COMPUTATIONAL MATERIALS SCIENCE

Soft heaps and clumpy crystals

A detailed simulation of the packing behaviour of deformable particles settles the debate about whether soft matter can adopt an unconventional crystal structure at high densities — it can. The hunt is now on for a real-world example.

FRANCESCO SCIORTINO & EMANUELA ZACCARELLI

Imagine the Rome metro at rush hour: passengers are squeezed into close contact with one another. But there is a physical limit beyond which they cannot go, because their bodies cannot occupy the same space. This common experience has an equivalent at the molecular scale, in what physicists call excluded volume — strong repulsive forces, of quantum-mechanical origin, that prevent atoms from occupying the same space. Because of this phenomenon, dense arrangements of atoms and molecules result in solids that have lattice structures, in which each particle excludes neighbours from its site in the lattice. It is therefore surprising to read Lenz and colleagues' paper[1] in *Physical Review Letters*, which reports that the packing of soft particles may result in unusual crystals in which each lattice site is occupied not by a single particle, but by clumps of particles.

Soft particles are nanometre- or micrometre-sized macromolecules that have a deformable shape. Focusing on polymers, for example, one can envisage several different soft particles of increasing complexity (Fig. 1). These could be: linear chains; rings, in which the ends of a polymer chain are connected; stars, in which several polymer chains are joined at a common centre; and dendrimers, in which several stars are linked together. For a fairly small energy cost, the structures of soft particles can rearrange and interpenetrate to cope with excluded-volume constraints at the molecular scale. This allows the centres of mass of different soft particles to coincide, without any overlapping of the monomers (Fig. 1).

To predict the collective behaviour of soft particles, scientists typically use one of two theoretical approaches. The first approach is to perform calculation-intensive, monomer-resolved simulations that provide an accurate description of a system's properties but are at the limit of today's computational capabilities. The second is to use the tools of statistical mechanics to develop a simplified (coarse-grained) model of a soft particle and its interactions with other particles. Such simplifications are often so crude that each particle is represented as a single site at the particle's centre of mass, but they allow predictions to be derived more easily.

Theoretical investigations using coarse-grained models suggest that, in the dense fluid state[2], soft particles prefer to sit on top of each other, forming heaps or clumps. Indeed, beyond a certain density it becomes energetically preferable for a particle to completely overlap with a few others, rather than be subjected to the cumulative repulsion of many more neighbours (Fig. 2). Similarly, passengers on the metro could consider piling up on top of one another rather than suffering from excessive squeezing. In fact, parents often do this with their children, by holding them in their arms!

Further work[3] has shown that if such a 'clumpy' fluid crystallizes, the resulting solid retains the clumpy structure to form a regular arrangement of heaps. The number of particles in each heap varies, giving rise to solids that are spatially ordered (as is typical of standard crystals), but also locally disordered because of the random number of particles in the clumps. However, predictions based on coarse-grained models are built on approximations that typically become progressively less accurate as the particle system gets denser, and so are open to question. The prediction of clumpy crystals from coarse-grained models has therefore been seen by some as an academic curiosity, especially given that monomer-resolved simulations of polymer rings[4] did not confirm the predicted formation of such crystals.

Lenz and colleagues' monomer-resolved simulations for dendrimers now provide unmistakable evidence that clumpy crystals really can form. The authors' work builds on lessons learned from the earlier computational study of polymer rings[4], which revealed that the particles shrank as density increased. The shrinkage progressively invalidated predictions made using coarse-grained simulations. To overcome this problem, the authors modelled dendrimers that have a dense core, which prevents the particles' size from varying significantly as particle packing increases. The researchers' monomer-resolved simulations of the dendrimers closely follow the theoretical predictions from corresponding coarse-grained models — that is, they confirm that clumpy crystals can develop.

