four additional honey sticks, and told them that any stick that was contributed to a common pool for their band would be tripled and the sticks distributed equally among band members. The Hadza could anonymously contribute any number of these four sticks (from zero to four), thereby pitting self-interest against the common good. Cooperators contribute sticks to the pool whereas egotists contribute nothing and free-ride on others' contributions.

Let's begin by considering those models that are not supported by the authors' results. They find that Hadza do not preferentially pick more cooperative individuals as future campmates or stick-receivers. They also do not preferentially network with those possessing complementary attributes, at least as indicated by age, food preferences or various physical measures. Thus, these findings do not favour existing models based on social selection or complementarity.

On the positive side, the most striking findings emerge when the variation in cooperative behaviours is partitioned within and among the 17 Hadza bands. There is substantially more variation among the bands, and substantially less variation within them, than would be expected by chance. Despite the fluidity of band membership, it seems that some combination of similarity-based association, social learning and sanctioning establishes differences in cooperative tendencies among different bands. This pattern is particularly interesting in light of experiments[9] showing that larger Hadza bands evince more fairness in anonymous interactions. Consistent with this, Apicella and co-workers' data from both the campmate and gift networks suggest that high contributors associate with other high contributors, and low contributors choose other low contributors. In fact, the gift-network results indicate that this extends to friends of friends: if your friend's friend is highly cooperative, you are likely to cooperate more, too.

As is the case in other primates[10], Apicella *et al.* also found that kinship and reciprocity contribute to assortment in Hadza social networks. No surprises there.

The crucial insight from this work[4] is that understanding distinct aspects of cooperation among these hunter-gatherers must incorporate an analysis of the dynamic processes at the population level that influence association, cultural transmission and band formation, instead of focusing tightly on purely individual actions within bands — the emphasis of much previous work. ■

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NANOTECHNOLOGY

Shape matters

The ligand-mediated binding of colloid particles to each other is more effective if the particles are flat rather than curved. This finding opens up opportunities for the design of self-assembling materials.

SHARON C. GLOTZER

From the invention of the wheel to the stacking of cannonballs and the design of stealth aircraft, humans have long known that shape matters. On a much smaller scale, the shapes of molecules affect their ability to form crystals, and enzyme shape is central to the binding of their substrates. Writing in the *Journal of the American Chemical Society*, Mirkin and colleagues[1] report a way in which shape can also affect the binding forces that hold nanometre-scale particles together — a discovery that suggests new approaches for constructing potentially useful architectures from these tiny building blocks.

Metallic and semiconductor nanoparticles grow as tiny crystals from solutions of precursor ions. Facets arise naturally from the anisotropic (directionally dependent) growth of the nanocrystals, producing particles that have a range of convex and concave shapes. These nanocrystals can be stabilized by coating them with small organic ligand molecules, or modified by the attachment of larger molecules such as DNA. Ligand coatings can conspire with the atoms in nanoparticles to produce net inter-particle forces (either attractive or repulsive) through van der Waals, hydrophobic and electrostatic interactions. DNA modification can also confer specificity on inter-particle forces — particles to which single-stranded

