Universality of Random Close Packing?

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**Recommended with a commentary by Daan Frenkel,
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Universality of Random Close Packing?...
...or: is it time for a new Kepler conjecture?

In 1611 Kepler proposed that the densest packing of spheres could be achieved by stacking close-packed planes of spheres. In such a packing, the spheres occupy $\pi/\sqrt{18}$ ≈74.05% of space. The Kepler conjecture was (almost certainly) proved in 1998 by Thomas Hales. When we pour a large number of equal-sized spheres in a container and shake them down, we do not obtain the Kepler packing. Rather a disordered structure forms in which the spheres occupy approximately 64% of the available space. It has long been debated if this density of "random close packing" (RCP) is well defined. The Bible seems to suggest it is: "Give, and it will be given to you. A good measure, *pressed down, shaken together* and running over, will be poured into your lap" (Luke 6:38) - but, of course, we should not use the Bible as a source of scientific information (otherwise we would have to accept that π=3). The quantitative study of random close packing seems to have started with J.D. Bernal's experiments on the packing of ball bearings [1]. His experiments (and those of many others) suggested that it is impossible to compress disordered sphere packings beyond a volume fraction of approximately 64%. However, this observation does not necessarily imply that there is a well-defined density of random close packing. It could just as well be that the rate at which the density of a disordered hard-sphere packing increases with "shaking" becomes very slow around a volume fraction 64% – very slow, but not zero. If that were the case, RCP would not have a clear mechanical definition. Indeed, in 2000, Torquato, Truskett and Debenedetti [2] argued that states with a density above 64% can always be obtained by increasing the local order. This observation implies that the "mechanical" route to random close packing is ill defined. At high-enough densities, ordered structures are always favored because they occupy a larger fraction of configuration space than disordered structures.

A recent preprint by Liu and Kamien [5] makes it plausible that what counts is the number of distinct, disordered states - not their volume in configuration space. Can we count the number of such states? The answer is: Not quite yet, but the approach of ref. [5] seems to point the way. The basic idea (see [3, 4]) is the following: start with a random configuration of N ideal-gas particles in a volume V. Now switch on a soft repulsive interaction between

the particles with a finite range σ (σ is equal to the diameter of the hard spheres that we consider). For instance:

$$\begin{aligned} v(r) &= (\epsilon/\alpha)\,(1-(r/\sigma))^{\alpha} && \text{for } r \leq \sigma \\ &= 0 && \text{for } r > \sigma \end{aligned}$$

where ϵ is an arbitrary positive number that sets the energy scale and α is a positive exponent (usually between 3/2 and 5/2 – the precise value should be irrelevant). For every ideal-gas configuration, we can now determine the nearest minimum or zero of the potential energy. It is convenient to use scaled coordinates ($\mathbf{s}$) to characterize the configurations of an ideal gas in (say) a cubic box of diameter L, in such a way that the real Cartesian coordinate x_i of particle i is equal to $s_x(i)L$, with $0 \leq s_x < 1$.

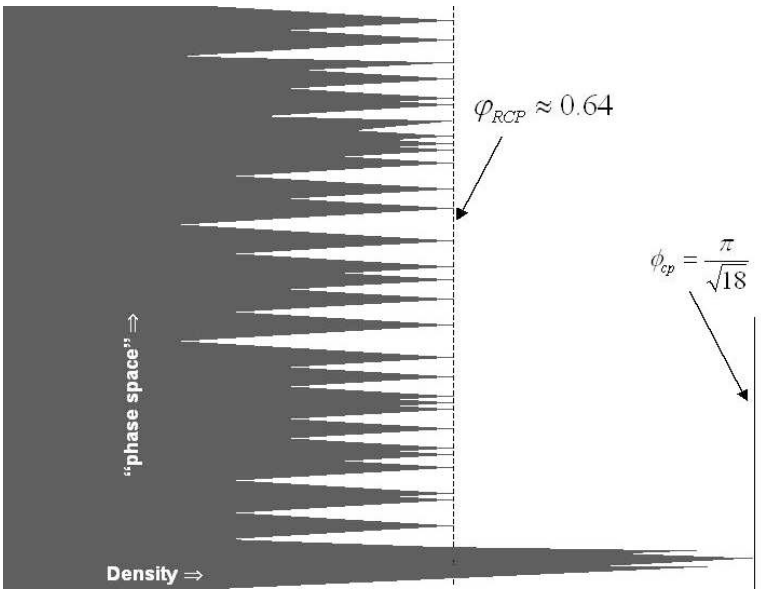

Figure 1: Sketch to illustrate that at the volume fraction of random close packing ($\phi_{RCP} \approx 0.64$), the overwhelming majority of allowed inherent structures disappear. The number of allowed crystalline structures (including structures with defects) is much smaller, and an even smaller number persists all the way up to the density of regular close packing (ϕ_{cp}).

At low densities, the states with zero potential energy will occupy a finite fraction of configuration space. However, as we decrease the volume of the system (by decreasing L), the nearest local energy minima (the "inherent structures", to use of language of ref. [6]) will one-by-one take on a finite

value of the potential energy. For every set of scaled coordinates, there is a unique density where this first happens. If we consider the limit $\epsilon \to \infty$ (hard spheres), then this density is the point where this specific inherent structure is no longer allowed. Note that every such inherent structure has its own "basin of attraction" in the space of scaled coordinates. The size of this basin of attraction may depend on the parameters of the soft repulsive potential but not the number of such basins. The key observation in refs. [3, 5] is that the simulations show that the rate at which allowed inherent structures disappear with increasing density, has a sharp maximum at a particular density. Moreover, this peak becomes sharper as the system size becomes larger. In the thermodynamic limit, the decrease of allowed inherent structures appears to be discontinuous at a hard-sphere volume fraction that happens to be very close to existing estimates of the density of random close packing (see figure 1). Note that this analysis is not affected by the fact that allowed states exist in the crystal at densities above RCP, because the *number* of distinct inherent structures in the crystal is very much smaller than of those in the disordered phase (up to RCP) – the fact that, close to the density of RCP, the total phase-space volume of the crystalline states is much larger than that of disordered states is irrelevant for the determination of RCP. However, it does imply that the entropy of the crystal at ϕ_{RCP} is much higher than that of the disordered phase – that is why hard spheres freeze above a certain volume fraction (49.4%).

The crucial point to note is that the counting of the rate of disappearance of the number of distinct, allowed inherent structures provides an unambiguous definition of RCP – there is no longer any need to specify the degree of "disorder" of the states to disentangle ordered and disordered packings. The fact that a sharp transition appears to exist implies that the evaluation of the density of RCP is now becoming a deep theoretical problem - it is a property of three-dimensional space. Finding an analytical expression for the density of RCP could become the modern sequel to the Kepler problem.

References

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