

infrared (Fig. 2b; orange-shaded regions). Within this spectral range, hBN is also a naturally hyperbolic material, whereby optical modes with very large momenta can be confined and propagated within the sub-diffractive volume of the material<sup>11,12</sup>. As a result, optical confinement to volumes that are arbitrarily small with respect to the free-space wavelength should be feasible; in fact, 2D confinement to a 3-monolayer-thick (~1 nm) flake via s-SNOM<sup>12</sup>, and 3D confinement to volumes  $2 \times 10^5$  times smaller than the free-space wavelength using far-field measurements of hBN nanostructures<sup>11</sup>, have been demonstrated. When coupled with graphene, strong plasmon–phonon interactions are anticipated, with hybridized modes between these two materials<sup>13,14</sup>. The dispersion relationship of these hybridized surface plasmon–phonon polaritons was also theoretically predicted by Koppens and collaborators<sup>2</sup> (Fig. 2b) and independently reproduced<sup>14</sup>. Therefore, not only does hBN improve the graphene plasmons, but graphene can provide the potential for

tuning the hyperbolic polaritons in hBN via electrostatic gating<sup>14</sup>. This results in tunable behaviour that is not practical within hBN-only designs due to the extremely large bandgap of hBN.

These efforts underline the exceptional potential of van der Waals crystals<sup>15</sup> for nanophotonic and metamaterial designs. In addition to the hybridization of these polariton modes, there is still the open question of how the in- and out-of-plane vibrational modes of 2D crystals are modified when confined within such heterostructures. Since the operating frequency range for surface phonon–polaritons is defined by the corresponding frequencies of the optically active crystal vibrations (optic phonons), it begs the question whether such high-quality heterostructures can provide a pathway to realize tailored nanophotonic devices. Such approaches could also lead to further polariton hybridization effects incorporating plasmons and phonon–polaritons within other van der Waals crystals, thereby opening up an entire

toolbox for the design of mid- to far-infrared optics. □

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## ORIGAMI

# Folding creases through bending

The folding of origami structures involves bending deformations that are not explicit in the crease pattern.

Talal Al-Mulla and Markus J. Buehler

**E**mulating the principles of paper folding and translating them to the design of new materials and advanced applications can be a disciplined, rigorous career. From DNA origami to the folding of macroscopic sheets<sup>1–3</sup>, the concepts of ‘material’ and ‘structure’ fuse in objects containing hierarchical features that can span from molecular lengths to the macroscale. Yet formalizing the rules of origami for use in computer modelling and simulation has been challenging. This is because theoretical models tend to be oversimplified, often erroneously classifying a foldable origami structure as unfoldable. This is the case for the square-twist crease pattern<sup>4</sup>: whereas mathematical models predict that the structure can’t fold, a simple experiment with paper shows that this origami structure is indeed foldable (Fig. 1). Unfortunately, errors in such mathematical models are not readily apparent because the reasons of why a structure is actually

foldable cannot be reconciled with the models<sup>5</sup>. Hence, to avoid theoretical and computational shortcomings, researchers studying origami mechanics routinely need to experiment with articulate physical abstractions of origami structures. Writing in *Nature Materials*, Jesse Silverberg, Itai Cohen and colleagues now show how and why the square twist is foldable<sup>6</sup>. On the basis of the interplay of plastic and elastic deformations, they show that the difficulties do not lie in the actual folding events, but in the abstraction of the folding rules. Through an example application, the researchers show the potential of taking an origami structure, understanding its mechanics, and applying what is learned to update theoretical models and produce origami metamaterials that offer new functions.