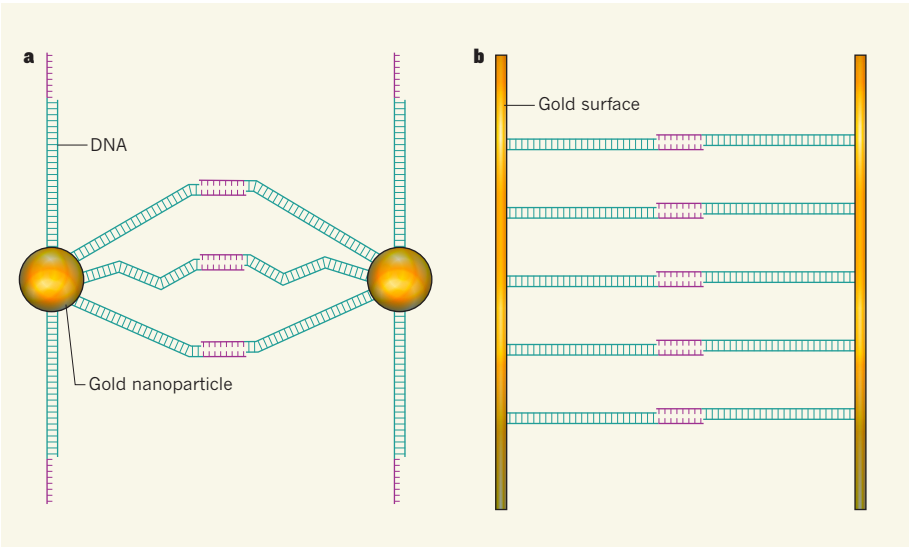

Figure 1 | DNA-mediated binding of nanoparticles. Mirkin and colleagues[1] prepared nanoscale gold particles of different shapes to which DNA molecules were attached. Although the main bodies of these molecules were duplexes (turquoise), the free ends of the DNA were single-stranded 'sticky ends' (pink). These could bind the particles together by forming duplexes with complementary sticky ends on other particles. The authors observed that particles with flat surfaces bound to each other more strongly than did spherical nanoparticles. This effect depends on how easily the sticky ends on different particles can approach each other. **a**, On spherical particles, relatively few sticky ends can come together to form duplexes, and the DNA molecules need to bend to allow duplex formation. **b**, When attached to flat surfaces, the DNA molecules can align so that more sticky ends form duplexes, without any bending.

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DNA is attached bind only to other particles that have complementary DNA sequences appended, because of the resulting DNA duplex formation.

Depending on their interactions, anisotropically shaped nanoparticles can serve as building blocks for self-assembled materials suitable for many applications, including solar cells, computer chips and even camouflage. There are various recent examples of nanoparticles whose anisotropic shape controls the structures that assemble from them: octopods[2], cuboctahedra (shapes formed by cutting the corners off a cube to create a polyhedron that has only squares and triangles for faces) and related polyhedra[3], and rounded squares and cubes[4–6], to name just a few.

Mirkin and co-workers[1] now add to our knowledge of the shape dependence of nanoparticle self-assembly. They made triangular gold nanoprisms — essentially, two-dimensional triangular objects — whose faces were modified with a layer of single-stranded DNA. When the authors combined these nanotriangles with others bearing complementary DNA, the particles 'hybridized' quickly and strongly with their counterparts. The researchers observed that particle–particle binding was several million times stronger, and happened 100 times faster, than in the case of similarly modified gold nanospheres.

The reason the triangular-shaped particles bind so much better to each other than do the spheres is just what one might expect. Mirkin and colleagues found that the large, flat faces of triangles align to allow many more DNA–DNA binding interactions than are possible for the curved surfaces of the spheres (Fig. 1). Additionally, the authors observed that the binding affinity of each DNA molecule for its complementary strand seems to be higher for the flat particles than for the round ones, so that greater numbers of duplex linkers can form per unit area. Finally, they found that flat surfaces allow many complementary DNAs to form duplexes without first having to bend; such bending is necessary for the binding of multiple ligands of similar length attached to two curved surfaces. It is remarkable that simple geometrical principles are at play even on such small length scales.

Intuitively, plate-like particles of any shape should be just as effective as triangles in maximizing the available interaction area for the ligands. In fact, any particles that have flat facets should bind together more easily using ligands than do spheres. And it is not just ligands such as DNA — which bind to each other through a precise combination of interactions — that should be able to maximize ligand–ligand interactions, and thus particle–particle interactions, when attached to flat surfaces. Ligands of any sort that attract each other should similarly benefit.

Mirkin and co-workers demonstrated this generality using ligands that terminate in carboxylic acid groups (COOH) in place of DNA. In this case, hydrogen bonds between the acid groups allow particle–particle association. The authors again observed that inter-particle attraction was considerably stronger for triangular gold particles than for spherical ones. Faceted particles could thus offer a new way of making 'patchy' particles[7], which contain interaction sites in patches at prescribed locations. By varying the patterns of the patches, the self-assembly of such particles can be controlled to make particular structures.

