Local structure of colloidal crystal-fluid interfaces

Verslag van Bachelorproject Natuur- en Sterrenkunde, omvang 12 EC, uitgevoerd in de periode 1-10-2009 tot 17-08-2010

Van der Waals-Zeeman Instituut, Faculteit der Natuurwetenschappen, Wiskunde en Informatica, Universiteit van Amsterdam

Begeleiders:

Auteur en studentnummer: Peter Schall en Duc Nguyen
Bart Weber 5619939
Tweede beoordelaar: Ben van Linden van den Heuvell

August 19, 2010
Abstract

In this writing we report a numerical method for the subdivision of hard-sphere structure into geometrical building blocks, formed by connecting the centers of touching particles (also known as canonical holes or Bernal holes). We apply this method to a colloidal crystal-fluid interface system to calculate the relative occurrence of tetrahedral, half octahedral and octahedral holes as a function of the distance to the interface. We find a typical FCC or HCP crystal signature on the solid side of the interface: 70% tetrahedral, 25% octahedral. The fluid side of the interface displays an increased level of tetrahedral holes: 85%, while octahedral holes completely vanish. We interpret this lack of octahedral holes in the context of nucleation: the octahedral hole, completed with eight tetrahedral hole forming neighbors makes an FCC unit cell, leading us to believe it can give rise to crystal nuclei.

In addition, we present a study of icosahedral order in the fluid part of our colloidal system as well as in a granular hard-sphere packing used for comparison. We find significant icosahedral order in the colloidal fluid. The icosahedral configurations do however, turn out to be fragmented in most cases. We suspect that the Brownian motion displayed by the colloidal particles in our system leads to the constant breaking and forming of icosahedral configurations. Consequently, fragmented icosahedra are measured more frequently than full icosahedra in the colloidal fluid. The granular packing used for comparison with the colloidal fluid contains mainly full icosahedra, confirming the notion that the fragmentation of icosahedral configurations in the fluid is induced by thermal fluctuations.
# Contents

1 Introduction .................................................. 3

2 Identifying Holes ............................................... 4

3 Results .......................................................... 10
   3.1 Test case: ideal crystal lattice .......................... 11
   3.2 Colloidal crystal ........................................... 11
   3.3 Colloidal Fluid .............................................. 14
   3.4 Icosahedral hard-sphere configurations ................. 18
   3.5 The colloidal crystal-fluid interface .................. 22

4 Discussion ...................................................... 24

5 Conclusions ................................................... 25
1 Introduction

Suspensions of micrometer size spherical colloids in liquid are model systems used for, among other applications, the study of crystal growth. In contrast to real solids and liquids, colloidal systems have time and length scales that are experimentally accessible: the individual particles in such systems can be visualized and tracked using confocal microscopy.

The phase behavior of colloidal suspensions is entropy driven and solely volume fraction dependent. At volume fractions above 0.545 only crystals occur. Below 0.494 colloids form a fluid and in between of these values there is a coexistence of both fluid and crystal state[1].

In our experiment we use hydrogel particles suspended in water that have a temperature dependent size. Because of a transition into a hydrophobic state, the particles shrink with increasing temperature. By applying a temperature gradient to a colloidal suspension that is in the fluid state, we grow a crystal that, at the interface where the growing stops, coexists with it’s melt. The tracking of individual particles in space and time, at and around this interface, enables us to study the local structure in both bulk crystal and bulk fluid, as well as the transition in local structure across the interface. We present a numerical method to subdivide the structure of any dense hard sphere system into geometrical building blocks that are formed by connecting the centers of touching particles, also known as canonical holes. The numbers of these different types of building blocks in our sample will be calculated to analyze the relation between local and global structure.


2 Identifying Holes

In dense hard sphere systems, the centers of touching particles can be connected to form polyhedra. Such polyhedra are basic geometric building blocks of the 3-D structure. They are also known as canonical holes\cite{2}. Figures 1 through 3 display a tetrahedral, a half octahedral and an octahedral hole, respectively. The edge length of these regular polyhedra is equal to the particle diameter.

![Figure 1: A tetrahedral hole: side view and upper view.](image1)

![Figure 2: A half octahedral hole: upper and side view.](image2)

![Figure 3: An octahedral hole.](image3)
In this work, holes are identified in the structure of dense hard-sphere systems. We find the holes from the positions of particle centers determined in 3-D with confocal microscopy. As a starting point for identifying holes, we use the Delaunay tessellation. In 2-D, the Delaunay tessellation connects points to form a triangle net that fills the plane entirely. The tessellation is chosen such that the circumcircles of the triangles in this net do not contain any other points. Delaunay triangulation is the dual structure of the Voronoi diagram. In figure 4, we show the Delaunay tessellation of ten black points in a plane and it’s relation to the Voronoi diagram.

![Figure 4: (a) Delaunay triangulation (black lines) of a set of points (black dots). The red dots are the centers of the circumcircles of the triangles. By connecting these red dots, the Voronoi diagram of the black points is made. (b) illustrates the Delaunay triangulation (black lines) and Voronoi diagram (red lines).](image)

The Delaunay triangulation (figure 4(a)) extends naturally to higher dimensions. In 3-D, the simplices are tetrahedra with empty (i.e. containing no other points) circumspheres. Figure 5 shows the Delaunay tessellation of a three-dimensional point set.

