Structure of the Hard Sphere Solid

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We show that near densest packing the perturbations of the hexagonal close packed (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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Introduction.—We are interested in the solid phase of the hard sphere 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 Letter. See [1,2] for reviews of the earliest computational work, showing the transition, and [3–10] for more recent work trying to determine the internal structure. See [11] 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 Letter we use the more convenient terminology of spheres rather than particles. In particular, instead of the "density" of a configuration of spheres we will use the packing fraction, 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 packing fraction variable, d, and consists of the uniform distribution on all configurations of the unit spheres at packing fraction 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 $S_{N,d} = (\ln V_{N,d})/N$, 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 d around 0.54, but with the nature of the solid near maximum possible d, $d_c = \pi/\sqrt{18} \approx 0.74$. The configurations for $d = d_c$ are known to be those obtained from two-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 packing fraction. 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 d. 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 [10], and experimental evidence based on colloids [11], 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 compare results in the last section.

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. All close packing configurations, including fcc and hcp, give exactly the same result to this order, proportional to the volume of the Voronoi cell. However, and this a main point of this Letter, the shape of the cell varies with the stacking, and this variation makes itself felt in the next approximation, 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 two-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 this asymmetry allows the motion of each sphere in the hcp lattice to impinge 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.

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 following six sites:

$$a = \left(\frac{1}{2}, \sqrt{\frac{3}{4}}, 0\right), \qquad b = (1, 0, 0),$$
$$c = \left(\frac{1}{2}, -\sqrt{\frac{3}{4}}, 0\right), \qquad d = \left(-\frac{1}{2}, -\sqrt{\frac{3}{4}}, 0\right), \qquad (1)$$
$$e = (-1, 0, 0), \qquad f = \left(-\frac{1}{2}, \sqrt{\frac{3}{4}}, 0\right).$$

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

$$A^{\pm} = \left(0, \sqrt{\frac{1}{3}}, \pm\sqrt{\frac{2}{3}}\right), \qquad D^{\pm} = \left(0, -\sqrt{\frac{1}{3}}, \pm\sqrt{\frac{2}{3}}\right),$$
$$B^{\pm} = \left(\frac{1}{2}, \sqrt{\frac{1}{12}}, \pm\sqrt{\frac{2}{3}}\right), \qquad E^{\pm} = \left(-\frac{1}{2}, -\sqrt{\frac{1}{12}}, \pm\sqrt{\frac{2}{3}}\right),$$
$$C^{\pm} = \left(\frac{1}{2}, -\sqrt{\frac{1}{12}}, \pm\sqrt{\frac{2}{3}}\right), \qquad F^{\pm} = \left(-\frac{1}{2}, \sqrt{\frac{1}{12}}, \pm\sqrt{\frac{2}{3}}\right). \qquad (2)$$

See Fig. 1.

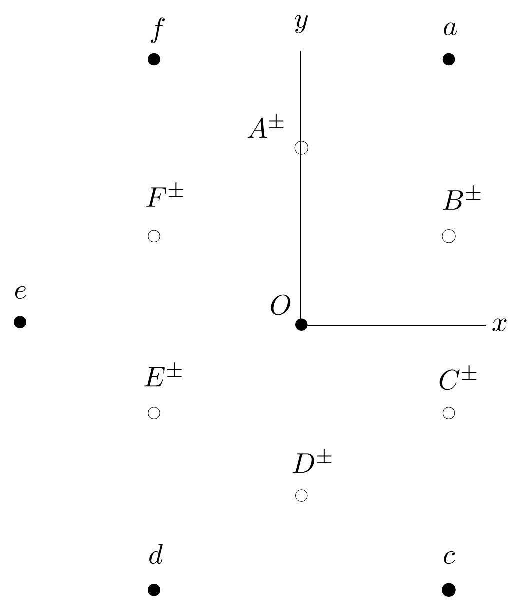

FIG. 1. $A^{\pm}, B^{\pm}, \ldots, F^{\pm}$ are centers of spheres above or below the x-y plane; $a, b, \ldots, f$, and O are in the plane.

