THE STRUCTURE OF THE HARD SPHERE SOLID

by

Charles Radin * and Lorenzo Sadun **

Abstract

We show that near densest-packing the perturbations of the HCP structure yield higher entropy than perturbations of any other densest packing. The difference between the various structures shows up in the correlations between motions of nearest neighbors. In the HCP structure random motion of each sphere impinges slightly less on the motion of its nearest neighbors than in the other structures.

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I. Introduction.

We are interested in the solid phase of the hard sphere gas model, a phase which is generally agreed to exist based on computer experiments refined over the past 50 years, as well as certain experiments with monodisperse colloids. Although the existence of the solid phase is uncontroversial, the internal structure of the solid is not well understood, and is the object of this paper. See [1-2] for reviews of the earliest computational work, showing the transition, and [3-9] for more recent work trying to determine the internal structure. See [10] for a relevant experiment with colloids.

The model consists of the classical statistical mechanics of point particles for which the only interaction is a hard core: the separation between particles must be at least 1. We use the canonical ensemble, corresponding to fixed density d and temperature T. (For the remainder of the paper we use the more convenient terminology of spheres rather than particles. In particular, by the "density" of a configuration of spheres we will mean the fraction of space occupied by the spheres.) In the usual way we can integrate out the velocity variables and consider the "reduced" ensemble associated only with the spatial variables. This ensemble is independent of temperature, effectively leaving only the density variable d, and consists of the uniform distribution on all configurations of the unit spheres at density d. (For a finite system of N spheres, constrained to lie in a container $C \subset \mathbb{R}^3$ of volume N/d, a configuration can be represented by the point in C^N corresponding to the centers of the spheres, and the uniform distribution is understood in the usual sense of volume in $\mathbb{R}^{3N}$.) The entropy density of the finite-sphere ensemble is then $S_{N,d} = (\log V_{N,d})/N$, where $V_{N,d}$ is the subvolume of C^N available to the (centers of the) spheres.

We will not be concerned with the solid/fluid transition, associated with density around 0.54, but with the nature of the solid near maximum possible density, $d_c = \pi/\sqrt{18} \approx 0.74$. The configurations of density d_c are known to be those obtained by 2-dimensional hexagonal layers, as follows. If we denote one such layer by α, then on either side of it we can choose either of the two ways of "filling the gaps", either β or γ. The FCC lattice corresponds to the choice $\ldots, \alpha, \beta, \gamma, \alpha, \beta, \gamma, \alpha, \beta, \gamma, \ldots$, the HCP structure is obtained from the choice $\ldots, \alpha, \beta, \alpha, \beta, \alpha, \beta, \ldots$, and there are infinitely many other "layered configurations" of the same optimal density. Since we will be concerned with an expansion of the ensemble in the deviation $\Delta d = d_c - d$, there is a minor problem with nonuniqueness of the configuration at the optimal density d_c. The ensemble is, by construction, the distribution which maximizes entropy. Our objective then is to show that, to lowest order in the deviation Δd, perturbations of the HCP layering yield the highest entropy compared with perturbations of other layerings. There is computer evidence, and experimental evidence based on colloids, that, however, it is the FCC layering which is optimal, by roughly the same magnitude effect that we obtain, 0.1%. We make many fewer assumptions than these works, and will spell out our assumptions unambiguously.

The essential question is how much "wiggle room" is available to each sphere. To first approximation, this can be computed by freezing the positions of all spheres but one, and computing the volume available to the single unfrozen sphere. FCC, HCP and all other close packing configurations give exactly the same result to this order, proportional to the volume of the Voronoi cell. The next approximation is to consider the effect that the motion of one sphere has on the volume available to its nearest neighbors. To compute this effect, we freeze the (equilibrium) positions of all but two nearest-neighbor spheres and exactly compute the volume, in $\mathbb{R}^6$, of the allowed 2-sphere configurations. When the two nearest-neighbor spheres are in the same layer, the results are the same for FCC and HCP or indeed any layering. However, when the two spheres are in adjacent layers there is slightly more available volume in the HCP case than in the FCC or any other layering. We conclude that the motion of each sphere in the HCP lattice impinges less on the motion of its neighbors than the motion of each sphere in the FCC lattice, and hence that small perturbations of the HCP lattice have more entropy than small perturbations of the FCC lattice.