The Delaunay tessellation of the particle centers in our system provides us with a space filling set of tetrahedra. Every tetrahedron has six edges which can either connect touching particles or non-touching particles. A distance threshold, $d$, is used to distinguish between these two cases. Distances larger than $d$ are considered non-touching. Distances smaller than $d$ are considered touching. A tetrahedron with six edges that connect touching particles, gives a tetrahedral hole (see figure 1).

The relation between half octahedral hole and Delaunay tessellation is illustrated in figure 6. The set of points made by the vertices of a half octahedral hole are tessellated into two neighboring tetrahedra that share a (triangular) face (figure 6), which contains one non-touching edge.
Figure 5: Delaunay tessellation of seven points positioned in 3-D-space. The vertices of the tetrahedra form the point set. This tessellation counts eight tetrahedra.

Figure 6: Relation between Delaunay tessellation and half octahedral hole. Two tetrahedra share a non-touching edge and a third vertex. The thick edges connect touching particles. The thin edge connects non-touching particles.
Octahedral holes are couples of half octahedral holes that share their square base. In the Delaunay tessellation, four tetrahedra with a common non-touching edge make an octahedral hole. Figure 7 shows that the four tetrahedra in an octahedral hole can also be viewed as two half octahedral holes.

![Figure 7: A Delaunay tessellated octahedral hole with numbered tetrahedra. The octahedral hole can be divided into two half octahedral holes. Tetrahedron couples 1,2 and 3,4 or 1,4 and 2,3 make half octahedral holes. Thick lines connect touching particles, while the thin line connects non-touching particles.](image_url)

At this point, the necessity of the octahedral hole may not be clear. After all, any octahedral hole in the structure can be viewed as two half octahedral holes. Our choice to identify octahedral holes as unique entities is motivated by the importance of full octahedral holes in crystal structure. In our analysis, octahedral holes do not count as two half octahedral holes but as single, unique entities.

The mentioned three hole types: tetrahedral, half octahedral and octahedral hole, are the dominant building blocks of hard-sphere crystals and fluids. Using their unique descriptions, we can identify and count tetrahedral and (half) octahedral holes in a system. Other local configurations are also present in dense hard-sphere systems. Such other (i.e. non tetrahedral or (half) octahedral), larger holes require additional analysis. In contrast to the simple hole types identified earlier, for larger holes, the specific shape is not a priori known. In order to construct these larger holes, we start with the remaining Delaunay tetrahedra that are not part of the holes identified before. We identify the bounding faces of these larger holes.

From figure 6, we see that the bottom face of the half octahedron is made
by four points that lie in a plane. In general, the points that make a hole face, are positioned in one plane on the vertices of a regular polygon with side length equal to the diameter of the particles. Most hole faces are triangular, as in the tetrahedral hole (4x) and the half octahedral hole (4x), others are square (1x in the half octahedral hole). Pentagonal and hexagonal hole faces exist, but since space is scarce in dense hard sphere systems, holes and therefore hole faces are kept small.

In all cases, hole faces are triangulated in the Delaunay tessellation. Figure 8 displays a triangular, a square, a pentagonal and a hexagonal hole face as they appear in the Delaunay tessellation. The diagonal on the square hole face in figure 8(b), or the edges that triangulate the pentagon and the hexagon in figures 8(c) and 8(d) are examples of non-touching edges on hole faces.

Figure 8: Hole faces. Thick lines connect touching particles, thin lines connect non-touching particles. Tetrahedral holes have triangular faces (8(a)). Half octahedral holes also have a square face (8(b)). Larger faces, such as pentagonal (8(c)) and hexagonal (8(d)) are also possible, but scarce. All faces appear triangulated in the Delaunay tessellation.
From all non-touching edges in the system, we want to disregard those that lie along hole faces, because the remaining edges (that lie inside holes) can be used to find groups of tetrahedra that represent large holes. In two steps we attempt to build a hole face around every non-touching edge:

1. Find two neighboring triangles, "connected" by the non-touching edge that lie in one plane and therefore form a quadrilateral:

   Every edge in the Delaunay tessellation takes place in several triangles. For non-touching face edges, there are two such triangles that lie in one plane.

2. If this quadrilateral does not already make a square hole face (figure 8(b)), we investigate the possibility of attaching additional coplanar triangles on the non-touching side(s) of the quadrilateral to form a larger hole face (figures 8(c) and 8(d)).

In the Delaunay tessellation, the two ends (points) of a non-touching edge make a triangle with each of their nearest neighbor points. To find coplanar triangles (step 1), we first define nearest neighbor points as those points, that occur in Delaunay tetrahedra together with both ends of the non-touching edge under consideration. Whether or not two such triangles lie in the same plane, is verified by taking the cross product of the normal vectors of these triangles (see figure 9):

\[
\frac{|\mathbf{n}_1 \times \mathbf{n}_2|}{|\mathbf{n}_1||\mathbf{n}_2|} = \sin \theta
\]

This expression, in which \( \theta \) is the angle between normal vectors \( \mathbf{n}_1 \) and \( \mathbf{n}_2 \), allows us to test for coplanarity. \( \mathbf{n}_1 \) and \( \mathbf{n}_2 \) are computed from the triangle vertices, which are all known. A coplanarity threshold, \( c \), is introduced to limit the allowed deviation from coplanarity: if \( \theta \) is smaller than \( c \), triangles are considered to be coplanar, if \( \theta \) is larger, we consider triangles non-coplanar. Every combination of two nearest neighbor points around a non-touching edge
is checked. If none of the combinations give two coplanar triangles, the central non-touching edge cannot be a face edge. If there is one or more nearest neighbor combinations that result in coplanar triangles we have to take, for each of them, step 2.

