Abstract

In this seminar we discuss some of the properties of densely packed 3D shapes, studied both in simulations and experiments. Starting with the ancient problem of stacking spheres, we move on to more recent developments in the field of macro- and microparticles, with the last chapter concentrating on thermodynamics and spontaneous ordering of quasicrystalline states of matter.
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1 Historical background

Packing problems, such as how densely objects can fill a volume, are among the most ancient and persistent problems in mathematics and science. The first known mathematical study of face-centred cubic arrangement of spheres is found in a Sanskrit work from 499 AD.\footnote{1} In geometry, close-packing of identical spheres is a dense arrangement of congruent spheres in an infinite, regular arrangement (or lattice). The problem of close packing of spheres was first mathematically analyzed by Thomas Harriot around 1587, after he was posed a question on piling cannonballs on ships.\footnote{2} Cannonballs were usually piled in a rectangular or triangular wooden frame, forming a three-sided or four-sided pyramid. Both arrangements produce a face-centered cubic lattice (fcc) – with different orientation at the base.

![Figure 1.1 Cannonballs piled on a triangular (front) and rectangular (back) base. In both cases, the balls form a fcc lattice.\footnote{2}](image)

Carl Friedrich Gauss proved that the highest average density – that is, the greatest fraction of space occupied by spheres – that can be achieved by a regular lattice arrangement is \( \phi = \pi / 3\sqrt{2} \approx 0.74048 \). The Kepler conjecture states that this is the highest density that can be achieved by any arrangement of spheres, either regular or irregular. This conjecture is now widely considered proven by T. C. Hales (2005). Hales' proof is a proof by exhaustion involving the checking of many individual cases using complex computer calculations. Referees have concluded that they are "99% certain" of the correctness of Hales' proof, so the Kepler conjecture is now very close to being accepted as a theorem.\footnote{3}

The problem of dense stacking is a notoriously difficult one, even for spheres as the simplest convex 3D bodies. Attention has very recently turned to finding the maximum density packings of nonspherical particles in \( \mathbb{R}^3 \), including ellipsoids, tetrahedra, and superballs. Very little is known about the densest packings of polyhedral particles that do not tile space, including the
majority of the Platonic and Archimedean solids. Of particular interest is the random packing, which relates to the ancient (economically important) problem of how much grain a barrel can hold.

2 Dense packings of identical ellipsoids

First, let us examine the experimental and numerical results for a dense random packing of spheres. Many experimental and computational algorithms give a packing fraction (relative density) of \( \phi = 0.64 \). This number, commonly referred to as the random close packing (RCP) density, is not universal but generally depends on the packing protocol. It is also an ill-defined concept because higher packing fractions are obtained as the system becomes ordered, and a definition for randomness has been lacking. A more recent concept is that of the maximally random jammed (MRJ) state, corresponding to the least ordered among all jammed packings.[4]

2.1 Simulation

A simulation run by Donev et al. (2004) explored MRJ density of ellipsoid packings.[4] For both oblate and prolate spheroids, the packing fraction, \( \phi \) and the average number of touching neighbors per particle, \( Z \), increased rapidly as the particles deviated from perfect spheres. Both reached large densities such as \( \phi = 0.71 \) and sometimes even as large as \( \phi = 0.735 \), approaching the density of the crystal with the highest possible density for spheres \( \phi = \pi/3\sqrt{2} \approx 0.74048 \). They suggested that the larger density is directly related to the large number of degrees of freedom per particle and thus the larger number of particle contacts required to mechanically stabilize the packing. It is important to note that the increases of packing fractions were unrelated to any observable increase in order in these systems and developed neither crystalline (periodic) nor liquid-crystalline (nematic or orientational) order.

Figure 2.1.1 (A) An experimental packing of the regular candies. (B) Computer-generated packing of 1000 oblate ellipsoids.[4]
2.2 M&M experiments

Donev and his team took on a very experimental approach – with M&M Milk Chocolate Candies. The candies are oblate spheroids with an aspect ratio of \( \alpha = b/a \). They experimented with both: regular and mini varieties of M&Ms. Both are oblate spheroids with small deviations from true ellipsoids: \( \Delta r/r \ll 0.01 \), with the ratio \( \alpha = 1.93 \) for regular and \( \alpha = 1.88 \) for minis.