Shape is also beginning to be used to control depletion interactions, which occur when entropy effects cause small particles or polymers to be excluded from the spaces between larger colloid particles. This exclusion increases the osmotic pressure outside — and so provides an effective attraction between — the larger particles. Micrometre-scale discs stack up[8] readily into columns when mixed with nanometre-scale micelles in water, demonstrating that the discs bind more strongly face to face through depletion, rather than edge to edge or edge to face. Similar principles have been used for the assembly of nanoscale octahedra[3]. The idea of matching the shapes of colloid particles to maximize the strength of depletion interactions between them has also been applied to particles that have curved surfaces, allowing the preparation of Pac-Man-shaped particles that specifically bind smaller spheres in their dimple-shaped 'mouths'[9].

Shape and the alignment of facets are crucial factors in particle assembly, even when the only interactions between particles are those that prevent them from overlapping. For example, computer simulations have shown that hard, regular tetrahedrons[10] and triangular bipyramids[11] each self-assemble into quasicrystals (aperiodic crystals) once the fraction of space occupied by the particles within a given volume exceeds roughly one-half.

The thermodynamically stable assemblies of truncated tetrahedra — a series of polyhedra formed when the four tips of a tetrahedron are progressively truncated until an octahedron is produced — are also dramatically influenced by the precise shape of the objects[12]. The resulting crystals can be quasicrystalline, or can have a similar structure to the atomic structures of diamond, of the metallic form of tin (β-tin) or of high-pressure lithium. They can also form what are known as body-centred cubic crystals. Taken together, these assemblies represent the most complex and diverse set of structures ever predicted to form from hard shapes.

In contrast to the alignment of nanoprisms discovered by Mirkin and colleagues[1], which is driven by the minimization of potential energy, the faces of hard polyhedra align to maximize entropy. This results in entropically 'sticky' patches that effectively provide attraction between particles without the need for ligand binding. Such behaviour is

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possible only when the particles are confined to a fixed volume or pressure, but it serves as another recently discovered example of how shape matters.

In fields ranging from biology to engineering, the importance of shape has long been appreciated, but not always fully understood. Through work such as that of Mirkin and coworkers, we are starting to get a sense of how shape affects objects on the nanoscale — and so a glimpse of the shapes of things to come. ■

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LASER SCIENCE

Even harder X-rays

With the laser just over half a century old, another dream of the pioneers of this light source has been fulfilled. An atomic X-ray laser with unprecedentedly high photon energy has been demonstrated. SEE LETTER P.488

JON MARANGOS

Writing in this issue, Rohringer *et al.*[1] report the first demonstration of atomic X-ray lasing at a photon energy of 849 electronvolts. The X-ray laser emission in this case is based on atomic population inversion, which arises when more members of an ensemble of atoms exist in a higher-energy state than in lower-energy states. Rohringer and colleagues created population inversion in a sample of neon gas using a device known as an X-ray free-electron laser, operating at 960 eV. Although its photon energy falls in the 'soft' X-ray part of the electromagnetic spectrum, the authors' X-ray source paves the way to making practical atomic lasers in the 'hard' X-ray regime (energies beyond 5 keV).

The X-ray free-electron laser (FEL) used by Rohringer and colleagues was the Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Laboratory in Menlo Park, California. The LCLS, which is based on self-amplified spontaneous X-ray emission from a high-quality, high-energy (up to 14 GeV) electron beam, was essential for creating the population inversion; that is, for 'pumping' the new atomic X-ray laser.