In step 2 we consider the four sides of the quadrilateral that two coplanar triangles form together. If all four sides of the quadrilateral connect touching particles, the two triangles make a square and the non-touching edge they share is a face edge (figure 8(b)).

From figure 8(c) and 8(d), we can see that hole faces can also contain more than two triangles. If our initial non-touching edge lies along a such larger hole face, the quadrilateral around it has one or two sides connecting non-touching particles. An example would be the upper non-touching edge that lies along the hexagonal hole face in figure 8(d). The two triangles in figure 8(d) that are connected by this edge, form a quadrilateral with one non-touching side: the bottom side. Had we picked the non-touching edge in the middle of figure 8(d), the respective quadrilateral would have had two non-touching sides. Either way, step 2 requires us to investigate the possibility of extending such a quadrilateral (which can only have one or two non-touching sides) along it’s non-touching side(s). To do so, for each non-touching side of the quadrilateral we search for a nearest neighbor point, with which the non-touching side of the quadrilateral forms a new triangle coplanar to the quadrilateral. If we cannot find any coplanar triangle(s) to extend the quadrilateral, we can be certain that the initial non-touching edge is not a face edge. A quadrilateral that, on the other hand, can be extended with one or two extra triangles, makes a pentagon or a hexagon, respectively. Step 2 is again applied to these larger polygons: either they are pentagonal or hexagonal hole faces, or they need additional extension. Our algorithm contains a loop that can construct arbitrarily large hole faces.

Non-touching edges that fail to qualify as face edges are contained inside holes. Hence, by disregarding, from all non-touching edges, those that take place on the faces of holes, we obtain a collection of non-touching ”body” edges. In figure 10 we display both an example of a non-touching face edge and a non-touching body edge.

We make the distinction between non-touching edges on hole faces and non-touching edges inside holes, because the neighboring tetrahedra that share an edge that is a member of the latter group, must all be part of one and the same hole. For every non-touching body edge we find the surrounding tetrahedra. If two groups of surrounding tetrahedra around two body edges have one or more tetrahedra in common they are (part of) the same hole. The two groups should then be combined into one, bigger group. Once such overlaps have been compensated for through this merging process, each group of tetrahedra constitutes a single hole. As such, these holes can be counted and visualized.

This second method only works for holes that contain a non-touching edge. We can therefore not apply it to find tetrahedral or half octahedral holes. The octahedral hole is a special case. It does contain a non-touching edge, but since the octahedral hole can be viewed as two half octahedral holes, this edge would
Figure 10: A large hole found in the crystal. All but one of the edges inside the body that connect non-touching, opposite particles, have been taken out for clarity.

qualify as part of a hole face. Octahedral holes are identified separately from half octahedral holes because they are characteristic for crystal structure.
3 Results

A broad variety of physical systems can be constructed using hard spheres. The resemblance between a hard-sphere potential and the strong repulsion that atoms experience at very close distances makes such systems ideal models for real atomic materials. In this section we analyze the local structure in several different hard sphere packings. We put the emphasis on our colloidal system: a thermodynamic equilibrium between crystal and fluid state. In this system a close packed hard-sphere crystal coexists with it's melt. It enables us to investigate crystal-fluid coexistence at the "atomic" level, as well as local fluid and crystal structure and it's relation with bulk state.

To place our results in the colloidal system in perspective, a computer generated FCC lattice as well as a granular random hard-sphere packing is analyzed. These two systems are similar to the colloidal crystal and colloidal fluid, respectively. The main difference between the colloids and the packings used for comparison is that the colloidal system exhibits Brownian motion due to the sufficiently small size (\(\sim 1 \mu m\)) of the colloidal particles. Our colloids form a "real" physical system with crystal particles that fluctuate around their equilibrium positions in the lattice and fluid particles that can flow through the bulk, driven by that same Brownian motion (fluctuation). The larger granular particles do not move. The possibility of a structural difference between the granular packing and a snapshot of the fluid, resulting from this lack of motion is investigated.

As for the crystal, our comparison system is computer generated. The computer generated FCC lattice is close packed at a volume fraction of 0.74. Nearest neighbours in this system do actually touch and there is no free volume available for insertion of an extra particle. FCC packing occurs in real solids such as crystal lead, aluminum, copper, silver and gold. Section 3.1 treats the ideal FCC crystal. From there we will continue with the real colloidal crystal and the colloidal fluid in sections 3.2 and 3.3 respectively. The latter of these sections will include a comparison with the granular system. In section 3.4 we present a study of icosahedral order in both colloidal fluid and granular packing. We close this results chapter with a section on the colloidal crystal-fluid interface (3.5).
A computer algorithm has been written that executes the hole identification methods described in the previous section. This algorithm requires two parameters:

- $d$, the distance threshold that distinguishes non-touching distances from touching distances.
- $c$, the coplanarity threshold that limits the allowed inclination that two triangles on a hole face may possess.