A square box, 8.8 cm by 8.8 cm, was filled to a height of 2.5 cm while shaking and tapping the container, in order to guarantee the randomness of position. The actual measurements were performed by adding 9.0 cm to the height and excluding the contribution from the possibly layered bottom. After measuring the average mass, density, and volume of the individual candies, the number of candies in the container and their volume fraction could be simply determined by weighing. These experiments yielded \( \phi = 0.665 \pm 0.01 \) for regulars and \( \phi = 0.695 \pm 0.01 \) for minis. The same technique was used for 3.175 mm ball bearings (spheres) and yielded \( \phi = 0.625 \pm 0.01 \).

The second set of experiments were performed by filling a 5-liter round flask (to minimize ordering due to wall effects) with candies by pouring them into the flasks while tapping. The volume fractions found in these more reliable studies were \( \phi = 0.685 \pm 0.01 \) for both the minis and regulars. Using this same procedure for 30,000 ball bearings in the 0.5-liter flask gave \( \phi = 0.635 \pm 0.01 \), which is close to the accepted MRJ density.

To make sure orientations of the candies were random, the 5-liter round bowl was scanned using a magnetic resonance imaging device. For several planar slices, the direction \( \theta \) of the major ellipsoid axis with respect to some fixed direction (say z axis) was computed, and the two-dimensional nematic order parameter calculated: \( S_2 = \langle (\cos \theta)^2 - 1 \rangle \), yielding \( S_2 \sim 0.05 \). This was consistent with the absence of orientational order in the packaging.

![Figure 2.2.1](image)

**Figure 2.2.1** (A): Packing fraction \( \phi \) of prolate (circles), oblate (squares) and fully aspherical ellipsoids (diamonds) versus aspect ratio \( \alpha \). (B): Average coordination Z number versus aspect ratio \( \alpha \). Inset: as asphericity is introduced, a locally jammed particle becomes free to rotate and escape the cage of its neighbours.\(^4\)
From the results we notice that the volume fraction increases as the shape of particles deviates from spherical. Why is this so? Due to the larger number of rotational degrees of freedom, the state of particles is much more jammed compared to spheres. This also gives rise to more contacts per particle as the aspect ratio is increased, and more contacts require a denser packing of the particles. By introducing orientational and translational order, the density of the packings can be further increased at least up to 0.74.

The number of contacts with neighboring particles $Z$ for spheres was determined by Bernal and Mason by coating ball bearings with paint, draining the paint, letting it dry, and counting the number of paint spots per particle when the system was disassembled. Their results gave $Z = 6.4$.\cite{4} The Donev team performed the same experiments with the M&M, counting the number of true contacts between the particles. The average number was $Z = 9.82$.

![Figure 2.2.2 Comparison of experimental (black bars, from 489 regular candies) and simulated (white bars, from 1000 particles) distribution of particle contact numbers.\cite{4}]

### 3 Dense packings of Archimedean and Platonic solids

Let us turn to more complex shapes. In 2009, Torquato and Jiao reported a theoretical study of packings of Archimedean and Platonic solids. Using a variety of initial configurations, they have found the densest known packings of the four non-tiling Platonic solids in three-dimensional Euclidean space.\cite{5}

First of all, let us recall the definition of a Platonic solid. It is defined as a convex polyhedron with all faces being congruent convex regular polygons. There are exactly five such polyhedra: tetrahedron, cube, octahedron, dodecahedron and icosahedron. An Archimedean solid is composed of two or more types of regular polygons. Studies of close-packed structures of these polyhedra are difficult due to their complex rotational degrees of freedom and the non-smooth nature of their shapes.
Of utmost importance in studying close packing of these polyhedra is the notion of central symmetry. A particle is centrally symmetric if it has a centre C that bisect every chord through C connecting any two points of the particle. A Bravais lattice packing is defined as one in which the centroids of the non-overlapping particles are located at the same points that define the Bravais lattice, each centroid oriented in the same direction. The space $\mathbb{R}^3$ can then be geometrically divided into identical regions $F$ called fundamental cells, each of which contains the centroid of a single particle. The problem was solved within an adaptive fundamental cell subject to periodic boundary condition as an optimization problem. Torquato and Jiao called this optimization scheme the adaptive shrinking cell (ASC).

