MATERIAL WITNESS

The materials of history

Although it would be too much to say that the history of materials technology has been largely an amateur pursuit of scientists, it hasn't enjoyed much support from professional historians. Yet the sophistication of some of the field's pioneers, despite lacking any formal grounding in the study of history, is remarkable.

Take the English metallurgist Cyril Stanley Smith, who worked on fissionable metals for the Manhattan Project before making reconstructions of ancient metallurgical techniques and translations of historical crafts manuscripts. With a fluent command of Latin, Smith was a member of both the humanities and metallurgy departments at MIT, and his translation, with John Hawthorne, of the treatise *On Divers Arts* by the twelfth-century Benedictine monk Theophilus remains a central reference on medieval craft methods. (Smith benefited perhaps from marriage to an eminent historian of science, Alice Kimball Smith.)

Then there is Trevor Williams, a chemist at the British chemicals company ICI, who was managing editor of the magisterial five-volume *History of Technology* in the 1950s. And the pre-eminent historian of chemistry in the twentieth century, James Partington, was a chemist who worked for a time with Walther Nernst.

That the history of materials culture has tended to rely on scientists rather than historians obviously has its pitfalls, for not all such enthusiasts acquire the historical nous of a Smith or a Partington. As archaeologist Marcos Martinón-Torres of University College London points out in a recent collection of papers on early modern chemistry (L. M. Principe (ed.) *Chymists and Chymistry* Science History Publications, 2007), "Many of the pioneer historians of alchemy and chemistry were chemists with an interest in the past. Most conducted outstanding work but, due to a lack of education as professional historians, sometimes committed oversights or anachronisms."

But Martinón-Torres goes on to say that today the tables are being turned: the study of chemical and materials history tends to focus on texts while "ignoring the fundamentals of chemistry and materials science." Martinón-Torres's own work illustrates what we risk losing with such neglect — his scientific analysis of the renowned crucibles of Hesse used by chemists in early modern Europe shows that they were made from mullerite, a refractory aluminium silicate that was not formally discovered until the twentieth century (M. Martinón-Torres *et al. Nature* **444,** 437; 2006).

A disjuncture between historians working from text and image, and scientists and archaeologists using quantitative analytical methods, is no recent complaint — in the 1980s the art historian Jan van der Meulen criticized studies of Gothic buildings for their indifference to the physical evidence. But why does this happen? It's tempting to blame the notorious fear of science in humanities departments, and there is probably some truth in that. But the wider reason is perhaps that an interest in 'materials culture', and a recognition that technologies are not only powerful forces of social and political change but also shapers of art, literature and philosophy, have not yet reached as far as they might.

Philip Ball

GRAPHENE

Buckle or break

The isolation of free-standing graphene sheets seems to contradict common belief about the existence of two-dimensional crystals. Monte Carlo simulations confirm that the sheets may be stabilized by the formation of finite-sized ripples.

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Can two-dimensional crystals exist in our three-dimensional world? This question has been the topic of a number of theoretical studies in the past. Mermin and Wagner concluded that, because the periodic order of the atoms cannot be maintained in an infinite two-dimensional crystal, such crystals may not exist[1,2]. Similarly, elasticity theory has predicted that two-dimensional membranes are unstable at finite temperatures (>0 K), such that large membranes, in particular, suffer severe buckling[3,4].

In contrast to these predictions are recent observations of individual layers derived from layered materials such as BN, MoS_2 and graphite[5]. The exfoliation of single graphene layers from graphite[6] has particularly given new life to our initial question. Graphene is a prime example of a two-dimensional crystal, as it is a single layer of carbon atoms and the building block of graphite and carbon nanotubes. The carbon atoms in a graphene sheet are depicted ideally as a flat hexagonal lattice, exactly one atomic layer thick, contrary to the predictions by Mermin and Wagner. Whether a graphene sheet is completely flat or not, however, has been difficult to prove experimentally because it may crumple, like a piece of paper, if not treated carefully. Experimental

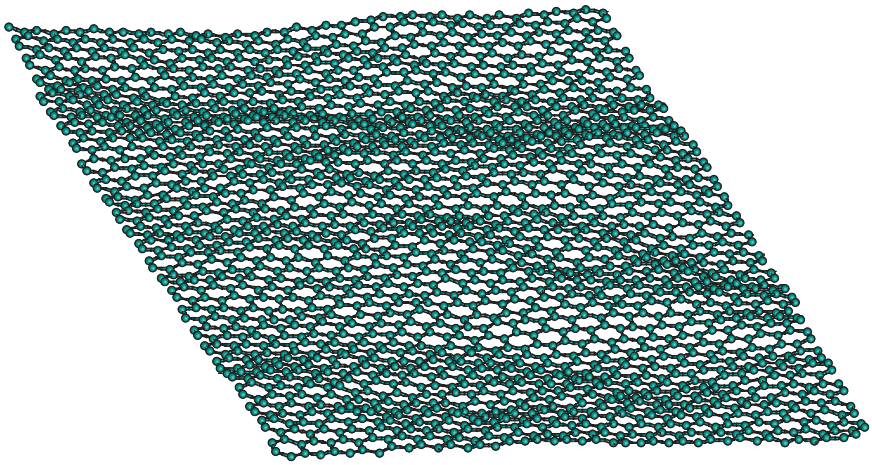

Figure 1 Section of a graphene sheet showing ripples of a finite size as obtained by Monte Carlo simulations.

reports that a free-hanging graphene sheet is buckled rather than flat[7] are therefore debated.