Once these parameters are fixed, the algorithm identifies holes from a set of particle coordinates.

### 3.1 Test case: ideal crystal lattice

As a first test, we applied our code on a computer generated FCC lattice. In the computer generated lattice, particles are sitting on perfect lattice positions, and the above mentioned parameters can be defined easily. It is known that hard spheres, packed in FCC or HCP crystals, give 67% tetrahedral and 33% octahedral holes[3]. The absence of other hole types in such lattices precludes the necessity of the coplanarity threshold, $c$, as $c$ is only used in the identification of larger holes. For $d$, any value between the diameter of the particles, $a$, and $\sqrt{2} \cdot a$, the length of a non-touching edge in an octahedral hole, suffices.

As the size of the generated crystal increases, we observe relative hole frequencies that approach the predicted values (figure 11). At the boundaries of the crystal, octahedral holes are cut off. The resulting half octahedral holes decrease the relative frequency of tetrahedral holes, because they are smaller than full octahedral holes (figure 12). At the edges of the sample, we also observe ”quarter octahedral holes” (see figure 13). Such tetrahedra only make holes as duo’s (half octahedral) or quartets (octahedral).

### 3.2 Colloidal crystal

Moving on from the computer generated FCC lattice to the real crystal we first note that a good value of $d$ is more difficult to find. Our colloidal crystal exhibits a volume fraction of 0.54 in contrast to the 0.74 of the perfect FCC lattice. This means that every particle has some free volume. The particles used in our experiment have a diameter of roughly 1 $\mu$m, small enough to display Brownian motion within this free volume. We see thermal vibrations of the crystal lattice meaning that the instantaneous positions of the particles have some deviations from the regular crystal lattice. Although the confocal microscope averages over time in order to reduce these deviations, the difference between our real hard sphere crystal and the ideal FCC configuration remains visible. Particles are not always ”seen” by the microscope at their equilibrium positions. In addition to Brownian motion, the $\sim$ 3% polydispersity of our particles causes a broader range of nearest neighbor distances.
Figure 11: Tetrahedral, octahedral and half octahedral holes were counted in the perfect FCC lattice. As the sample size, in unit cells cubed, increases, boundary effects become marginal and the expected values are approached.

Figure 12: An image of one of the bounding faces of our cubic FCC lattice. Half octahedral holes completely fill the plane.
To find the best value for the threshold \( d \), we count tetrahedral and (half) octahedral holes at variable \( d \), and plot their frequency relative to the total number of Delaunay tetrahedra present in the sample, in figure 14.

At \( d = 1.04 \mu m \), the number of octahedral holes is maximized. We choose \( d \) to maximize the number of octahedra identified, because octahedra are the signature of crystal packing. Increasing \( d \) further than \( 1.04 \mu m \), the non-touching edge inside the body of the octahedral hole (see previous section) may for some, more tightly packed, octahedral holes be identified as an edge connecting touching particles. Such octahedral holes would then, according to our definitions, turn into congregates of four tetrahedral holes. Reducing \( d \) below \( 1.04 \mu m \), we would throw out tetrahedral and octahedral configurations that are too loosely packed (i.e. not completely touching). To strengthen our choice for \( d \), in addition to figure 14 we have also determined the pair correlation function \( g(r) \) in the crystal, which gives the probability that particle centers are separated by the distance \( r \) (figure 15). The first peak in the \( g(r) \) plot represents "touching" neighbors of the central particles. Because we want our program to consider all particles within this peak as touching neighbors, the distance threshold \( d \) should coincide with the first minimum, which it does.

In contrast to the computer generated FCC lattice, the real crystal contains large (i.e. other than tetrahedral and (half) octahedral) holes. Therefore, to calculate relative hole frequencies, we need to, in addition to the \( d \) parameter, provide a value for the \( c \) parameter. An order of magnitude estimate for \( c \) can
Figure 14: The fraction of all Delaunay tetrahedra that are (part of) tetrahedral, half octahedral or octahedral holes in the real crystal, plotted as a function of $d$.

Figure 15: Pair correlation function calculated for particles in the crystal. The first minimum is situated at roughly 1.04 $\mu$m.
be made with the help of figure 15. The first peak in figure 15 gives the mean distance between "touching" particles. Given the 0.54 rather than 0.74 volume fraction in our system, this distance is larger than the average particle diameter. The distance between the first peak and the first minimum in figure 15 illustrates the deviation from mean "touching" distance that is allowed by the $d$ threshold.

If we allow candidate particles for the formation of coplanar triangles to have an equal positional deviation in the out of plane direction, a coplanarity threshold of $\frac{d-a}{a}$ follows, where $a$ is the mean touching distance (see figure 16).

