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[11]. Origami constructs with tailored hierarchical energy levels may also allow for the control of failure modes in engineering structures[12]. ❑

Talal Al-Mulla and Markus J. Buehler are in the Laboratory for Atomistic and Molecular Mechanics (LAMM), Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Room 1-290, Cambridge, Massachusetts 02139, USA.
e-mail: mbuehler@mit.edu

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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,
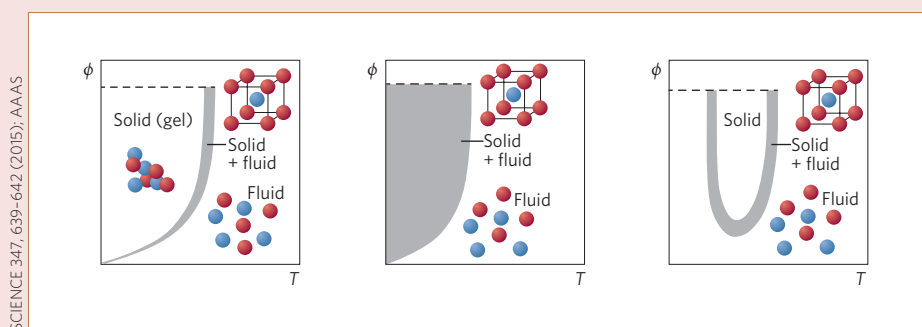
B. M. Mognetti and D. Frenkel *Nature Mater.* **11**, 518–522; 2012). Because the two types of strand hybridize at different temperatures (which can be tuned by designing the sequence of the binding segments), temperature shifts the balance of the competitive binding. This strategy leads to the melting 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 Vinothan 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 disfavouring 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.

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