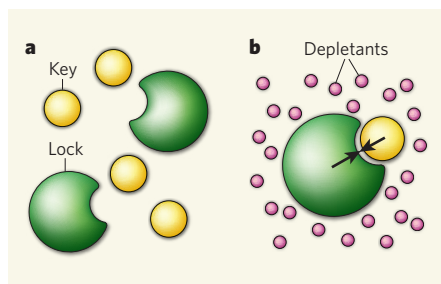


own radius, thus creating an ‘exclusion zone’ around each colloid particle that depletants can’t penetrate. When pairs of colloid particles come into contact, parts of their exclusion zones overlap, reducing the total volume of the colloid system that is inaccessible to depletants. Colloidal pairs are therefore attracted to each other because this increases the free volume of the depletants, a thermodynamically favourable effect.

Sacanna *et al.*<sup>1</sup> recognized that the complementary binding of key particles into the dimples of locks maximizes the depletants’ total free volume relative to nonspecific binding modes (in which keys bind to locks at positions other than the dimples). The attraction between the two types of colloid particle is therefore greatest along an axis that connects the centroids of the lock, the key and the dimple’s radius of curvature (Fig. 1b), and forms the basis of a truly directional bond. The authors do not report the relative strength of the directional interaction compared with nonspecific binding modes, but the directional effect must be substantial, judging by the lack of nonspecific binding in their system at the lowest depletant concentrations in which lock-and-key binding is observed.

So how could such a bond be used? Sacanna *et al.* demonstrate that the interaction is selective — key colloid particles do not bind efficiently to locks if they are larger or smaller than the lock’s pocket. This suggests that locks could pluck specifically sized colloid particles from a mixture. But this is probably not the most interesting use for this technology. Instead, the mechanical origin of the lock-and-key interaction indicates that the bond will form even when the two particles have different compositions or surface chemistry. This would



**Figure 1 | Lock-and-key binding in colloids.** **a**, Sacanna and colleagues<sup>1</sup> have made colloids in which ‘lock’ particles contain a dimple into which appropriately sized spherical ‘key’ particles can fit. Both types of particle were typically in the range of 1–3 micrometres in diameter. **b**, The authors added nanometre-scale polymers, known as depletants (not shown to scale), to their colloids. All the particles in the resulting system are in random motion, but when locks and keys come close to each other, depletants are excluded from the gap between the two larger particles. The imbalance in depletant density between the inside and outside of the gap generates a difference in osmotic pressure that attracts the pair of colloid particles to each other (arrows). The strength of the interaction is maximized when the key fits into the lock’s dimple, effectively forming a directional bond along the axis that connects the centres of the lock, the dimple and the key.

therefore be a straightforward way to produce anisotropic particles, for example, that would respond to an external electric or magnetic field. Such field susceptibility would be useful for self-assembly processes, because it would allow particles to align collectively relative to the field’s direction.

The fact that several locks may bind to a single key increases the possibilities of

lock-and-key bonds still further. Multiple pockets on lock particles, if achievable, would introduce the colloidal equivalent of extended coordination complexes — two- and three-dimensional molecular arrays that self-assemble in fixed geometries from atoms and ligand molecules. The assembly of colloidal particles into similar arrays might allow access to desirable, but so far elusive, complex colloidal structures<sup>9</sup>.

It is possible, however, that lock and key particles will form glasses or gels, rather than regular lattices, through a process known as kinetic trapping. But the fact that each bond functions as a ball-and-socket joint — the key colloid is free to rotate in its binding pocket — should help to prevent this. Such flexibility will probably provide some essential ‘wiggle room’ in the later stages of particle assembly processes, in the same way that it is often helpful to be able to bend the final piece of a model aeroplane in order to manipulate it into place.

Colloid scientists are used to working in a sequential manner: first they make their building blocks, then they assemble them. In other words, once synthesized, the building blocks are fixed items that can’t be changed. Happily, the building blocks of Sacanna and colleagues’ system<sup>1</sup> — the lock-and-key complexes — can be reconfigured at any point during a self-assembly process. To do this, the authors exploit the fact that the strengths of depletion interactions are linked to the size of the depletant particles. Using established methods to modulate the sizes of these particles *in situ* in their colloidal systems — for example, by making depletants from polymers that swell or shrink in response to temperature — the authors were able to form or break

## SURFACE SCIENCE

# Liquid marbles

Being two-faced isn’t always a bad thing. In the case of Janus microspheres — micrometre-sized particles whose two hemispheres have distinct properties — it can be extremely desirable, as Shin-Hyun Kim and colleagues show (S.-H. Kim *et al. Angew. Chem. Int. Edn* doi:10.1002/anie.201000108; 2010). They report Janus microspheres that form a flexible, superhydrophobic barrier on the surface of water.

The process of making the particles began by forming equally sized droplets of a light-reactive compound in water. The droplets also contained silica particles, which migrated to the droplets’ surface. The authors irradiated the droplets

with ultraviolet light, triggering a polymerization reaction, and then etched away the silica from the resulting polymeric microspheres, creating dimpled surfaces.

Kim *et al.* deposited the microspheres onto a film to prevent them from moving, then treated them with a compound that attached fluorine atoms to the upper, exposed surface of the spheres. Once detached from the film, the particles had two distinct faces — a hydrophilic (water-attracting), non-fluorinated side and a superhydrophobic (water-repelling), fluorinated side. The dimples on the surfaces of the spheres were essential for generating superhydrophobicity.

Kim *et al.* found that the Janus particles form hexagonal arrays on water surfaces, with their hydrophilic hemispheres facing the water. The resulting monolayers of particles are surprisingly robust: when the authors dropped a small amount of water onto a monolayer, it didn’t pass through, but instead formed spherical droplets up to 2.4 millimetres in diameter. Larger droplets were heavy enough to force their way through the monolayer by widening the gaps between the particles.

If poked with a hydrophilic glass rod, the monolayer deformed to prevent the rod from coming into direct contact with the water. What’s more, when water droplets were rolled on a bed of microspheres, the droplets became coated with the particles, creating ‘liquid marbles’. The marbles could be picked up



and squeezed by tweezers, without bursting (pictured).

The authors speculate that their microspheres could be used to form buoys for floating micromachines, or size-dependent, semipermeable membranes at the interfaces of immiscible fluids. They might even find their way into rain-resistant cosmetics.

Andrew Mitchinson