![Diagram](image)

**Figure 16:** Coplanarity parameter $c$ equals $\frac{d-a}{a}$ for small angles. $a$ is the mean "touching" distance.

Hence, $c$ is of order 0.1 rad. We have calculated the relative hole frequencies in both the colloidal crystal and colloidal fluid using $c$-values around this estimate. In the crystal the results do not depend strongly on $c$. Large holes are rare and the coplanarity threshold does therefore not play an important role in this part of our sample. However, when subdividing the structure of our colloidal crystal into canonical holes, a certain number of Delaunay tetrahedra is not designated to any hole. The abundance of such left over Delaunay tetrahedra is influenced by the value of the $c$ parameter. The left over Delaunay tetrahedra can originate from near octahedral configurations, in which two opposite particles are slightly more distant from the center of the hole, than the other four particles. If the four particles closest to the center of a such configuration are non-coplanar by the slightest bit, which, in practice, they always are, the Delaunay tessellation of the whole contains a fifth, very flat, tetrahedron (figure 17). Consequently, the octahedral hole is lost according to our description of octahedral holes in the previous section. Instead, a congregate of two half octahedral holes with a fifth unidentified Delaunay tetrahedron in between is recognized.

As the tetrahedron in between of two half octahedral holes is not in contact with any body edges and clearly it is not a tetrahedral hole, it cannot be designated to a hole and remains a "left over" Delaunay tetrahedron.

Although these near octahedral configurations do not account for all left over tetrahedra (those Delaunay tetrahedra that are not designated to any hole), they do illustrate how small deviations from perfect lattice positions can lead to errors in the acquisition of holes.
3.3 Colloidal Fluid

In the colloidal fluid relative hole frequencies depend more sensitively on the coplanarity threshold than in the colloidal crystal. The average hole size (in tetrahedra per hole) decreases with increasing $c$. Increasing the coplanarity parameter allows for more hole faces to be constructed. Therefore, the drop in average hole size was expected.

Like the colloidal crystal, the colloidal fluid contains left over Delaunay tetrahedra. Although these tetrahedra do generally not take place in between of octahedral holes with somewhat distorted particle positions (figure 17, octahedral holes are very rare in the fluid), we do suspect that they arise in similar ways as a result of noise in the data. Left over tetrahedra do not contribute to the hole statistics. We therefore adjusted $c$ to minimize undivided regions and left over tetrahedra while the total number of holes identified is maximized.

Using our code with the values of $d = 1.04 \mu m$ and $c = 0.16$ rad we can successfully divide most of the hard-sphere fluid into canonical holes. The regions that fail to divide can contain up to 100 particles. Possibly, these regions are less dense than the regions in the fluid that do divide into holes nicely. Extra free volume for the particles would cause fewer "touching" neighbors to be identified. The construction of holes requires such touching neighbors. Therefore, it is more difficult to subdivide a low density region into separate holes. Whatever the cause of undivided regions in the fluid, they have little effect on the hole statistics.
In table 1, we display the relative hole frequencies obtained in the colloidal crystal and the colloidal fluid as well as the hole frequencies in a perfect FCC lattice and the dense, granular, randomly packed hard-sphere system that was used for comparison with the colloidal fluid.

<table>
<thead>
<tr>
<th></th>
<th>tetrahedral (%)</th>
<th>octahedral (%)</th>
<th>half octahedral (%)</th>
<th>other (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC/HCP lattice</td>
<td>67</td>
<td>33</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>real crystal</td>
<td>70</td>
<td>23</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>real fluid</td>
<td>83</td>
<td>1</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>random packing</td>
<td>82</td>
<td>4</td>
<td>8</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 1: Relative hole frequencies.

The real colloidal crystal, according to our calculations, contains fewer octahedral holes than the computer generated FCC lattice. Our explanation for this discrepancy is not based on possible structural differences between the two systems, but on the noise in our data that results from:

- In the first place, the Brownian motion that particles display within their free volume.

- Tracking inaccuracy: the confocal microscope used for tracking the colloidal particles in this experiment has limited precision. Especially in the z-direction (along which the microscope focuses) it can be difficult to accurately measure particle positions.

- The polydispersity of the particles in our system (3%).

We have done some tests on computer generated FCC lattices with noise. Adding random numbers, drawn from a normal distribution with controllable spread and average zero, to every coordinate of every particle we simulated an FCC lattice with noise resulting from the above mentioned sources.

Tests on such computer generated FCC lattices with Gaussian noise, tuned to make the width of their first $g(r)$ peak resemble that of the real colloidal crystal, reveal relative hole frequencies similar to those in the real crystal. This confirms that the nature of the discrepancy between relative hole frequencies in the perfect FCC lattice and in the colloidal crystal is not structural.

Whether or not half octahedral holes in the colloidal crystal appear as couples with fifth tetrahedra in between (see figure 17) has also been investigated. Although such couples certainly appear, only a small minority of the half octahedral holes is coupled as such, to make near octahedral configurations.

Interestingly, when comparing the relative hole frequencies in the colloidal crystal to those in the colloidal fluid, full octahedral holes seem to, almost completely, disappear. Clearly the octahedral hole is a strong indicator of crystal structure. In fact, it may play an important role in nucleation. In the FCC lattice, all eight triangular faces of an octahedral hole form bases of neighboring tetrahedral holes. In the fluid, the eight faces of an octahedral hole would
also be likely to form tetrahedral holes with the particles in their surrounding. Especially since the tetrahedral hole is the densest possible local configuration of hard spheres and density is maximized locally in the fluid, this is likely to happen. Figure 18 illustrates how completing the potential tetrahedral holes surrounding an octahedral hole, gives the FCC unit cell.