II. Calculations

We choose Cartesian (x, y, z) coordinates such that there are hexagonal layers parallel to the x, y plane. In particular we will call that layer a β-plane which contains sphere centers at the origin $O = (0,0,0)$ and the six sites:

$$\begin{array}{rcl} a = (\sqrt{\tfrac{1}{4}}, \sqrt{\tfrac{3}{4}}, 0) & b = (1,0,0) & c = (\sqrt{\tfrac{1}{4}}, -\sqrt{\tfrac{3}{4}}, 0) \\ d = (-\sqrt{\tfrac{1}{4}}, -\sqrt{\tfrac{3}{4}}, 0) & e = (-1,0,0) & f = (1\sqrt{\tfrac{1}{4}}, \sqrt{\tfrac{3}{4}}, 0) \end{array} \qquad 1)$$

See Figure 1. The centers for spheres in the layers above or below this layer are possible at some of:

$$\begin{array}{rr} A^{\pm} = (0, \sqrt{\tfrac{1}{3}}, \pm\sqrt{\tfrac{2}{3}}) & B^{\pm} = (\sqrt{\tfrac{1}{4}}, \sqrt{\tfrac{1}{12}}, \pm\sqrt{\tfrac{2}{3}}) \\ C^{\pm} = (\sqrt{\tfrac{1}{4}}, -\sqrt{\tfrac{1}{12}}, \pm\sqrt{\tfrac{2}{3}}) & D^{\pm} = (0, -\sqrt{\tfrac{1}{3}}, \pm\sqrt{\tfrac{2}{3}}) \\ E^{\pm} = (-\sqrt{\tfrac{1}{4}}, -\sqrt{\tfrac{1}{12}}, \pm\sqrt{\tfrac{2}{3}}) & F^{\pm} = (-\sqrt{\tfrac{1}{4}}, \sqrt{\tfrac{1}{12}}, \pm\sqrt{\tfrac{2}{3}}) \end{array} \qquad 2)$$

See Figure 1.

Consider the Voronoi cell of the sphere centered at O. Without loss of generality, we assume there are spheres in the layer above O, with z-coordinate of the centers equal to $2/3$, at sites A^+, C^+ and E^+. We will call this an α-plane. In the layer below O, $z = -2/3$, there are spheres at either A^-, C^- and E^- (another α-plane, for instance for HCP), or at B^-, D^- and F^- (a γ-plane, for instance for FCC). In the latter case the Voronoi cell is a rhombic dodecahedron, with the 14 vertices:

$$\begin{array}{cc} (\pm\tfrac{1}{2}, -\sqrt{\tfrac{1}{12}}, \sqrt{\tfrac{1}{6}}) & (\pm\tfrac{1}{2}, \sqrt{\tfrac{1}{12}}, \sqrt{\tfrac{1}{24}}) \\ (\pm\tfrac{1}{2}, \sqrt{\tfrac{1}{12}}, -\sqrt{\tfrac{1}{6}}) & (\pm\tfrac{1}{2}, -\sqrt{\tfrac{1}{12}}, -\sqrt{\tfrac{1}{24}}) \end{array} \qquad 3a)$$

$$\begin{array}{ccc} (0, 0, \sqrt{\tfrac{3}{8}}) & (0, \sqrt{\tfrac{1}{3}}, \sqrt{\tfrac{1}{6}}) & (0, \sqrt{\tfrac{1}{3}}, -\sqrt{\tfrac{1}{24}}) \\ (0, 0, -\sqrt{\tfrac{3}{8}}) & (0, -\sqrt{\tfrac{1}{3}}, -\sqrt{\tfrac{1}{6}}) & (0, -\sqrt{\tfrac{1}{3}}, \sqrt{\tfrac{1}{24}}) \end{array} \qquad 3b)$$

and in the former case it is a trapezo-rhombic dodecahedron, with 14 vertices:

$$\begin{array}{cc} (\pm\tfrac{1}{2},\sqrt{\tfrac{1}{12}},\sqrt{\tfrac{1}{6}}) & (\pm\tfrac{1}{2},-\sqrt{\tfrac{1}{12}},\sqrt{\tfrac{1}{24}}) \\ (\pm\tfrac{1}{2},-\sqrt{\tfrac{1}{12}},-\sqrt{\tfrac{1}{24}}) & (\pm\tfrac{1}{2},\sqrt{\tfrac{1}{12}},-\sqrt{\tfrac{1}{6}}) \end{array} \tag*{4a)}$$

