices such as switches and rectifiers have a realistic chance to reach the market.

**Sitting on a Graphene Mine**

There has been an explosion of ideas that suggest graphene for virtually every feasible use. This is often led by analogies with carbon nanotubes that continue to serve as a guide in searching for new applications. For example, graphene powder is considered to be excellent filler for composite materials (6). Reports have also been made on graphene-based supercapacitors, batteries, interconnects, and field emitters, but it is too early to say whether graphene is able to compete with the other materials, including nanotubes. Less expectedly, graphene has emerged as a viable candidate for use in optoelectronics (10, 39). Suspensions offer an inexpensive way to make graphene-based coatings by spinning or printing (Fig. 1B). An alternative is the transfer of films grown on Ni (9, 10). These coatings are often suggested as a competitor for indium tin oxide (ITO), the industry standard in such products as solar cells, liquid crystal displays, etc. However, graphene films exhibit resistivity of several hundred ohms for the standard transparency of ~80% (9, 10, 39). Such resistivity is two orders of magnitude higher than for ITO and is unacceptable in many applications (e.g., solar cells). It remains to be seen whether the conductivity can be improved to the required extent. Having said that, graphene coatings also offer certain advantages over ITO. They are chemically stable, robust, and flexible and can even be folded, which gives them a good chance of beating the competition in touch screens and bendable applications.

There is also fast-growing interest in graphene as a base material for nanoelectromechanical systems (NEMS) (32, 40), given that lightness and stiffness are the essential characteristics sought in NEMS for sensing applications. Graphene-based resonators offer low inertial masses, ultrahigh frequencies, and, in comparison with nanotubes, low-resistance contacts that are essential for matching the impedance of external circuits. Graphene membranes have so far shown quality factors of ~100 at 100-MHz frequencies (40). Even more encouraging are data for drum resonators made from reduced graphene oxide films (32). These nanometer-thick polycrystalline NEMS (Fig. 4C) exhibit high Young’s moduli (comparable to those of graphene) and quality factors of ~4000 at room temperature. The films can be produced as wafers and then processed by standard microfabrication techniques. Further developments (increasing the frequency and improving quality factors) should allow graphene NEMS to assail such tantalizing challenges as inertial sensing of individual atoms and the detection of zero-point oscillations.

Among other applications that require mentioning are labs-on-chips (electronic noses) and various resistive memories. The high sensitivity of graphene to its chemical environment is well acknowledged, now that sensors capable of detecting individual gas molecules have been demonstrated (29). Imagine an array of graphene devices, each functionalized differently to be able to react to different chemicals or biomolecules. Such functionalization has been intensively researched for the case of carbon nanotubes, and graphene adds the possibility of mass-produced arrays of identical devices. Furthermore, there are several enticing reports on nonvolatile memories in which graphene-based wires undergo reversible resistance switching by, for example, applying a sequence of current pulses (41, 42). The underlying mechanism remains largely unknown, but such nanometer-scale switches present an attractive alternative to phase-change memories and deserve further attention. Reports on graphene–ferroelectric memories (43) are also encouraging, given the basic simplicity of their operation.

**More Room in the Flatland**

Graphene has rapidly changed its status from being an unexpected and sometimes unwelcome newcomer to a rising star and to a reigning champion. The professional skepticism that initially dominated the attitude of many researchers with respect to graphene applications is gradually evaporating under the pressure of recent developments. Still, it is the wealth of new physics—observed, expected, and hoped for—that is driving the arena for the moment. Research on graphene’s electronic properties is now mature but is unlikely to start fading any time soon, especially because of the virtually unexplored opportunity to control quantum transport by strain engineering and various structural modifications. Even after that, graphene will continue to stand out in the arsenal of condensed matter physics. Research on graphene’s non-electronic properties is just gearing up, and this should bring up new phenomena that may well sustain, if not expand, the graphene boom.