Figure 18: An octahedral hole imaged in the crystal part of our sample. The eight particles that complete tetrahedral holes neighboring the octahedral hole also form the vertices of an FCC unit cell. Those vertex particles are shown at 10% of the distance threshold. The larger particles make an octahedral hole and (for clarity) are displayed at 60% of the distance threshold. The octahedron formed by connecting touching particles is shown in red. One of the eight tetrahedral holes around the octahedral hole is highlighted in black.

An octahedral hole in the fluid part of our sample may be too small to be called a nucleation site. The FCC unit cell that forms when a such octahedron receives nearest neighbors on it’s faces however, constitutes a significantly large ordered region that can serve as a nucleation site. We therefore see octahedral holes as starting points of crystal nuclei, which explains their scarcity in the bulk colloidal fluid.

Not scarce at all in the colloidal fluid are tetrahedral holes (earlier literature mentions the same abundance of tetrahedral holes in random hard sphere packings[2, 3]). Being the densest configuration, tetrahedral holes are always favored in random hard sphere packings. However, space cannot be filled with regular tetrahedra. To compensate for the high abundance of tetrahedral holes in the fluid state, larger holes have to be formed. Although we certainly observe these other holes in the fluid (see table 1) it is not their numbers so much as their size that changes across the solid-fluid interface: the average size of other holes in the fluid is larger than that of other holes in the crystal.

In the fourth row of table 1 we display the relative hole frequencies found in the granular random hard sphere packing. The particles in this system have size \( \sim 4 \text{ mm} \) and their positions are measured using laser sheet imaging. Especially
the absence of Brownian motion in this system, allows for more accurate position measurements. In figure 19 we compare the $g(r)$ plots of the granular system and the colloidal fluid.

![Graph showing $g(r)$ plots](image)

Figure 19: Red line: $g(r)$ Plot of the granular random hard sphere packing. Black line: $g(r)$ Plot of the colloidal fluid. In both cases the distance $r$ is plotted in units of $D$, the first maximum. The fluid has a less sharp $g(r)$ function.

The pair correlation functions in figure 19 give the probability that particle centers are separated by the distance $r$. The curve of the granular system has a much sharper first peak that comes out further above the other peaks than that of the colloidal system. The sharpness of the first peak indicates the range of nearest neighbor distances that can be considered touching according to our earlier definition. In the granular packing this range is small because the particles do not have a lot of free volume to move around in. The colloidal particles on the other hand, have more free volume. Also, these particles take place in a real fluid, meaning they wiggle and flow. Both effects cause the pair correlation function to smear out. The consequence of this smearing out pair correlation function for the execution of our program is that some areas, as mentioned before, fail to subdivide into canonical holes. We indeed observe such failure to a lesser degree in the granular system than in the fluid.

It is difficult to tell whether or not the structure in the granular random close packing is any different from that in the colloidal fluid. The difference in relative hole frequencies between the two systems may be noise induced. The crystal
data reveals octahedral holes to be more easily measured in low noise systems (table 1). This could explain the increase in octahedral holes in the granular system, compared to the colloidal fluid. On the other hand, the increase in octahedral holes may also reflect a higher degree of crystallization within the granular system with respect to the colloidal fluid. In our section on Icosahedral hard sphere configurations we will further elucidate possible structural differences between colloidal fluid and granular packing resulting from flow.
Subdividing hard sphere structures into canonical holes does lead to significant insight into the relation between local packing and global structure. Not all aspects of this relation can however be caught with this method. The clustering of tetrahedral holes into larger, polytetrahedral structures is a phenomenon that cannot be investigated through the canonical hole approach\cite{4,5}. Perhaps the most important manifestation of this tendency to form clusters of tetrahedral holes is the icosahedral configuration that Frank, among other authors, has highlighted before\cite{6,7}. This configuration, in which 12 particles closely surround a central particle, forming an icosahedron around it, displays a very high packing fraction. It can be subdivided into 20 tetrahedral holes, all sharing the central particle (figure 20).

Icosahedral configurations are of importance in liquid structure because of their high density\cite{6}. Where possible, the fluid tries to form icosahedral configurations. The five fold rotational symmetry of such icosahedral configurations does however make it impossible to tile 3-D space with them\cite{8}. Therefore random hard sphere packings are frustrated in the sense that their locally preferred structure (icosahedral configuration) cannot be extended globally.

In order to test whether this frustration\cite{7} also occurs in the random packings we investigated before, we have written an algorithm that can identify fragmented or full icosahedra from the coordinates of a set of particles. For the purpose of identifying (fragmented) icosahedra, the Delaunay tessellation was again selected as a first step. Icosahedral configurations are tessellated, as shown in figure 20, into 20 tetrahedral holes. It is important to notice at this point, that these 20 tetrahedra are identical. Each of the twenty tetrahedra has
the exact same environment. We have programmed a precise description of this environment in order to determine whether neighboring tetrahedral holes make (fragmented) icosahedra. The algorithm that includes this description works as follows:

1. A tetrahedral hole in the system is selected as starting point.

2. We choose one out of the four particles that make this tetrahedral hole. This particle will serve as the central particle in the to be formed icosahedral fragment (or full icosahedron).