But doesn't the need to use an X-ray FEL somewhat undermine the authors' new laser demonstration? Yes and no. The LCLS has already generated[2] laser-like X-rays of unprecedented brightness — having a photon energy that can be tuned from 500 eV to more than 8 keV in pulses lasting 5–80 femtoseconds (1 femtosecond is 10^{-15} s) and containing up to 10^{13} photons. The LCLS has enabled the first laboratory studies[3,4] of matter exposed to intense keV-energy X-rays, and has been used to image single nanocrystals[5] and viruses[6]. Nevertheless, like any FEL based on self-amplified spontaneous X-ray emission, the LCLS has inherent limitations in the quality of its output radiation. These limitations are principally due to the stochastic nature of the process, which leads to poor temporal coherence (meaning that the waves comprising the X-ray field are not well synchronized) and strong spectral and temporal jitter from sequential laser pulses.

It has long been common practice to use one type of visible-light laser to provide the energy for pumping the population inversion needed to operate another laser that has different optical properties. For example, nanosecond visible lasers are regularly used to pump femtosecond visible lasers. In their study (page 488), Rohringer *et al.* extend this idea to the X-ray region of the spectrum. Earlier X-ray lasers operating at lower photon energies, from 20 to 300 eV (ref. 7), have been pumped by physical processes, such as electron

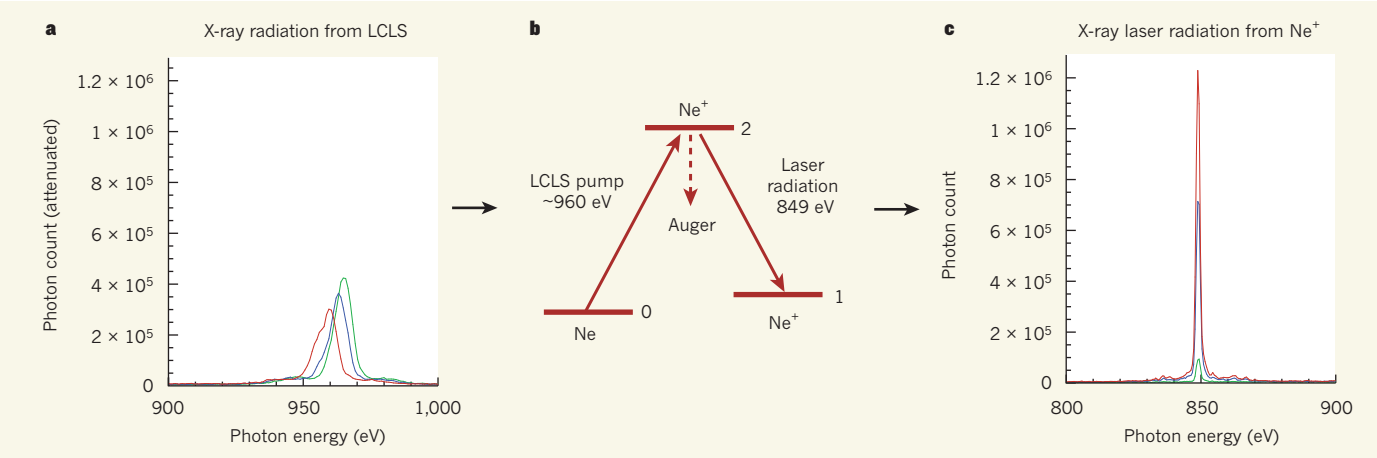

Figure 1 | Atomic X-ray lasing. Rohringer *et al.*[1] have demonstrated X-ray lasing at a photon energy of 849 electronvolts by creating atomic population inversion in a sample of neon gas using the Linac Coherent Light Source (LCLS), which is an X-ray free-electron laser. **a**, The LCLS X-ray radiation has a large spread in photon energy and considerable fluctuation in the average photon energy (about 960 eV) obtained from sequential laser pulses (shown in different colours). Photon count is measured after transmission through the neon sample and is strongly attenuated. **b**, The LCLS 'pumps' many of the neon atoms from the ground state (state 0) into a higher-energy state of ionized neon (state 2). Most of the ions in this excited state decay through an Auger process, but some will make the radiative transition to a state (state 1) that has a lower energy than state 2. This transition is accompanied by the emission of laser radiation that has a precise average photon energy (849 eV). **c**, The laser radiation has a smaller energy spread than that of the LCLS.

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