Silverberg and co-authors found that to properly model the folding of the square-twist pattern they needed to consider two distinct modes of deformation: creasing

and facet bending (the square twist could not be folded by creasing alone). In their model, creasing is differentiated from bending in that creases represent a plastic mode of deformation, whereas bending is reversible (put simply, creases, but not the bending of facets, leave a mark on the folded paper). Indeed, folding a piece of paper entails first the formation of a fold through bending, and then the creation of a crease. Importantly, the authors show that facet bending and other such intermediate reversible steps are crucial for modelling the underlying mechanical principles of origami. As with the bending of shoelaces when tying one’s shoes, bending in paper acts as a crutch for the folding of origami, and allows for motions that would otherwise be impossible (in fact, certain origami structures, such as the square twist, cannot be made if paper were rigid).

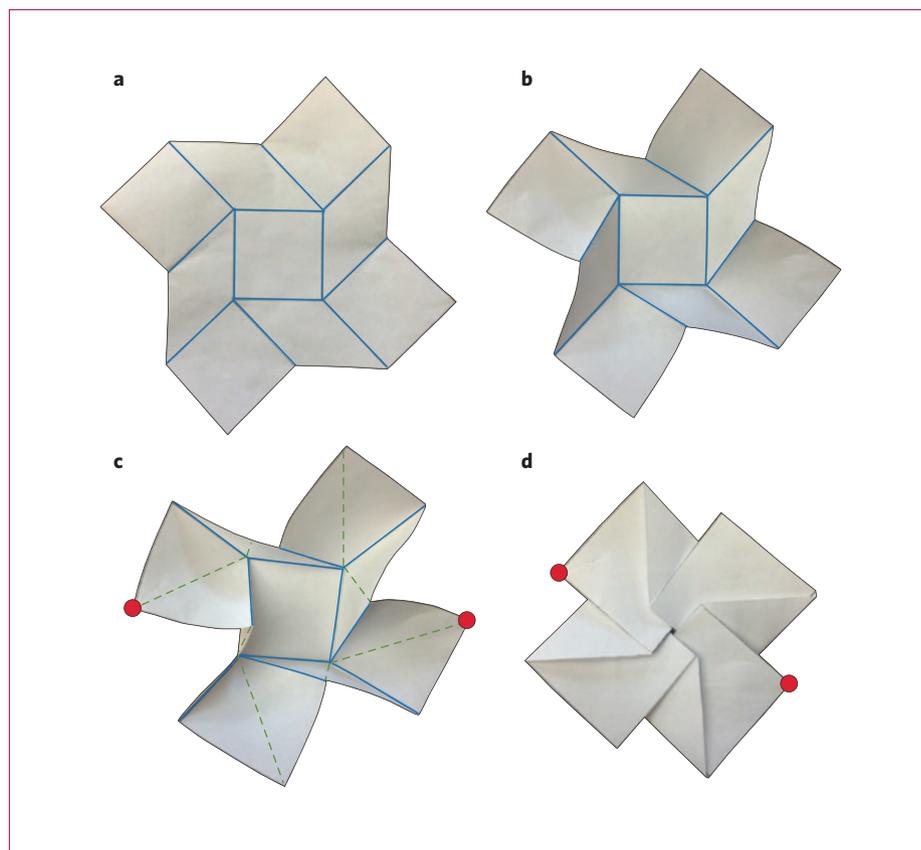
Moreover, by coupling origami rules with the inherent material properties of

hydrogels — in particular, temperature-dependent swelling — Silverberg and colleagues demonstrate that both creasing and bending play a major role in origami mechanics. The researchers fabricated a hydrogel composite with a square-twist crease pattern that could fold (the creases were actuated by temperature-induced swelling) but that did not allow for facet bending (this can be done because the composite is more rigid than paper). They found that after application of stress the composite exhibited hysteresis in the folding behaviour, and that the hysteresis could be removed by introducing additional creases where bending would otherwise occur. Silverberg and colleagues' work thus exemplifies how origami rules can be abstracted for application in other materials.

