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THE FORCE OF SHAPE

Entropic forces feature throughout condensed-matter science. The depletion force has its origins in solution chemistry, and is generally considered to be an entropic effect of the steric exclusion of solutes close to and between surfaces¹ — although deducing the relative importance of entropic effects in real systems that also exhibit enthalpic effects is not trivial². Helfich's seminal work on membrane fluctuations³ revealed that their suppression in adjacent membranes can induce an entropic repulsion — although here too the details remain unclear⁴. The entropic consequences of confinement also supply one way of understanding the critical Casimir force between surfaces that confine fluid mixtures⁵. The hydrophobic interaction, central to biophysics, has been given an entropic interpretation⁶, although there's debate over the details^{7,8}.

The crystallization of colloidal hard spheres is also considered to be an entropically driven phase transition⁹. Here the hexagonal crystal structure observed experimentally is a simple consequence of close-packing requirements. But if the particles are non-spherical, the optimal packing geometry is not always clear. Damasceno *et al.* have recently shown that arbitrarily shaped hard polyhedra display considerable predictability in their dense packing arrangements, but that the influences on these structures are subtle and the outcomes diverse¹⁰. Depending on their shape, some polyhedra will form ordered crystals, while others form liquid crystals, 'plastic' crystals in which the particles rotate freely,

or disordered glasses. The entropic forces promoting the dense phases here heed details of particle shape: in particular, there is often a propensity for particles to sit face to face with facets aligned, creating directional preferences that can lead to ordered self-assembly.

These processes of non-spherical particle packing are relevant to the crystallization of viruses, many of which are faceted polyhedra, and also of proteins, the shapes of which are less geometric but often strongly anisotropic. For synthetic nanoparticles an increasing ability to control shape permits the exploration of diverse packing phenomena¹¹, while the use of DNA to make complex molecular polyhedra adds a new dimension bridging the biological and the nanotechnological¹². There is good reason, then, to seek a clear grasp of how shape exerts an entropic influence.

This is what van Anders *et al.* now provide¹³. Using computer simulations of polyhedral packings, they clarify the concept of a shape-dependent directional entropic force, showing that it can be given a rigorous description based on the role of shape and faceting in maximizing the entropy of dense packings. As such, the force is an emergent property of local particle configurations, and it typically manifests itself for polyhedra as a repulsion between corners and an attraction between faces. For these systems the force is typically of the order of a few kT (where k is Boltzmann's constant and T is temperature), making it comparable to van der Waals and depletion



PHILIP BALL

forces. It should, the researchers say, be experimentally measurable.

The directional entropic force offers a way to distinguish simple packing, driven by global density considerations, from self-assembly that is sensitive to local geometry. It helps rationalize why a self-assembled system doesn't necessarily seek the densest packing, and offers a tool for designing such assembly processes. □

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