$$\begin{array}{ccc} (0,0,\sqrt{\tfrac{3}{8}}) & (0,-\sqrt{\tfrac{1}{3}},\sqrt{\tfrac{1}{6}}) & (0,-\sqrt{\tfrac{1}{3}},-\sqrt{\tfrac{1}{6}}) \\ (0,0,-\sqrt{\tfrac{3}{8}}) & (0,\sqrt{\tfrac{1}{3}},-\sqrt{\tfrac{1}{24}}) & (0,\sqrt{\tfrac{1}{3}},\sqrt{\tfrac{1}{24}}) \end{array} \tag*{4b)}$$

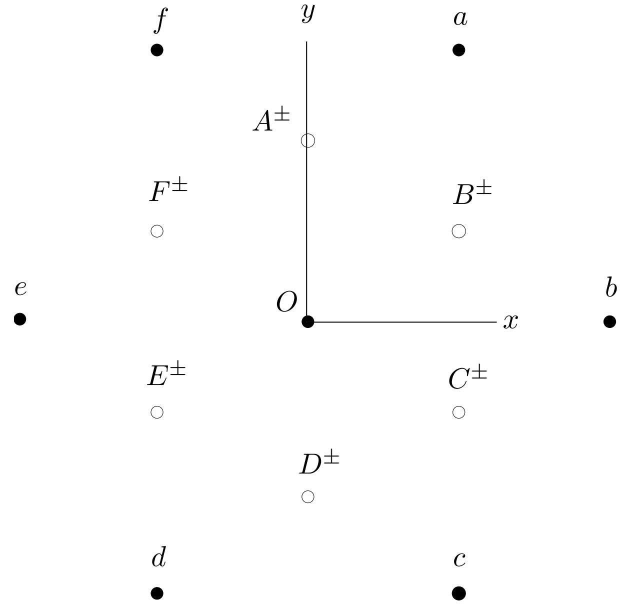

Figure 1. $A^{\pm}, B^{\pm}, \ldots, F^{\pm}$ are centers of spheres above or below the $x-y$ plane; $a, b, \ldots, f$, and O, are in the plane.

Neighboring spheres of diameter 1 centered at the sites 3) or 4) actually touch. To deal with densities below d_c it is convenient to shrink the spheres rather than move the centers. Without loss of generality we need only consider five cases of pairs of neighboring spheres as follows. As noted above, the spheres in the $z = 2/3$ plane are an α-plane, and those in the $z = 0$ plane are a β-plane. The five cases of pairs of spheres can then be chosen with centers at: O and b, with the $z = -2/3$ plane being either α or γ; or centered at O and A^+ with one of three possibilities:

α for the $z = -2/3$ plane and β for the $z = 4/3$ plane, or γ for the $z = -2/3$ plane and β for the $z = 4/3$ plane, or γ for both the $z = -2/3$ plane and the $z = 4/3$ plane. Again, our aim is to free up such a pair of spheres, leaving their environment frozen in place, and compute the volume in $\mathbb{R}^6$ available to the centers of the pair.

Imagine first that only the sphere at O is freed up from its lattice position, and consider the volume in $\mathbb{R}^3$ available for its center. The boundary of this region consists of portions of 12 spherical surfaces – think of the free sphere rolling on the surface of its frozen neighbors. If the density is close to d_c then the region is very small, and to lowest order in Δd we can linearize these surfaces, obtaining a small copy – volume of order $(\Delta d)^3$ – of the Voronoi cell of the (frozen) central sphere. Now free up the other sphere also, the one centered at A^+. Then each sphere is in part constrained by its 11 frozen neighbors, but also by the other free sphere. Again to lowest order in Δd we can assume that the constraint on each free sphere due to the other free sphere only depends on one degree of freedom, a coordinate along the line separating their frozen centers. In other words, the region available to one of the free spheres is, to lowest order in Δd, the polyhedron obtained by moving inward or outward one of the faces of the (small) Voronoi cell, simultaneously extending the faces that touch the moving face. At maximum separation each sphere is then constrained by an 11-sided polyhedron $\tilde{P}$. In Figure 2 we give an analogous 2-dimensional version of this process for a pair of circles freed up from an hexagonal packing.

