of strand added: one possibility explored by the authors was to add equal amounts of X and Y strands such that they could hybridize randomly to all nanoparticles. The resulting effect on the overall interactions was twofold: the increased density of the secondary DNA layer led to a steeper osmotic repulsion, and the new bridges formed increased the entropic attraction. This caused a diffusion-free, first-order solid–solid transition into a clear fcc structure with unchanged nearest-neighbour distance. Such behaviour is reminiscent of the phase transition observed in micellar suspensions interconnected via telechelic polymer bridges[5], and suggests that the transformation corresponds to a uniform deformation of the crystal unit cell (that is, to a Bain transformation[6]), where the central particle of the bcc unit cell ends up in the centre of an fcc face (Fig. 1).

Atomic systems usually allow for only moderate strains, and in many metallic crystal transformations these strains are only a fraction of the lattice spacing. In Gang and colleagues' DNA–nanoparticle system, however, the strains are large. The DNA strands allow for the considerable strain imposed because close to their melting temperature the hybridization of double-stranded DNA is dynamic: bonds break and form continuously, and hence the system can easily anneal to accommodate strain. Yet a different scenario is observed when the added strands can directly bridge X and Y nanoparticles (the overall interactions are then shifted towards stronger attractions). Depending on the annealing, dense hexagonal planes form randomly stacked layers that can be twisted, and that register into an fcc stacking when heated. Finally, if the added strands are such that they only increase the X–Y repulsion, the mother phase breaks apart into finite-sized clusters.

As Gang and colleagues show, the crystal-to-crystal transition can also be tuned in terms of composition, forming alternating hexagonal layers of, say, gold nanoparticles and quantum dots. Clearly, the ability to make different structures starting from a single parent phase opens the prospect of reprogramming crystal structures on demand. Although the present work focuses on nanocolloids, one can imagine that a similar approach, when applied to micrometre-sized colloids, could be used to switch the photonic properties of such materials, with potential applications as reflective colloidal coatings or metamaterials. ❑

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DNA–NANOPARTICLE CRYSTALS

Exploiting shape complementarity

Improved control over the shape of nanoparticles and the interactions between them allows the rational construction of intricate microscale assemblies.

Jean-Philippe Sobczak and Hendrik Dietz

Two recent studies report the co-crystallization of binary mixtures of anisotropic gold nanoparticles into microscale 3D crystals[1,2] (Fig. 1). In both works, shape complementarity and weak DNA-mediated interactions between the particles were key in making the crystallization process possible.

Writing in *Nature Materials*, Chad Mirkin and collaborators hypothesized that the interplay of complementarities in nanoparticle size and shape should dictate to what extent co-crystallization of different nanoparticles occurs[1]. First, the authors describe the preparation of a series of monodisperse, anisotropic gold nanoparticles (these included cubes with flat, convex, and concave faces, as well as discs and octahedra, with dimensions ranging from 30 to 120 nm) functionalized with a densely packed shell of double-helical DNA molecules bearing specific, single-stranded overhangs (these mediate specific interactions between different nanoparticles through hybridization of complementary DNA sequences). Then, by using small-angle X-ray scattering (SAXS) and direct imaging with electron microscopy (EM), Mirkin and co-authors demonstrate the formation of co-crystallites from binary mixtures of these nanoparticles. Mixtures of differently sized cubes with flat faces consistently formed crystal structures, even at large size differences of up to 81%. However,
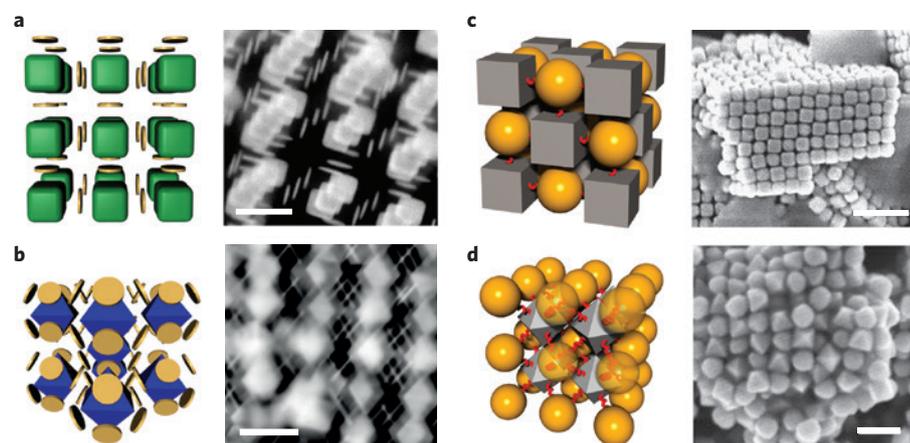