3. We then search for other tetrahedral holes that share this central particle. All 20 tetrahedra in the Delaunay tessellation of an icosahedral configuration possess the central particle as one of their vertices, so this is a first condition any neighboring tetrahedra have to satisfy in order to be added to the fragment.

4. For each of the tetrahedra that were found in the previous step, we test whether or not they fit in the description of the environment of a tetrahedron that takes part in an icosahedral configuration. This description was mentioned before, it is written in terms of the Delaunay tessellation. That’s why the environment is tested tetrahedron by tetrahedron. It could be, for instance, that one of the tetrahedral holes that turns out to share the particle we choose as central particle, also shares two other particles with the initial tetrahedral hole. It would then be added to the icosahedron fragment because any tetrahedron in the icosahedral configuration has three such neighbors (here we mean neighbors that share three particles (see figure 20)). Of course there are also other types of neighbors that only share two particles (or just one, the central one). Those neighbors have increasingly complex descriptions in the program.

5. If neighboring tetrahedra are positioned such that they contribute to an icosahedral fragment together with the initial tetrahedral hole, they will be recognized and added to the initial four particle fragment.

6. As such, fragments are formed. Each of the four initial particles is used as a central particle. Each central particle leads to a different but partly overlapping fragment. One of the four central particles will lead to the largest icosahedral fragment. The initial tetrahedron is labelled with the size of the largest possible fragment it can form. The size of this fragment can range from four particles, a single tetrahedral hole (this means no other tetrahedra were added), to thirteen particles, a full icosahedral configuration.

All tetrahedral holes in the system are labelled with the largest possible icosahedral fragment they take part in. We can then plot the distribution of fragment size throughout the system. This has been done for our colloidal fluid and our granular random packing. The result is displayed in figure 21.
The granular random close packing contains mainly full icosahedral configurations while our colloidal fluid’s fragment size peaks at about ten out of thirteen particles. The difference between these two results can be understood from the thermal fluctuations that are present in the colloidal fluid while lacking in the granular packing. It is these thermal vibrations that cause icosahedral configurations to constantly form and break down in the colloidal fluid. The mobility of the particles in the fluid remains visible despite the fact that we look at a snapshot of the structure. In figure 22 we display full icosahedral configurations as they are found in the colloidal fluid (figure 22(a)) and in the granular packing (figure 22(b)).
Figure 22: Real icosahedral configurations found in the colloidal fluid (a) and in the granular packing (b). The particles in the colloidal fluid are displayed at a smaller diameter than those in the granular packing in order to indicate their additional free volume. The icosahedron in figure 22(a) is clearly more distorted than that in figure 22(b). The difference is caused by Brownian motion within the extra free volume.

The free volume available for particles in the fluid results in distorted and fragmented icosahedra. We suspect that in contrast to those in the granular packing, icosahedra in the fluid never last for long. They are constantly broken apart and built up again. Consequently their size distribution differs as can be seen in figure 21.
3.5 The colloidal crystal-fluid interface

Our experiment, in which a colloidal crystal coexists with its melt, exploits the excellent properties of colloids\(^1\), to directly visualize the crystal-fluid interface and the bulk phases between which it is buried, at the "atomic" level. This direct visualization, gives us the unique opportunity to study local structure in a real crystal-fluid equilibrium system. Canonical holes have proven to be a successful means of doing so. In figure 23 we illustrate the transition in local structure (in our colloidal crystal-fluid interface sample) from a solid environment into a fluid environment. It clearly shows how at around \(x = 35\) the local structure in our sample changes completely. This is where the solid-fluid interface is located. Moving away from the interface both into the fluid and into the crystal part of our sample, we observe a constant bulk structure that doesn’t change. On the right side of this transition, octahedral holes hardly occur, while tetrahedral holes become more abundant, indicating fluid structure. On the left side, though somewhat distorted by the noise (as discussed earlier), a clear crystal signature (67% tetrahedral and 33% octahedral) is present.

Icosahedral fragments larger than nine particles were also counted at and around the colloidal crystal-fluid interface. In figure 23 the concentration of icosahedral fragments is normalized by the maximum concentration found in the sample at about \(x = 38\). In agreement with the transition of relative hole frequencies, the concentration of icosahedral fragments consisting of more than nine particles increases significantly at around \(x = 35\). Indeed the colloidal fluid forms many icosahedra, confirming their favorable configuration.

In the ideal crystal lattice no icosahedron fragments larger than nine particles would be found. We argue that the presence of such fragments in our colloidal crystal merely reflects the additional free volume the particles in this crystal have with respect to ideal FCC packing: the strictness of our definition of an icosahedron overlaps in part with the natural fluctuations of the crystal, meaning particles can fluctuate into what we define as fragmented icosahedral configuration. However, the icosahedron program works well enough to outline the sharp transition between crystal and fluid state in our sample.