The time is now ripe for an experimental search for clumpy crystals composed of specially synthesized soft particles. DNA dendrimers[5] — nanometre-scale particles designed to self-assemble from single-stranded DNA molecules — may be the optimal candidates for realizing this unconventional state of matter. If so, the resulting clumpy crystals would enter the fast-growing pantheon of DNA constructs with potential uses in nanotechnology[6].

Clumpy crystals shed light on fundamental physical principles, but they may also have practical applications. The variation in the number of particles at each lattice site favours mass transport, in the form of individual particles hopping from one site to another (Fig. 2). This could be valuable for applications in which lattice rigidity and mass transport need to be coupled. Another fascinating possibility is that the number of particles occupying clumps in a crystal could be controlled by compressing the crystal. Indeed, a theoretical study has suggested[7] that a sequence of crystal phases, with differing occupancy numbers, occurs as the density of the particles increases.

The peculiar nature of clumpy crystals should be shared by disordered solids — those that do not have lattice structures — such as glasses. Glassy states[8] offer unique opportunities to tailor the viscoelastic properties of

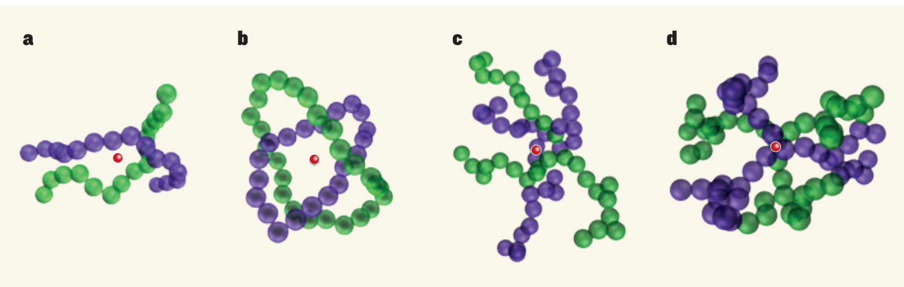

Figure 1 | Two particles, one centre. a–d, Soft particles formed from polymers can change shape and interpenetrate in such a way that their centres of mass coincide, as shown here for pairs of: polymer chains (**a**); polymer rings (**b**); three-armed polymer 'stars' (**c**); and dendrimers (connected stars; **d**). The centres of mass (red dots) of the green and purple particles coincide, even though not all of the monomers overlap. (Graphic courtesy of Lorenzo Rovigatti.)

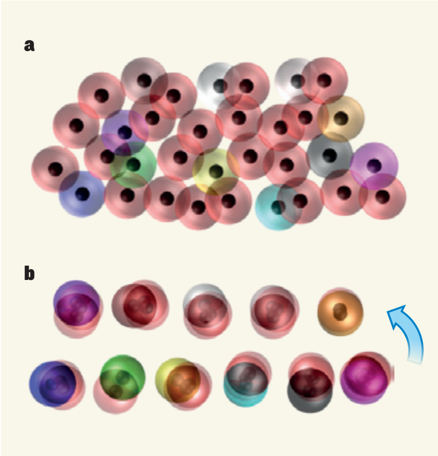

Figure 2 | The formation of clumpy crystals in two dimensions. **a**, At high density, soft particles (shown as transparent spheres; diameter corresponds to each particle's typical size) might adopt an arrangement in which they partially overlap with several neighbours. The total repulsion exerted on each particle by its neighbours is high. **b**, Alternatively, the same particles might form a regular lattice of 'clumps'; in this case, each clump contains an average of three overlapping particles. Particles belonging to distinct clumps do not interact, so that the overall repulsion exerted on each particle is less than that in **a**. Particles might also be able to hop between lattice sites (arrow). Lenz and colleagues' numerical simulations[1] reveal that dendrimeric soft particles form clumpy crystals. (Graphic courtesy of Lorenzo Rovigatti.)

materials. For example, glasses can be melted by applying a 'shear' deformation force parallel to a sample's surface (an effect known as shear melting). Analogous to what has been reported for clumpy crystals[9], the viscosity of shear-melted clumpy glasses should increase with the intensity of the applied deformation, a phenomenon known as shear thickening. This behaviour is at odds with that of most materials, in which the application of shear decreases a sample's viscosity. Finally, the link between soft particles and quantum mechanics should be noted: boson particles have been predicted[10] to form supersolids, the quantum analogue of clumpy crystals, although such supersolids have not yet been observed. Perhaps an experimentally realized clumpy crystal could give insight into some aspects of such mysterious quantum solids.