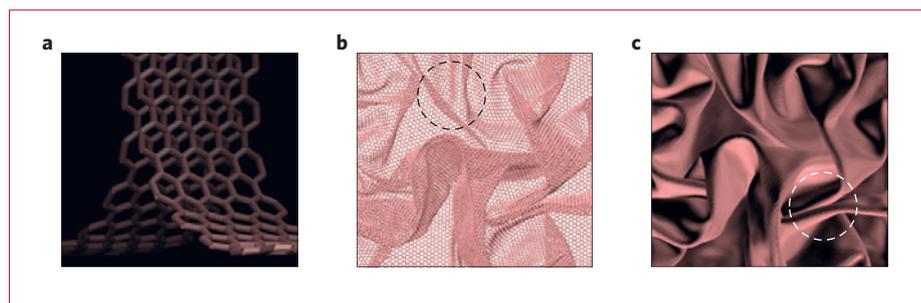
Another core finding of the work of Silverberg and collaborators is the recognition that, in the same origami building block (the square-twist pattern) and at the same length scale, there exist a hierarchy of mechanically accessible energy levels that grant access to hierarchies in structure. Such hierarchies in structure and energy can be exploited further to engineer even more hierarchical levels by incorporating additional origami building blocks, each with its own intrinsic hierarchy of energy levels. And accessibility between hierarchies may be different for different materials. For paper, it is enabled by bending; for the stiffer hydrogel composite, by the addition of extra creases.

Origami principles have already helped in DNA nanofabrication<sup>1</sup>, the design of batteries<sup>2</sup>, and the study of large-scale structural systems and even architecture<sup>3</sup>. Silverberg and colleagues' study may spur the use of origami in other materials and make origami structures more accessible to computational manipulation and optimization. For instance, origami methods could enrich computational-modelling algorithms for the design of composite materials with prescribed functional states. And hierarchies of energy levels in origami structures, which have been used in the design of beam elements<sup>7</sup>, could be used to design various types of structural unit. Moreover, the origami-inspired design of mechanical devices could potentially lead to tailored mechanisms in other systems, such as self-folding polymers<sup>8</sup>.

Furthermore, understanding and accounting for overlooked aspects of paper folding should facilitate the translation of folding mechanisms into practical applications. For instance,



**Figure 1** | Folding of the square-twist structure. **a–d**, The square twist consists of a central square connected to four rhombi that are in turn connected to adjacent rhombi by four outer squares. Although only creases (blue lines) are visible on the paper origami, bent facets lead to folds (dashed green lines) that are largely responsible for the compliance and foldability of the structure. Once creases are made, the initially un-creased structure (**a**) no longer remains flat in the absence of external forces (**b**). When compressed (by pushing the ends marked by red dots closer to each other, for example), the structure starts to fold by bending, except for its central facet (**c**), until it reaches an unbent folded configuration (**d**).



**Figure 2** | Origami with two-dimensional materials. **a–c**, Graphene and other flexible two-dimensional materials may be able to be folded analogously to paper origami. Because of its atomic scale, creases (**a**) and folds (**b**; dashed black circle) in graphene are completely reversible rather than involving plastic deformations. Graphene can also exhibit self-adhesive folds (which can lead to multilayer graphene), thus effectively creating creases that adhere to other creases (**c**, dashed white circle).

two-dimensional micro- and nanoscale materials could benefit from principles distilled from origami models. In fact, Silverberg and colleagues' material-

independent approach suggests that graphene, which can take many different conformations and shapes<sup>9</sup> owing to its high strength and flexibility<sup>10</sup> (Fig. 2),

could make elaborate nanomaterial structures. Also, the approach holds promise for algorithms not related to origami. For example, computer-aided engineering design can benefit from improved origami modelling to enable the creation of strong yet light, reconfigurable structures for applications in civil engineering<sup>11</sup>. Origami constructs with tailored hierarchical energy levels may also allow for the control of failure modes in engineering structures<sup>12</sup>. □