Figure 1 | Binary crystals from anisotropic nanoparticles. a–d, Co-crystals formed from binary mixtures of nanoparticles shaped as cubes and disks[1] (**a**), as octahedra and disks[1] (**b**), as cubes and spheres[2] (**c**), and as octahedra and spheres[2] (**d**). All scale bars, 100 nm. Figure reproduced from: **a,b**, ref. 1, Nature Publishing Group; **c,d**, ref. 2, Nature Publishing Group.

increasing the size mismatch between the nanoparticles resulted in reduced long-range order and decreasing co-crystal domain size (from ~4.5 μm to ~3 μm). The authors also show that a decreasing long-range order resulted from decreasing shape complementarity between cubes of the same size but with convex, concave or flat faces. In a system consisting of convex cubes only (the most extreme case of shape non-complementarity), amorphous assemblies were observed. When disks were co-crystallized with cubes with flat faces, size complementarity and the thickness of the interaction-mediating DNA shell determined whether disordered, 1D-ordered or 3D-ordered assemblies (Fig. 1a) formed. When disks were co-crystallized with octahedra, 3D lattices formed (Fig. 1b), but only when the disks were of the same size or smaller than the octahedra.

Reporting in *Nature Communications*, Oleg Gang and co-authors describe the co-crystallization of binary mixtures of spherical and anisotropic nanoparticles[2]. The authors prepared monodisperse gold spheres, cubes, and octahedra with dimensions ranging from 27 to 46 nm, and functionalized them with a densely packed shell of single-stranded DNA molecules (instead of double-stranded DNA as in Mirkin and colleagues' work). Through SAXS and EM analyses of the resulting assemblies, they found that when the spheres were mixed in a 6:1 stoichiometric excess over cubes, finite-size clusters comprising one cube and six spherical nanoparticles arranged in cubic symmetry, and that when the sphere-to-cube ratio was set to 1:1, ~1-μm co-crystal domains with a NaCl lattice formed (Fig. 1c). In the case of octahedra with spheres, body-centred, CsCl-type co-crystallites were observed (Fig. 1d), as expected from the octahedral arrangement of facets. Interestingly, the authors could not obtain assemblies with long-range order when using stiff double-helical DNA linkers between the nanoparticles. Thus, they conclude that the flexibility of the linkers is essential for accommodating DNA bonds between the surfaces of the spheres and cubes. Moreover, in agreement with Mirkin and colleagues' work, Gang and co-authors observed a reduction in long-range order with increasing nanoparticle-size mismatch, and that this reduction in long-range order could be compensated for (up to a certain degree) by using longer flexible DNA linkers.