The (entropic) volume V_S in $\mathbb{R}^6$ which we want to compute can then be represented as:

$$V_S = \int_{B_1}^{1} \Big[\int_{B_2}^{\frac{1}{2}-w} A_{\bar{w}}\, d\bar{w} \Big] A_w\, dw \tag*{5)}$$

where A_w represents a cross-sectional area of one of these maximal regions $\tilde{P}$, cut by a plane midway between the two spheres, and B_j refers to the end of $\tilde{P}_j$ which is opposite the other free sphere.

We have determined these cross-sectional areas, as follows. The polyhedron $\tilde{P}$ is associated with the sphere near the origin, and there are four cases to consider: whether the frozen configuration is FCC or HCP – note that every other layering would produce the same effect as one of these for this computation – and whether the second sphere is in the $z = 0$ plane or the $z = 2/3$ plane. The results are as follows.

For three of the cases, namely: FCC and the second sphere in the $z = 0$ plane, FCC and the second sphere in the $z = 2/3$ plane, and HCP and the second sphere in the $z = 0$ plane, we get the same results:

$$\frac{\pi^2}{2(\Delta d)^2} A_w = \begin{cases} \sqrt{\frac{1}{32}}(6+8w), & -\frac{1}{2} \le w \le 0 \\ \sqrt{\frac{1}{32}}(6-8w), & 0 \le w \le \frac{1}{2} \\ \sqrt{\frac{1}{32}}(8-16w+8w^2), & \frac{1}{2} \le w \le 1 \end{cases} \tag*{6)}$$

The fourth case is different, HCP and the second sphere in the $z = 2/3$ plane:

$$\frac{\pi^2}{2(\Delta d)^2} A_w = \begin{cases} \sqrt{\frac{1}{32}(16 + 48w + 36w^2)}, & -\frac{2}{3} \le w \le -\frac{1}{2} \\ \sqrt{\frac{1}{32}(\frac{37}{4} + 21w + 9w^2)}, & -\frac{1}{2} \le w \le -\frac{1}{3} \\ \sqrt{\frac{1}{32}(\frac{21}{4} - 3w - 27w^2)}, & -\frac{1}{3} \le w \le -\frac{1}{6} \\ \sqrt{\frac{1}{32}(\frac{23}{4} + 3w - 9w^2)}, & -\frac{1}{6} \le w \le 0 \\ \sqrt{\frac{1}{32}(\frac{23}{4} - 5w - 9w^2)}, & 0 \le w \le \frac{1}{6} \\ \sqrt{\frac{1}{32}(6 - 8w)}, & \frac{1}{6} \le w \le \frac{1}{2} \\ \sqrt{\frac{1}{32}(8 - 16w + 8w^2)}, & \frac{1}{2} \le w \le 1 \end{cases} \tag*{7)}$$

We graph these two functions A_w in Figure 3.

