

occurs and the large number of interparticle bonds that need to be re-arranged during the disorder-to-order transition.

Therefore, in most experiments a careful yet ill-understood annealing process is needed to obtain crystals. Using computer simulations, Angioletti-Uberti and co-workers show that with their scheme to tailor the DNA shell around the particles so as they display re-entrant melting, the appearance of crystals at low volume fractions is highly promoted in a relatively broad temperature range. They also spelled out real DNA sequences that should bestow such unusual behaviour and considered the inclusion of inert strands to further tune the interparticle interactions. The researchers' approach has therefore far-reaching practical applications for the design of self-assembling systems with trouble-free pathways for crystallization. Furthermore, avoiding kinetic traps becomes an increasingly difficult problem

for systems with anisotropic particles and flexible chains because of the additional entropic contributions.

Moreover, despite the many structural similarities between atomic crystals and superlattices of DNA-coated particles, relatively few phase transitions between crystals of the latter have been observed. This is because, although thermodynamically favourable, such transitions are usually constrained not only kinetically but also physically (because of the necessary re-arrangement of DNA linkages). The re-entrant melting concept as a design principle promises to resolve this issue. Indeed, it may be possible to design multiple re-entrant melting scenarios that allow for the fabrication of novel crystal phases. The approach might also be expanded to systems containing different particle types, where heating and cooling could lead to the self-assembly

of different components, and thus to temperature-selective materials evolution. □

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## UPDATING THE EUREKA

One of the oldest genuine physical laws, and one of the few that most children learn, is the principle added in the third century BC by Archimedes of Syracuse. In his treatise *On Floating Bodies* he stated that “any floating object displaces its own weight of fluid”. This weight of displaced fluid can be equated with the object's buoyancy.

Buoyancy and its converse, sinking or sedimentation, supply the basis for a wide range of natural and technological processes. Sedimentation of particles in natural aquatic environments is a key aspect of marine geology and ecology, whereas centrifugation is widely used to separate particles of different density in food science and cell biology. A technique called density-gradient ultracentrifugation (DGU) is commonly used to separate components of a suspension into layers according to the particle densities. It uses a solute — a sugar, say, or a heavy salt, or colloidal nanoparticles — to set up a density gradient, so that the particles sink to the level at which their density matches that of the surrounding solution. This so-called isopycnic point should, in a simple picture, be set by Archimedes' principle.

But is it really? Even in some early protein-separation studies, the isopycnic point, or in other words the

apparent protein density, seemed to depend on the nature of the solvent<sup>1</sup>. Similarly, in fractionation of carbon nanotubes the density deduced for a standard DGU medium called Percoll differed from that for sugar or salt solutions<sup>2</sup>.

These discrepancies call into question what Archimedes' principle really means for a complex fluid containing many different species of various size and density. Is the “weight of fluid” displaced that of the pure solvent, or of the rest of the suspension? Both positions have been advocated; but what this really means is that the question of buoyancy becomes a many-body problem, like that of gravitation in star clusters, in which the behaviour of each particle depends on that of the others.

Piazza *et al.* have now attempted to clarify the matter by bringing the microscopic theory of liquids to bear on Archimedes' principle<sup>3</sup>. They acknowledge that the distribution of suspended particles around another particle is, at short range, not uniform but has a particular radial distribution due to mutual interactions, which is typically oscillatory owing primarily to packing effects. The true local weight of the medium within a given volume is therefore equal to the integral of this radial distribution function over



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that volume. In particular, there is an exclusion zone very close to the central particle within which the surrounding particles cannot go because of physical contact, so that the effective density of the central particle is increased.

This analysis allows Piazza *et al.* to derive a more generalized form of Archimedes's principle for complex fluids. It can give rise to some odd consequences, as their experiments demonstrate. The apparent density is size dependent, and this can lead to dense particles accumulating in a layer above less dense ones. Archimedes was not exactly wrong, but he needed a finer-grained theory to get it all right. □

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