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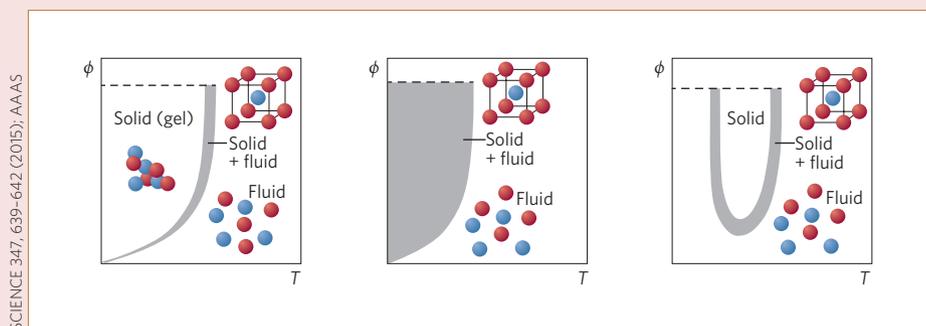
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## COLLOIDAL SELF-ASSEMBLY

# Programmable competitive binding

A much touted advantage of colloidal building blocks, in comparison to atoms and molecules, is that the interactions between them are tunable. Be it through the make-up of the solvent, or the chemistry and shape of the colloids, these can be designed to arrange into a variety of crystals (and also disordered solid structures) at suitable densities or compositions. However, designing crystal-to-crystal transitions that can be induced by varying the temperature, which is easier to control experimentally, has been much more challenging. This is because typical effective interactions between colloidal building blocks rely on attractive and repulsive forces (of entropic or electrostatic origin, for example) that are in practice independent of temperature. Hence, most phase diagrams of colloidal systems follow the archetypal topology — a fluid at high temperature and solids (crystals, often pre-empted by a glass or gel) at low temperatures.

The inherent programmability of the interactions between DNA-decorated colloids may change this situation. First, the binding force between the complementary ends of colloid-tethered DNA strands does change significantly with temperature (largely because of a loss in entropy; R. Dreyfus *et al. Phys. Rev. Lett.* **102**, 048301; 2009); second, the effective binding energy between the colloids can be adjusted by designing DNA strands that compete for binding. One such strategy involves decorating colloids with two types of DNA strand that compete for the formation of DNA bridges between colloidal particles (which promotes aggregation) or of DNA loops or hairpins on the same particle (S. Angioletti-Uberti,



B. M. Mognetti and D. Frenkel *Nature Mater.* **11**, 518–522; 2012). Because the two types of strand hybridize at different temperatures (which can be tuned by designing the sequence of the binding segments), temperature shifts the balance of the competitive binding. This strategy leads to the melting of a crystal both on heating and on cooling (also known as re-entrant melting).

Yet competing interactions can also allow for independent control of both the topology of the phase diagram and the temperature ranges in which transitions between phases occur, as recently demonstrated by W. Benjamin Rogers and Vinodhan Manoharan (*Science* **347**, 639–642; 2015). The researchers used strand displacement — a technique that employs free DNA strands to displace complementary strands in a duplex — to design the topology of the phase diagram of DNA-coated colloids. In particular, they demonstrate an arbitrarily wide temperature range for fluid–crystal coexistence, and re-entrant melting (pictured). To broaden the temperature width of the phase-coexistence region, the researchers designed the sequences of colloid-tethered and free DNA strands

so that the binding energy between tethered DNA strands and between free and tethered strands are roughly the same. To achieve re-entrant melting, they designed two types of free strand that compete for binding with colloid-tethered strands. In this case, temperature tilts the balance between the number of bound strands (which maximizes the enthalpy by disfavoring the formation of DNA bridges between colloids) and the number of unbound free strands (which increases the entropy by favouring bridge formation and thus crystallization). Using a variation of this scheme, Rogers and Manoharan also programmed a reversible temperature-induced transformation between two crystals of identical symmetry but different composition.

The versatility of strand-displacement binding reactions is of course not limited to tinkering with the topology of phase diagrams. In principle, there seems to be no obvious major impediment for similar strategies to achieve multistage self-assembly and disassembly, programmed actuation and stimuli-responsive reconfigurable systems.

PEP PÀMIES