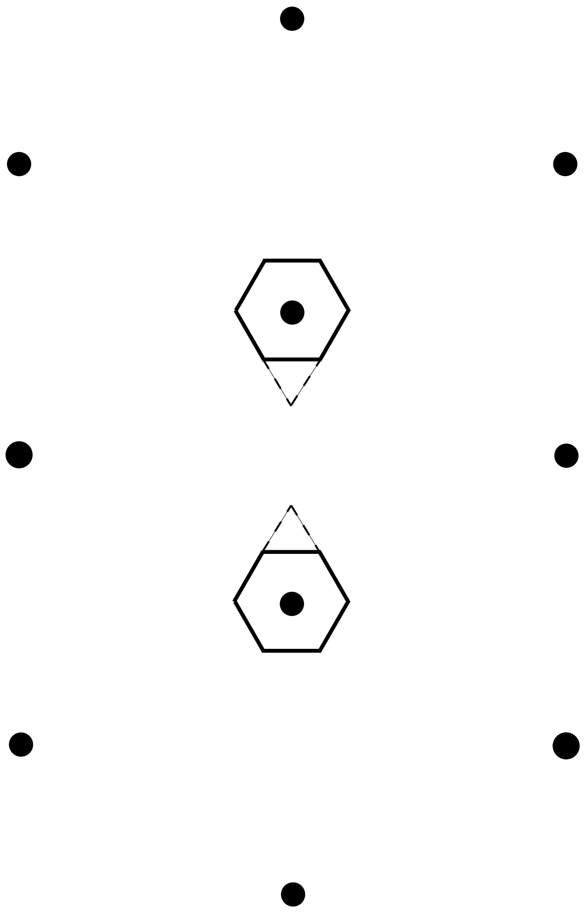

Figure 2. Small copies of the Voronoi cells of 2 disks, with dashed lines showing how they extend when the centers of the disks separate.

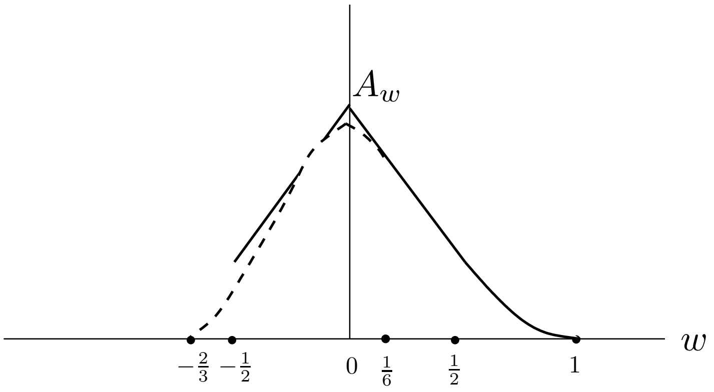

Figure 3. The 2 area functions of 6) and 7). They overlap for $w \geq 1/6$.

It only remains to compute V_S from 5) for each of the five distinct cases of pairs of neighboring spheres. We have done this and obtained the following results.

It is immediate from 6) that the two cases in which the second sphere is also in the $z = 0$ plane will have the same value, and that this value will be the same if the $z = 4/3$ and $z = -2/3$ planes are both γ – for instance FCC; this value of V_S is $(467/960)[2(\Delta d)^3/\pi^2] \approx 0.48646[2(\Delta d)^3/\pi^2]$.

If the second sphere is in the $z = 2/3$ plane, the $z = 4/3$ plane is β and the $z = -2/3$ plane is α – for instance HCP – then $V_S = (908179/1866240)[2(\Delta d)^3/\pi^2] \approx 0.48664[2(\Delta d)^3/\pi^2]$.

Finally, if the second sphere is in the $z = 2/3$ plane, the $z = 4/3$ plane is β and the $z = -2/3$ plane is γ, then $V_S = (1814587/3732480)[2(\Delta d)^3/\pi^2] \approx 0.48616[2(\Delta d)^3/\pi^2]$.

These results prove our assertion on the optimality of the HCP layering. They also allow us to quantify the entropy difference between HCP and FCC. Each off-layer "bond" in the HCP configuration has entropy $\log(908179/907848)$ greater than in the FCC configuration. Half of this difference is associated with each sphere. However, each sphere has 6 nearest neighbors in different layers, so the HCP entropy per sphere is $3\log(908179/907848) \approx 0.0011$ greater than the entropy of the FCC (and more for other layerings).

III. Summary

Our goal was to compare the entropies of certain families of perturbations of the perfect densest packings of unit spheres. We start with packings obtained from the densest packings, viewed as consisting of two dimensional hexagonal layers, by homogeneously lowering the density – for instance by uniformly shrinking the size of the spheres. From these various starting points – namely the various layerings, including FCC and HCP, which are lower density versions of the densest packings – we make two assumptions. First we look only for terms of lowest order in the deviation of density from densest packing. And second, we only consider those perturbations obtained by loosening isolated pairs of neighboring spheres from their lattice positions. Clearly the latter is our only nontrivial assumption. Our result is that perturbations of the HCP structure have the largest entropy, in contradiction with [9] in which it is claimed that the contributions from nearest neighbor spheres alone yields a preference for FCC.

IV. References

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Charles Radin, Mathematics Department, University of Texas, Austin, TX 78712
Email address: `radin@math.utexas.edu`

Lorenzo Sadun, Mathematics Department, University of Texas, Austin, TX 78712
Email address: `sadun@math.utexas.edu`