

COLLOIDAL PHASE TRANSITIONS

A switch for phase shifting

Temperature can switch the thermodynamic phase of colloid-polymer mixtures by tipping the balance between competing attractive interactions induced by polymer depletion or adsorption.

Ah-Young Jee, Boyce Tsang and Steve Granick

At heart, scientists working with colloidal particles are fascinated by how interactions between the particles lead to emergent behaviour. One of the most interesting (and useful) mechanisms to generate attractive forces between colloids (to induce them to crystallize^{1,2}, for example) is the so-called depletion interaction, in which the entropy of a mixture of colloidal particles differing in size is maximized when large particles squeeze together to increase the volume available to smaller particles³. In practice, the smaller particles are most often non-adsorbing, low-molecular-weight polymers. However, when the polymers adsorb to the large particles (occupying their surfaces sparsely), they glue them together. Classically, on the spectrum in between attractive interactions caused by depletion or adsorption, there is no interesting link; textbooks on colloid science discuss these matters in separate chapters. Yet in an age when physical scientists seek inspiration from cells and organisms, where function typically arises from a combination of activating and inhibiting pathways, can the competition between polymer depletion and adsorption lead to useful behaviour?

Writing in *Nature Materials*, Lang Feng, Bezia Laderman and co-authors now demonstrate the point at which depletion- and adsorption-induced attractions between colloidal particles are (almost) balanced². Whereas for non-adsorbing polymers the attractive interaction is entropic, for adsorbing polymers the interaction is of enthalpic origin, as it is induced by the simultaneous adsorption of the same polymer chains on more than one particle, with varying interparticle distances. In the clever experimental design of the authors, the adsorbing and non-adsorbing polymers are, in fact, the same polymer (polyethylene oxide; PEO). By exploiting the weak temperature dependence of adsorptivity of PEO, the authors find that at the crossing point between the entropic and enthalpic regimes there is an intermediate regime in which the colloids behave as if they were inert (that is, almost analogous to hard spheres; Fig. 1a). Such a phenomenon has been reported for other

polymer-colloid mixtures⁴, yet Feng and collaborators demonstrate that the strength of the interactions and the tipping direction between the entropic and enthalpic regimes can be switched at will by modulating the temperature. In fact, they show that solids, a crystal or an amorphous aggregate, can form from a liquid dispersion both on cooling and on heating, respectively.

Such a convenient control of interparticle interactions can open the door to stimuli-responsive functionality. For example, countless applications in materials science depend on sequestering an object of interest (such as an enzyme or, more generally, a molecular stimulus) and then

releasing it on demand. The control over competing interactions demonstrated by Feng and co-workers could in principle be used to design such types of system. Indeed, it should be possible, for instance, to design multistage delivery systems that release cargos at specific temperature set-points through configuration changes in the carrier. Such structural changes could be induced by temperature-dependent colloidal interactions, which should be open to fine engineering control, as depletion interactions are greatly influenced by shape⁵.

Furthermore, this fine control of interparticle interactions could be useful

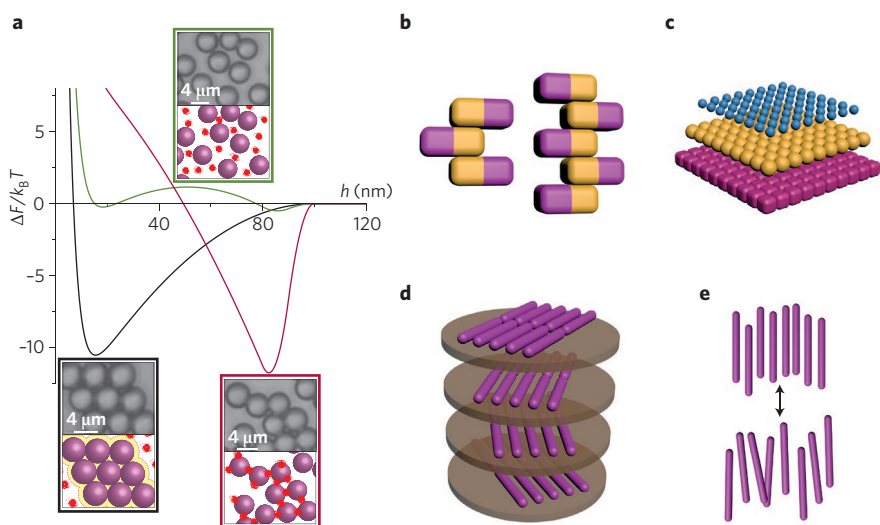


Figure 1 | Temperature-dependent attractive interactions between colloidal particles in colloid-polymer mixtures. **a**, Free energy ($\Delta F/k_B T$) between two colloidal particles in a polymer solution as a function of interparticle distance (h) and temperature, showing that temperature can act as a switch between a crystal (black curve; low temperature), a liquid-like dispersion (green curve; intermediate temperature) and a flocculated solid (red curve; high temperature)². The insets show microscopy (top) and schematics (bottom) of the structure of the three phases. The yellow area indicates the region around the colloids (purple) depleted from polymer (red spheres). **b**, Hypothetical example of a sequentially programmed assembly of Janus colloidal particles whose surfaces, of different chemical make-up (orange and magenta), switch at different transition temperatures (in the assembly shown, attractive interactions between the orange patches are switched on). **c**, The principle could be extrapolated to generate self-assembled three-dimensional structures in samples subject to a temperature gradient (colours indicate different particles). **d**, Because anisotropic particles can act as molecular analogues to liquid crystals, exhibiting conceptually similar (and sometimes diverse) phase transitions, three-dimensional structures of stacked liquid-crystal phases could also be assembled. **e**, Phase-switchable filament networks of anisotropic colloidal particles or macromolecules can in principle be used to replicate complex cellular behaviour under flow, shear or compression. Panel **a** adapted from ref. 2, 2015 Nature Publishing Group.