Finding the densest packing of regular tetrahedra is part of the eighteenth problem in Hilbert’s famous set of problems.$^5$ The densest Bravais lattice packing of tetrahedra, which requires all of
the tetrahedra to have the same orientations has a relative low density $\phi_{max}^{lattice} = 18/49 = 0.367...$ and each tetrahedron touches 14 others. Some previous results concerning this Platonic polyhedron yielded even higher densities, but were not Bravais lattices. The densest of these packings ($\phi = 0.7786...$) with a periodic structure is called a “wagon-wheels” packing because the basic subunits consist of two orthogonally intersecting “wagon wheels”. A wagon wheel consists of five contacting tetrahedra packed around a common edge. By using the ASC scheme, dense packings were obtained using low-density versions of the aforementioned packings. Initial conditions using periodic copies of the wagon-wheels packing with 72 particles per cell lead to the densest packing reported to date with $\phi = 0.782021...$. This packing is denser due to the face-to-face (not vertex-to-face) contacts and the lack of central symmetry.

With the packings of other three Platonic solids; icosahedra, dodecahedra and octahedra, Torquato and Jiao used a wide range of multi-particle configurations with $N$ ranging from 20 to 343. The packings again started off dilute with varying densities. For the above mentioned polyhedra, densities of packings obtained through simulations compared with the densest lattice packings are shown in Table 1.

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<th>icosahedra</th>
<th>dodecahedra</th>
<th>octahedra</th>
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<td>0.947003</td>
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<td>0.947368</td>
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<td>packings</td>
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**Table 1** Packing fractions $\phi$ of three Platonic solids computed using the ASC scheme and their corresponding optimal lattice packings.[5]

The simulation results strongly suggest that the optimal lattice packings of the centrally symmetric Platonic solids are indeed the densest packings of these particles, especially since these arise from a variety of initial dilute multi-particle configurations within an adaptive fundamental cell.

Furthermore we can show that the maximal density $\phi_{max}$ of a packing of congruent nonspherical particles of volume $v_{particle}$ is bounded:

$$\phi_{max} \leq \phi_{max}^{upper bound} = \min \left[ \frac{v_{particle}}{v_{sphere}} \frac{\pi}{\sqrt{18}}, 1 \right],$$

(1)

where $v_{sphere}$ is the volume of the largest sphere that can be inscribed in the non-spherical particle and $\pi/\sqrt{18}$ is the maximal sphere-packing density. In (Fig. 3.3) we can compare the densities of the densest lattice packings of the Platonic and Archimedean solids to the corresponding upper bounds on the maximal density of such packings.
Why should the densest packings of the centrally symmetric solids be their corresponding optimal lattice packings? First of all, face-to-face packings allow such polyhedral packings to achieve large densities because they enable the contacting centroids to come closer together. Second, face-to-face contacts are maximized when a pair of particles has the same orientation because of the central symmetry and the equivalence of the three axes of the solid. This is consistent with a lattice packing, the densest of which is the optimal one. These arguments led to the following conjecture: The densest packings of the centrally symmetric Platonic and Archimedean solids are given by their corresponding optimal lattice packings.