The unconventional behaviour of soft matter has often surprised scientists. Lenz and colleagues' study provides yet another example of how soft particles at the nano- and microscale do not simply reproduce phenomena known to occur in the atomic and molecular world. ■

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ASTRONOMY

Andromeda's extended disk of dwarfs

Deep-imaging observations of the Andromeda galaxy and its surroundings have revealed a wide but thin planar structure of satellite galaxies that all orbit their host in the same rotational direction. SEE LETTER P.62

R. BRENT TULLY

In this issue, Ibata and colleagues[1] report that roughly half the dwarf companion galaxies of the Andromeda galaxy are rotating coherently about it in a thin plane. Their finding provides a fascinating new constraint on theories of galaxy formation.

First, the observational facts. Andromeda, also known as Messier 31, is the nearest giant galaxy to our Galaxy. It is so near that a census of its companions by deep imaging with the Canada–France–Hawaii Telescope has been completed over a large area and to a faint level of detection. Because the system is close, distances to the companions can be measured and the velocities of constituent stars determined. Such a complete census for the Milky Way is impossible because candidates could be anywhere in the sky, even behind a zone obscured by the Galaxy. And other giant galaxies are too far away to be studied to such a level of detail.

Ibata *et al.* found that 13 of 27 dwarf companions (satellites), at distances from Messier 31 of between 35 and 400 kiloparsecs (114–1,305 light years), lie in a thin plane 13 kpc thick and share a coherent velocity pattern: those to the north of Messier 31 are moving away from Earth relative to the galaxy, and those to the south are moving relatively towards Earth. No theorist of galaxy formation would have dared to predict such a situation. What's more, the Milky Way is in the same plane as the 13 satellites. The discovery of this plane is a spectacular result, and the authors avoid the risk of diluting their message by not mentioning more speculative matters that add to the intrigue.

Although the disk of Messier 31 is tilted by about 50° from the plane of the satellites, the rotation in the galaxy is in the same direction of motion as the satellite-velocity pattern. Looking beyond Ibata and colleagues' survey region, the three galaxies that lie 250–500 kpc from Messier 31 — IC 1613, IC 10 and LGS 3 — and which were known before the advent of deep-imaging surveys, all reside in the same satellite plane. This is particularly interesting because these three more-distant galaxies contain substantial interstellar gas and are still forming stars, and so might be recent arrivals on the scene. All the satellites in the authors' survey region are gas deficient (except Messier 33, which is not on the plane being discussed) and, according to standard galaxy-formation models, would be presumed to have been in the vicinity of Messier 31 for some time and to have complex orbits.

But things are even stranger than Ibata and colleagues suggest. The remaining known Messier 31 satellites can be split roughly in equal numbers into those at lower and higher Galactic longitude. All of those at higher longitude than Messier 31, including the Local Group's third-largest galaxy Messier 33, lie in a separate common plane. This secondary plane is offset and tilted by about 13° from the primary plane through Messier 31.

Ibata *et al.* remark on earlier suggestions that satellites of the Milky Way also seem to lie in a plane[2,3]. It occurred to me that perhaps there was enough information in the data archives to evaluate the distribution of companions in the next-nearest groups of galaxies — those around the dominant galaxies Centaurus A and Messier 81. The regions around these galaxies have been closely studied in surveys for satellite candidates and in follow-up observations with the Hubble Space Telescope[4,5]. In the case of Centaurus A, 22 of 24 satellites within 600 kpc of the galaxy's centre separate into two equally populated planes that are roughly parallel but offset by 280 kpc. Centaurus A lies in