in sequential assembly⁶. For instance, one could design colloidal particles with varying surface affinity for polymers, such that a solidification transition occurs at a specific temperature that depends on the chemical make-up of the surface of the particles. The particles could assemble (solidify) into the designed structures in a sequential manner as temperature is decreased. And it may be possible to trap colloids at fixed, but non-touching distances from one another as a function of temperature. Also, patchy particles with multiple patches that differ in polymer affinity could self-organize into intriguing structures (Fig. 1b), and in the presence of a temperature gradient particles of appropriate surface make-up could be designed to self-organize, layer by layer, into three-dimensional assemblies (Fig. 1c), including complex binary, ternary, or higher-order structures with tunable stoichiometry.

Rod-shaped molecules are broadly useful in applications from advanced polymer materials to biological macromolecules, and the depletion force can be central to bringing filamentous molecules together in situations where pH or salt concentration must be kept constant. In fact, filamentous macromolecules can display ordered structures at a lower volume fraction than spherical particles because the excluded volume between two rods exceeds the volume of a rod⁷. Therefore, it is reasonable to anticipate that switching from polymer depletion to adsorption could convert a liquid-crystal phase (at low temperature) to an isotropic phase as temperature increases. Moreover, three-dimensional structures could be created by stacking liquid-crystal phases (Fig. 1d), and the type of liquid-crystal ordering could also be switched (Fig. 1e). The point where

attraction balances repulsion found by Feng and collaborators shows that the potential uses of depletion interactions in colloidal matter are far from being exhausted. □

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ICOSAHEDRAL QUASICRYSTALS

Assembled with one component

Computer simulations of one-component three-dimensional icosahedral quasicrystals will help to understand the mechanisms that may stabilize them in experiments.

Marc de Boissieu

Because of their long-range order in the absence of lattice periodicity, quasicrystals have intrigued researchers since Dan Shechtman's initial discovery¹. They have been found in many different systems², most of them consisting of intermetallic compounds (Al-, Zn-, or Cd-based). More recently, planar quasicrystals (that is, periodic stackings of quasicrystal planes) have been observed in soft-condensed matter, where the length scales are much larger and the formation of the quasicrystals is driven by a substantially different energy landscape than that of intermetallic compounds. Explanations for their formation have been based on simple interatomic potentials that model the core-shell structure of the elementary component³ (for example, a micelle). Writing in *Nature Materials*, Michael Engel, Sharon Glotzer and colleagues now show with molecular dynamics simulations that icosahedral quasicrystals that display quasiperiodic order in all three dimensions can be formed with just one component⁴.

Engel and co-authors used a simplified version of an empirical oscillating pair potential, fitted to *ab initio* data, that has proven to be extremely powerful in

explaining some of the physical properties of intermetallic quasicrystals⁵ (in particular, the binary CdYb and ZnSc systems), for which a detailed understanding of the atomic structure⁶ and the lattice dynamics⁷ had been achieved. The simplified potential has three maxima and two parameters that allow the strength of the first minimum and the distances between minima to be varied. By scanning the parameter space, the authors found that one-component three-dimensional icosahedral quasicrystals self-assemble in a region in phase space that is surrounded by a large variety of periodic phases, including clathrates and lattices with hexagonal, tetragonal and rhombohedral unit cells. Within the limits of the relatively small sizes of the systems they could simulate (about 20,000 particles), the authors show that the quasicrystals display a diffraction pattern that has all the characteristics of quasiperiodic long-range order⁸ (Fig. 1a). Also, their crystallographic-structure model shows frequent atom rearrangements known as phason flips, whose typical signature appears in the form of diffuse scattering in the diffraction pattern, and which have been observed in all icosahedral quasicrystals².

Could the simulated interparticle potential and obtained quasicrystals have experimental counterparts? Engel and colleagues speculate that the shape of the potential and the resulting structures may turn out to be realizable more easily in colloidal-matter systems, for which the fine-tuning of the shape of the effective pair potential is feasible. Still, a full understanding of the structures of the quasicrystals would need further analysis. Indeed, whereas all experimental icosahedral phases that have been found have a primitive face-centred icosahedral space group, Engel and co-workers' simulations lead to a body-centred icosahedral lattice. This structure, which had been proposed for tetrahedrally coordinated systems such as Si (refs 9,10), is also present in the surrounding crystal phases, such as the BC8 and clathrates, all of them tetrahedrally connected structures. It is, in fact, rather surprising that an isotropic potential leads to tetrahedrally coordinated structures, as usually angular-dependent potentials are deemed to be necessary. Also, the quasicrystals consist of double-shell atomic clusters, have an intriguing cluster distribution that is different to those of known structures, and their density