![Graph](image)

**Figure 3.3** Comparison of $\phi_{\text{lattice}}^{\text{max}}$ (blue circles) and $\phi_{\text{upper bound}}^{\text{max}}$ (red squares). The large asphericity and lack of central symmetry of the tetrahedron (P1) and truncated tetrahedron (A1) are consistent with the large gaps between $\phi_{\text{lattice}}^{\text{max}}$ and $\phi_{\text{upper bound}}^{\text{max}}$, while there are non-lattice densities that are appreciably greater (green triangles).\[^5\]

## 4 Thermodynamics and stacking of densely packed polyhedrons

### 4.1 Packing of micrometer-sized cubes

Let us move on to the packing of cubes. In an article published in 2012, Rossi et al. looked into self-ordering of synthesized micrometer-sized cubes in aqueous dispersions by an optical microscope. The particles that we will talk about here are the first ever realization of such a colloidal system.\[^6\]

Essential to the experiment was the fact that the cubes were large enough for optical microscopy but still small enough to exhibit Brownian motion such that equilibrium thermodynamics of the cubes was probed on the time scale (typically minutes to hours) of optical microscopy. The particles were synthesized in three steps as is shown in (Fig. 4.1.1.).
Figure 4.1.1 The synthetization process of the micrometer-sized cubes.\[^{[6]}\]

First, iron-oxide template cubes were prepared (a), which were then covered with an amorphous silica shell (b) to form what later became the hollow cube. The iron oxide templates were dissolved by hydrochloric acid (HCl) which diffused away through the nano-porous silica shell. The synthesis yielded particles with uniform size and shape with a typical side of 1338 nm with a polydispersity (deviations from uniform size) of 3% (c). These particles were in fact not real cubes but rather “supperballs”, a shape that smoothly interpolates between the cube and a sphere by varying one single parameter \( m \):

\[
\left( \frac{x}{a} \right)^m + \left( \frac{y}{a} \right)^m + \left( \frac{z}{a} \right)^m = 1
\]

where \( a \) denotes the size of the cubes. In the mentioned experiment, the parameter \( m \) was approximately 3.5. All aqueous dispersions observed in the experiment contained 10 mM NaCl, to reduce the Debye length to \( \kappa^{-1} = 3 \text{ nm} \); this was small enough to ensure the colloids the most anisotropic shape. As the dispersion also included polymers as depletants, we now recall the concept of depletion force.

The range and strength of the attraction between colloids can be varied by the addition of free non-adsorbing polymer to the colloidal dispersion. These polymers, when in an appropriate solvent, behave as random coils with a radius of gyration \( R_g \). On average, they are excluded from a shell of thickness \( R_g \) around the colloidal particle called the depletion zone. When two colloidal particles are brought together, these depletion zones will overlap and the total volume accessible to the polymer will increase. It is this increase in free volume that causes an effective attraction; the so-called depletion force. The range of the attraction is directly related to the radius of gyration \( R_g \), whereas the strength is proportional to the osmotic pressure of the polymers.

When two exclusion zones overlap, the volume accessible to the polymer increases by \( \Delta V \) resulting in an osmotic pressure imbalance that drives the cubes together. The attraction between two cubes can be derived simply from entropy definition \( S = N k_B \ln V_p \) and interaction energy equation \( F = -T \Delta S \)^{[7]}:

\[
F(n) = -\Delta V n k_B T
\]
where $V_o$ corresponds to volume available to the polymer and $n$ to the number density of the depletant. The overlap volume is approximated by

$$\Delta V \approx (L - 2\delta + 2R_g)^2 2R_g$$

and can be seen in (Fig. 4.1.2) where $L$ is the total length of the cube’s side and $(L - 2\delta)$ is the length of the flat faces; $\delta$ is a measure of the roundness of the cube.

Figure 4.1.2 A schematic to the derivation of the overlap volume of the micrometer cubes.\textsuperscript{[6]}

As a non-adsorbing polymer was added to the solution, within minutes simple cubic crystals nucleated and started to grow via coalescence with other nuclei to form cubic mosaics seen in (Fig. 4.1.3). The depleting polymers force the cubes together into close-packed structures that maximize the overlap volume mentioned above. Cubes may form close-packed mosaics that are not simple cubic (linear rows, translated rows), but surprisingly, the preferred close-packaging occurs in the form of

Figure 4.1.3 Some typical snapshots of mosaic-like crystals forming in the capillary. Surprisingly, the top right layer fits almost perfectly on the bottom one (top left). The bottom right diagram sorts the crystals by orientation as seen in the inset. The scale bar corresponds to 10 $\mu$m.\textsuperscript{[6]}
a simple cubic lattice in which the particles are quite precisely in register in the plane as well as in 3D. The formation of cubic lattices in 3D is a consequence of the fact that the cubes have slightly rounded corners. When four cube corners meet, they form a pore with a radius of about 160 nm, which is large enough to accommodate depletant polymers. Thus there is a free-energy penalty for a cube to cover such a pore, because when two layers of cubes shift on top of one another precisely to match the pores, so that the volume accessible for polymers increases, minimizing interaction energy.