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 $\sqrt{2/3}$, at sites A^+, C^+, and E^+. We will call this an α plane. In the layer below O, $z = -\sqrt{2/3}$, 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:

$$\pm\left(0, 0, \sqrt{\frac{3}{8}}\right), \qquad \pm\left(0, -\sqrt{\frac{1}{3}}, \sqrt{\frac{1}{6}}\right), \qquad \pm\left(0, \sqrt{\frac{1}{3}}, \sqrt{\frac{1}{24}}\right),$$
$$\pm\left(\frac{1}{2}, \sqrt{\frac{1}{12}}, \sqrt{\frac{1}{6}}\right), \qquad \pm\left(-\frac{1}{2}, \sqrt{\frac{1}{12}}, \sqrt{\frac{1}{6}}\right), \qquad (3)$$
$$\pm\left(\frac{1}{2}, -\sqrt{\frac{1}{12}}, \sqrt{\frac{1}{24}}\right), \qquad \pm\left(-\frac{1}{2}, -\sqrt{\frac{1}{12}}, \sqrt{\frac{1}{24}}\right);$$

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

$$\left(0, 0, \pm\sqrt{\frac{3}{8}}\right), \qquad \left(0, -\sqrt{\frac{1}{3}}, \pm\sqrt{\frac{1}{6}}\right), \qquad \left(0, \sqrt{\frac{1}{3}}, \pm\sqrt{\frac{1}{24}}\right),$$
$$\left(\frac{1}{2}, \sqrt{\frac{1}{12}}, \pm\sqrt{\frac{1}{6}}\right), \qquad \left(-\frac{1}{2}, \sqrt{\frac{1}{12}}, \pm\sqrt{\frac{1}{6}}\right), \qquad (4)$$
$$\left(\frac{1}{2}, -\sqrt{\frac{1}{12}}, \pm\sqrt{\frac{1}{24}}\right), \qquad \left(-\frac{1}{2}, -\sqrt{\frac{1}{12}}, \pm\sqrt{\frac{1}{24}}\right).$$

Neighboring spheres of diameter one centered at the sites (1) or (2) actually touch. To deal with d below d_c it is convenient to shrink the spheres to have diameter $1 - \epsilon$ rather than move the centers. Calculations to lowest order in Δd are equivalent to calculations to lowest order in ϵ, with the conversion $\Delta d = 3d_c\epsilon + O(\epsilon^2)$. Without loss of generality we need only consider five cases of pairs of neighboring spheres as follows. As noted above, the spheres in the $z = \sqrt{2/3}$ 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 $z = -\sqrt{2/3}$ plane being either α or γ; or centered at O and A^+ with one of three possibilities: α for the $z = -\sqrt{2/3}$ plane and β for the $z = \sqrt{8/3}$ plane, or γ for the $z = -\sqrt{2/3}$ plane and β for the $z = \sqrt{8/3}$ plane, or γ for both the $z = -\sqrt{2/3}$ plane and the $z = \sqrt{8/3}$ 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 d is close to d_c, then the region is very small, and to lowest order we can linearize these surfaces, obtaining a 2ϵ-scaled copy of the Voronoi cell of the (frozen) central sphere. In particular, the (frozen) sphere centered at a point p constrains the motion of the sphere at O only in the p direction, not in the directions perpendicular to Op.

Now free up, besides the sphere centered at O, the one centered at A^+. Each of these spheres is in part constrained by its 11 frozen neighbors, but also by the other free sphere. We introduce variables w and $\bar{w}$ to describe the constraints between the two free spheres. Let $2\epsilon w$ be the (variable) displacement of the sphere at O in the direction of A^+, and let $2\epsilon\bar{w}$ likewise be the displacement of the sphere at A^+ towards O. To lowest order in ϵ, the constraint that the free spheres place on one another is $w + \bar{w} \leq 1/2$. The 11 frozen neighbors of the sphere at O constrain it to lie in an 11-sided polyhedron $\tilde{P}$ (to leading order in ϵ), and likewise the sphere at A^+ is constrained to lie in a polyhedron $\tilde{P}'$. In Fig. 2 we give an analogous two-dimensional version of this for a pair of circles freed up from an hexagonal packing. We wish to compute the volume of the portion of the region of $\tilde{P} \times \tilde{P}'$ remaining after imposing the constraint $w + \bar{w} \leq 1/2$. Let A_w (respectively, $A'_{\bar{w}}$) be the cross-sectional area of $\tilde{P}$ ($\tilde{P}'$) for a fixed value of w ($\bar{w}$). The (entropic) volume V_S in $\mathbb{R}^6$ is

$$V_S = 4\epsilon^2 \int_{B_1}^{1} \left[\int_{B_2}^{(1/2)-w} A'_{\bar{w}} d\bar{w} \right] A_w dw, \tag{5}$$

where the lower limits of integration $B_{1,2}$, which are either $-1/2$ or $-2/3$, depend on the geometry of $\tilde{P}$ and $\tilde{P}'$.

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 $z = \sqrt{2/3}$ plane. The results are as follows.