These two studies provide insight into how to tailor the free-energy landscape for optimal co-crystallization of binary mixtures of anisotropic nanoparticles.
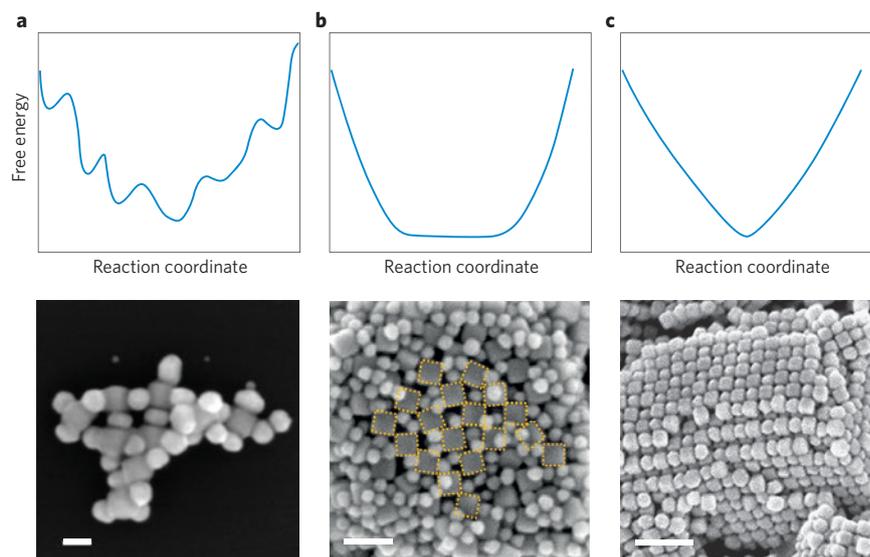

Figure 2 | Free-energy landscapes and degree of order for aggregates of DNA-coated nanoparticles. **a**, A rough free-energy landscape with many local minima prevents equilibration and typically leads to disordered aggregates. **b**, Incubation of the particles at temperatures near the 'melting' temperature of the DNA ligands smoothes the energy landscape and opens a pathway for equilibration. However, structural non-complementarity between particles can lead to a multitude of isoenergetic configurations. In this case, the assembled crystallites have short-range order only. Yellow outlines highlight the lack of long-range order. **c**, Tuning the structural complementarity between the particles narrows the energy-landscape funnel, increasing the long-range order of the crystalline aggregates. All three micrographs correspond to aggregates of cubes and spheres. Scale bars, 50 nm (**a**), 100 nm (**b**) and 200 nm (**c**). Micrographs reproduced from ref. 2, Nature Publishing Group.

First, it is important to obtain control over the kinetic routes to the target crystalline states, as previously recognized with single-component nanoparticle assembly[3]. As shown by Mirkin, Gang and their colleagues, the DNA shells should be dense to allow for the formation of many, individually weak hybridization bonds. Still, at room temperature the DNA shell acts like superglue, with particles adhering strongly on contact. This leads to a free-energy landscape that is rough and contains many local minima (Fig. 2a). The many energetic barriers slow down and ultimately inhibit equilibration into a low-energy valley. Hence, disordered aggregates are typically obtained on nanoparticle mixing at room temperature. At elevated temperatures, however, the DNA bonds between the nanoparticles are sufficiently reversible to allow for rapid bond exchange, the energy landscape is smooth, and equilibration into the low-energy valley becomes possible (Fig. 2b). Yet if many relative particle arrangements have a similar energy in this valley, particle placement will be ill-defined and only short-range order may be achieved. For example, a small cube may be placed on a sticky large cube in many positions and orientations that will have the same energy. As a designer

for high-quality nanoparticle crystals, to achieve large crystals with a high degree of order it is therefore important to reduce the number of states with comparable energy in the energy valley (Fig. 2c). In Mirkin and co-authors' work, this is achieved by using particle mixtures with a high degree of structural complementarity, and by communicating the shape information from particle to particle via a stiff double-helical DNA interaction shell. In Gang and colleagues' study, the more extensible single-stranded DNA shell compensates for geometrical non-complementarity between spheres and faceted particles, and creates an energetic gradient towards an optimal relative position that entails the maximization of hybridized bonds and the minimization of mechanical strain of the DNA chains.