4.2 Thermodynamics of quasicrystalline phases of densely packed tetrahedra

Apart from studies of packing, hard tetrahedra have been used to model the structure of water. Polytetrahedral networks of atoms are characteristic for Frank-Kasper phases, common in intermetallic compounds. Until 2009, no simulation or experiment has yet reported the spontaneous formation of an ordered phase of hard tetrahedra.\[1\]

Tetrahedra do not tile Euclidean space, but can be incorporated into clusters one tetrahedron at a time. These structures are locally dense, but the problem of arranging them into a space-filling bulk structures is non-trivial. In (Fig. 4.2.1, (A)), tetrahedral dice are stuck together with modelling putty to form various bodies.

![Figure 4.2.1](image)

**Figure 4.2.1** (A): The pentagonal dipyramid (a), the nonamer (b), the icosahedron (c), the extension of the icosahedron with large gaps between outer tetrahedra lower the density (d), tetrahelix (e).

(B-D): A quasicrystal obtained by 13,824 hard tetrahedra using numerical compression.\[1\]
The dense packings of hard regular tetrahedra were found by Monte Carlo simulations. An equilibrium of an initially disordered fluid of 13,824 tetrahedra at constant $\phi = 0.5$ was compressed to form an ordered structure. The structure was quasicrystalline, that is, it displayed order but no translational symmetry. It also has a packing fraction much higher than 0.5. What

\[ \frac{\text{Figure 4.2.2}}{} \]

followed was the probing of the thermodynamics of such a tetrahedron fluid. Figure 4.2.2 shows the equation of state of such a fluid $\phi (P^*)$, where $P^*$ is the reduced pressure $P^* = P\sigma^3/k_B T$ and $\sigma$ denotes the edge of the tetrahedron at a constant temperature. A simulation was carried out for a small system, containing 512 tetrahedra and a larger one with 4096 tetrahedra. From (Fig. 4.2.2) we can see that at $P^* = 58$ and $\phi = 0.47$ the small system exhibits an S-shaped transition from a simple fluid to a complex fluid. At higher pressures the systems jams and attains its highest packing fraction at infinite pressure ($\phi = 0.7858$). In contrast, the larger system undergoes a first-order transition on compression of the fluid phase and forms a quasicrystal.
Structural changes in the fluid are reflected in the unusual behaviour of its radial distribution function $g(r)$, as shown in (Fig. 4.2.2, e). The first peak near $r = 0.75\sigma$ disappears upon compression at low compression and then reappears at high pressure, splitting into two peaks at $r = 0.55\sigma$ and $r = 0.80\sigma$. The positions of these peaks are typical of face-to-face and edge-to-edge arrangements, respectively, within a single pentagonal dipyramid. This initial loss of structure with increasing pressure or packing fraction is strikingly different from the well-known behaviour of the hard sphere system depicted in (Fig. 4.2.2, f), and underscores the influence of shape in dense packings.

5 Conclusion

Recent years have seen development in the studies of dense packing of various 3D shapes. Dense particle packings serve as useful models of the structures of liquid, glassy and crystalline states of matter, granular media, heterogeneous materials, and biological systems. Probing the symmetries and other mathematical properties of the densest packings is an important part of material science. A revolution in novel nanoparticles and colloidal building blocks has already been enabled by recent breakthroughs in particle synthesis. New particles are poised to become the ‘atoms’ and ‘molecules’ of tomorrow’s materials if they can be successfully manipulated or assembled into useful structures. Of particular interest is the nature of random packings and the question whether such packings can ever be denser than ordered packings, especially in high spatial dimensions. The latter problem has direct relevance in communications theory.
6 Sources