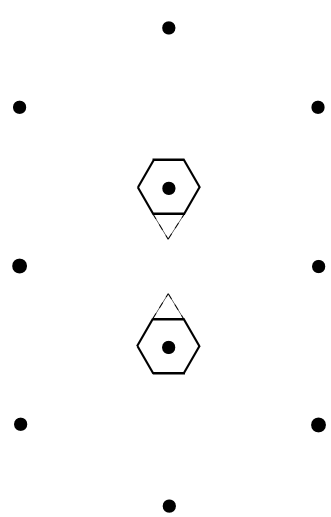

FIG. 2. Small copies of the Voronoi cells of two disks, with dashed lines showing how they extend to polygons $\tilde{P}$ and $\tilde{P}'$.

For three of the cases, namely, fcc and the second sphere in the $z = 0$ plane, fcc and the second sphere in the $z = \sqrt{2/3}$ plane, and hcp and the second sphere in the $z = 0$ plane, we get the same results:

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

The fourth case is different, hcp and the second sphere in the $z = \sqrt{2/3}$ plane:

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

We graph these two functions A_w in Fig. 3.

It remains only 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 $z = \sqrt{8/3}$ and $z = -\sqrt{2/3}$ planes are both γ—for instance, fcc; this value of V_S is $(467/960)[(2\epsilon)^6] = (467/960) \times [512(\Delta d)^6/\pi^6] \approx 0.486\,46[512(\Delta d)^6/\pi^6]$.

If the second sphere is in the $z = \sqrt{2/3}$ plane, the $z = \sqrt{8/3}$ plane is β and the $z = -\sqrt{2/3}$ plane is α—

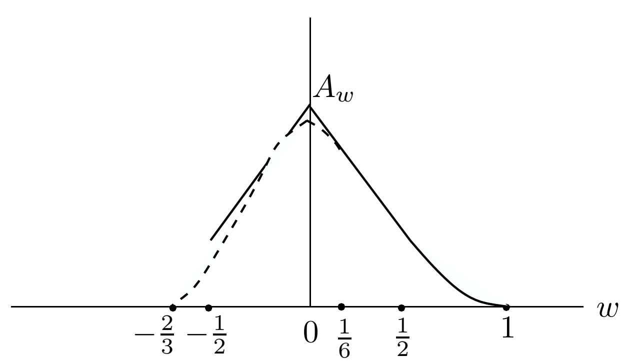

FIG. 3. The two area functions of (6) and (7). They coincide for $w \geq 1/6$.

for instance, hcp—then $V_S = (908\,179/1\,866\,240) \times [512(\Delta d)^6/\pi^6] \approx 0.486\,64[512(\Delta d)^6/\pi^6]$.

Finally, if the second sphere is in the $z = \sqrt{2/3}$ plane, the $z = \sqrt{8/3}$ plane is β and the $z = -\sqrt{2/3}$ plane is γ, then $V_S = (1\,814\,587/3\,732\,480)[512(\Delta d)^6/\pi^6] \approx 0.486\,16[512(\Delta d)^6/\pi^6]$.

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 $\ln(908\,179/907\,848)$ greater than in the fcc configuration. Half of this difference is associated with each sphere. However, each sphere has six nearest neighbors in different layers, so the hcp entropy per sphere is $3\ln(908\,179/907\,848) \approx 0.0011$ greater than the entropy of the fcc (and more for other layerings).

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 consider only those perturbations obtained by loosening isolated pairs of neighboring spheres from their lattice positions.

What we find is that a neighboring pair of free spheres, from different layers, has more room in hcp than in other layerings. As follows from our data, this is due to the asymmetry in their Voronoi cells: more than half the Voronoi cell represents the ball moving away from its neighbor than towards it. This is an important point. Although the centers of mass of the Voronoi cells are the centers of mass of the spheres, this is not the relevant average to be taking when one is simply computing the total volume; the fact that the median does not coincide with the mean here is significant. And this is where we feel that [10] goes astray. In that paper, an additional harmonic force is added to each sphere, tethering it to its nearby lattice site. But from what we have just seen this is reasonable for fcc but not for hcp, and goes to the heart of why hcp gives a small enhancement to the entropy. The effect we are analyzing is very small; in order to use the added harmonic forces, it should be demonstrated that they are negligible. But this is inherently difficult if not impossible; to show that the modified model with small but fixed coupling behaves the same as the hard sphere model, in spite of the way the added force affects hcp more than fcc, one has to analyze systems large enough to eliminate finite size effects.

Now we are claiming that the two-body effect is dominant for the entropy. There is some confirmation for this from the old paper [3] by Rudd *et al.* (not referenced in [10]), in which computer calculations show that in the hard sphere model the three-body correction is small compared to this two-body effect. We are extending those calculations to four-body and five-body corrections [12]; preliminary results show that the four-body correction is substantially smaller than the three-body correction, and that the five-body correction is smaller still.

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