Recently, it has been pointed out that the fields of nucleic acid nanotechnology and nucleic acid-mediated nanoparticle assembly have been evolving relatively independently[4], even though ultimately they both build on nucleic acid hybridization events. The works of Gang, Mirkin and their colleagues reminds us that there is significant conceptual overlap between these fields. Controlling kinetic routes to target states is similarly important in

nucleic acid nanotechnology. Invoking shape-complementarity principles and generic weak-contact interactions has also recently emerged as one strategy towards producing reconfigurable, higher-order DNA assemblies[5]. One clear goal in both fields is to produce large-scale 3D crystals by rational design. In DNA nanotechnology, this has been achieved in one singular case with DNA tensegrity triangles and variants of it[6]. In DNA-mediated nanoparticle assembly, many 3D crystallites have now been produced[4], but it appears to be difficult to prepare crystals that grow larger than ~5 μm. We speculate that further increasing

the nanoparticle uniformity and decreasing the degree of chemical defects in the sticky DNA shell will help to grow larger crystals. In DNA nanotechnology, the self-assembly of shape-complementary objects surrounded by a dense, generically weakly attractive envelope (as realized, for example, by using short single-stranded DNA tails) may prove to be a promising route to producing complex 3D crystals from defined-size DNA objects such as 3D DNA origami[7] or 3D DNA-tile bricks[8]. ❑

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MATERIAL WITNESS

LIQUID-STATE PARTICLE PHYSICS

The ability of condensed-matter physics to offer models for fundamental and particle physics has a distinguished history. Arguably it commenced with the liquid-droplet model of the atomic nucleus formulated in 1936 by Niels Bohr, which provided a simple approximation for thinking about nuclear stability and fission in terms of familiar concepts such as surface tension and heat of vaporization. Since then, real materials systems have offered all manner of laboratory analogues for exploring fundamental physical phenomena that lie outside the range of direct experimentation: for example, the use of liquid crystals to mimic the topological defects of cosmic strings and monopoles[1], the representation of graphene's electronic structure in terms of massless relativistic Dirac fermions[2], or the way topological insulators made from oxide materials might manifest the same properties as Majorana fermions, putative spin-1/2 particles that are their own antiparticles[3].

These cases and others supply an elegant demonstration that physics is unified not so much by reduction to a small set of underlying equations describing its most fundamental entities, but by universal principles operating at many scales, of which symmetry breaking, phase transitions and collective phenomena are the most obvious. It's perhaps curious, then, that particle physics has traditionally focused on individual rather than

collective states — as Ollitraut has recently put it, "on rare events and the discovery of new elementary particles, rather than the 'bulk' of particles"[4]. One indication that bulk properties are as important for high-energy physics as for materials science, he suggests, is the new discovery by the CMS Collaboration at CERN in Geneva that the plasma of quarks and gluons created by a proton collision with a lead nucleus has emergent features characteristic of a liquid[5].

It was initially expected that the quark–gluon plasma (QGP) — a soup of the fundamental constituents of nucleons — produced in collisions of heavy nuclei would resemble a gas. In this case, as in an ideal gas, the 'bulk' properties of the plasma can be derived rather straightforwardly from those of its individual components. But instead the QGP turns out to be more like a liquid, in which many-body effects can't be neglected.

Shades of Bohr, indeed. But how many many-body terms are relevant? Earlier studies of the tiny blob of QGP formed in lead–proton collisions, containing just 1,000 or so fundamental particles, showed significant two-particle correlations[6]. But in an ordinary liquid, hydrodynamic flow produces coherent structures in which the motions of many molecules are correlated. The new CMS results show that the QGP also has small but measurable six- and eight-body correlations — suggestive of

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collective flow effects — that are evident in the variations in particle numbers with the azimuthal angle relative to the line of collision. The azimuthal variations indicate that this flow is anisotropic, and the CMS team proposes that the anisotropy comes from a hydrodynamic amplification of random quantum fluctuations of the colliding particles.

So exactly what kind of liquid is this? Since the strong force between quarks and gluons doesn't diminish with distance, the QGP seems likely to be quite unlike any we know so far. But might it be within the wit of colloid scientists to tune interparticle forces so as to create a simple laboratory analogue? ❑

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