On page 858 of this issue, however, Fasolino *et al.* provide strong theoretical support for the experimental observations of ripples in graphene[8]. The researchers have performed large-scale Monte Carlo simulations to determine the equilibrium structure of an infinite single graphene sheet over a range of temperatures. The sheet spontaneously forms ripples with a characteristic wavelength as shown in Fig. 1, indicating that the ripples observed experimentally may not be an artefact but an intrinsic property.

To understand the origin of the ripples, the environment of the carbon atoms in graphene must be considered. Unlike a three-dimensional crystal, in graphene the carbon atoms do not have neighbouring atoms above or below the sheet, so there are no restoring forces from atoms in adjacent layers. The restoring forces perpendicular to the sheet are limited to the out-of-plane component of the forces between neighbouring atoms due to the bending of the sheet. These forces are much weaker than those along the bonds, such that the perpendicular vibrational modes are much softer than the in-plane modes. Thermal motion can then easily move the carbon atoms out of the plane, which could destroy the order in the graphene sheet even at very low temperature. To estimate the impact of these thermal fluctuations, the graphene sheet can be compared to a continuous membrane. Elasticity theory shows that there is a strain energy connected with the perpendicular displacements, because there is a coupling between bending and stretching of the membrane[9]. This strain energy limits the perpendicular displacements and keeps a finite membrane together. However, the membrane may become buckled at finite temperature as this is the most favourable way of diminishing the amplitude of the soft perpendicular vibrations. The connection between the vibration frequencies and the buckling can be understood by comparing a flat membrane to a nanotube. The acoustic vibration mode perpendicular to the membrane corresponds to the vibration of a nanotube in the radial direction. In smaller nanotubes with larger curvature, the tube is stiffer perpendicular to the wall and the frequency of the vibrations is higher. The membrane, in a similar way, becomes stiffer due to the buckling, which increases the frequency of the perpendicular vibrational modes.

The amplitude of the buckling, however, increases with the size of the membrane, because the restoring strain energy for a given deflection perpendicular to the membrane decreases with system size. Therefore, only small membranes are predicted to stay approximately flat, whereas macroscopic membranes would have significant ripples and infinite membranes would break up into smaller, finite membranes as a result of the thermal vibrations[3,4].

The results of Fasolino and colleagues[8], however, show that a graphene sheet is neither a flat two-dimensional crystal nor a homogeneous and featureless membrane. Graphene instead forms spontaneous ripples with a characteristic wavelength of around 80 Å at finite temperatures (Fig. 1). These ripples stand in stark contrast to the common belief that graphene is perfectly flat. The wavelength of the ripples corresponds to about 50 carbon–carbon bond lengths and this value falls well within the limits of the experimental estimate[7]. However, the calculated amplitude of the ripples is less than 1 Å even for an infinite sheet, in contrast to the prediction from elasticity theory. The reason is that graphene has an atomic structure that can respond to the thermal fluctuations by bond-length alternations in the plane. The calculated bond lengths deviate from the ideal value of 1.42 Å that is expected for bonds between sp^2-hybridized carbon atoms, and the deviation increases with temperature. The variation should be visible at room temperature where the bond-length distribution varies from 1.3 Å, similar to the average length of a double bond, up to 1.54 Å, which is the typical length of a single bond in diamond. This bond-length variation cannot be accommodated in the layer, so a slight displacement of the carbon atoms out of the plane occurs, leading to the small buckling observed. In addition, the variation in bond length leads to an overall lattice contraction that contributes to the bending rigidity. This limits the amplitude of the out-of-plane ripples such that they are not threatening to destroy the graphene sheet.

The ripples may have an impact on the electronic properties of graphene. For example, it has been proposed that the ripples can be scattering centres[10] and limit conductivity in the plane. The wider implication of the study by Fasolino *et al.* is that two-dimensional crystals can exist in a three-dimensional world as long as they find a mechanism to limit the thermal motion of the atoms perpendicular to the crystal plane. For graphene, a buckling mechanism that originates from the flexibility of the carbon–carbon bonds provides the answer. Whether this mechanism could work for other lattices remains an open question, but these results suggest that the stability of two-dimensional crystals is not a closed topic.

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