---

\(^1\)Colloidal particles are large enough to see with a microscope, yet small enough to have Brownian motion. Their Brownian motion enables colloids to go through entropy driven phase transitions and the transparency of our colloids allows us to use confocal microscopy to track individual particles in space and time.
Figure 23: Relative hole frequencies as a function of $x$, the axis perpendicular to the interface in the crystal-fluid equilibrium colloidal system. Left of the interface a crystal signature is present. Right of the interface, lack of octahedral holes and dominant tetrahedral holes indicate fluid structure. The coupled fraction gives the percentage of half octahedral holes taking place in full octahedral holes. For the calculation of this fraction we defined octahedral holes to be coupled half octahedral holes (in contrast to the usual distinction between full and half octahedral holes). From the ”Fraction Coupled” line we can tell that half octahedral holes in the fluid tend not to form couples. The yellow line indicates the relative concentration of icosahedral fragments containing 10-13 particles. This line is normalized to the concentration of fragments found at $x = 38$. 

28
4 Discussion

Our numerical approach to identifying holes works in the bulk of the real colloidal crystal and fluid. It is not free of problems though. We have already established that noise in the data points can lead to differing relative hole frequencies, as well as left over Delaunay tetrahedra and very large holes (see results section). In fact it has been illustrated how in particular octahedral holes, when exposed to noise, can create left over Delaunay tetrahedra and in the process be (wrongly) read as two half octahedral holes (figure).

In addition to these earlier mentioned problems, we should point out that to our knowledge, there are at least two hole types that cannot be identified with our current technique. The problem with these hole types is that when the coordinates of the particles that constitute them are Delaunay tessellated, no edges through the bodies of these holes are drawn. Since our large hole identification technique requires at least one such non-touching body edge to be drawn, the code fails in these instances and only delivers more left over tetrahedra.

The first example is the trigonal prism that’s illustrated in figure 24.

![Figure 24: Neighboring particles connected to form a trigonal prism. This hole cannot be identified by our code. Particle size is set to 90% of the touching distance.](image)

In the tessellation of this hole, any non-touching edge that may be drawn, lies along a square hole face. Such edges would, in our code, be characterized as face edges (which they are). Hence, no hole can be constructed with the tetrahedra into which this congregate is tessellated.

The second unidentifiable hole is illustrated in figure 25. This hole is sur-
rounded by six particles, five of which together make a pentagonal hole face. Just like the trigonal prism, this pentagonal hole is quite compact, causing it not to have any non-touching body edges when Delaunay tessellated. Again, the edges connecting non-touching particles would have to lie along the pentagonal hole face, so they would qualify as face edges.

Figure 25: Pentagonal hole. The Delaunay tessellation of this hole only gives non-touching face edges, along the pentagonal face.

If a hole like that in figure 25 is encountered by our code, the (usually) three Delaunay tetrahedra into which it is tessellated cannot be grouped into a hole. Instead they will be ignored and thereby added to the left over Delaunay tetrahedra, just like with the trigonal prism.

The final point we would like to address in this discussion concerns the construction of hole faces, that is used in the identification of other holes (by other holes we refer to those holes that are not classified as tetrahedral or (half) octahedral). In the identifying holes section we wrongly suggested that a quadrilateral with four equal sides makes a square. A quadrilateral with four equal sides makes a rhombus, which is not necessarily a square. However, because we are dealing with hard spheres, that cannot sit in a rhombic configuration and still touch each other, the assumption that, in our system, a quadrilateral with equal sides makes a square seems fair. In practice, of course the square hole faces may turn out to be a little rhombic here and there, because the spheres in our system are not completely touching. The same argument applies to larger hole faces: they may not be completely regular, but because the spheres do not have a lot of space to move around, hole faces are nearly regular.
5 Conclusions

We have presented a numerical method of subdividing a hard-sphere structure into canonical holes. Despite its shortcomings, this algorithm has proven to be a powerful tool in the analysis of local structure at a global scale. It has enabled us to conclude that although somewhat masked by the experimental difficulties, both real crystal and real fluid display a variety of local packings, the distribution of which is very similar to that in model solids and random packings respectively[2, 3]. In spite of its fluctuations, we find the structure of the colloidal crystal to be most similar to its ideal FCC (or HCP) counterpart.

The colloidal fluid, on the other hand, appears to contain some motion-induced structural differences with respect to the otherwise closely resembling granular packing. In particular, our icosahedron search has depicted the consequence that mobility of the particles has on local structure in a fluid. Icosahedral configurations were found to be breaking up and forming again, causing the average fragment size in the fluid to be below that in the granular packing. Clarke and Johnsson have earlier reported on a relation between icosahedral order and system volume fraction[9]. Our data, as displayed in figure 21, is in accordance with their findings which state that icosahedral order increases with system density.

Finally, we would once more like to stress the implicit relation between octahedral configuration and nucleation. As was displayed in figure 18, the octahedron is literally central to the FCC unit cell. Completed with its eight neighboring tetrahedral holes, the octahedron forms a significantly large ordered region. The tendency of a hard sphere fluid to form tetrahedral holes, leads us to believe that such neighbors are likely to take place around an octahedral hole in the fluid. The FCC unit cell, and thereby the octahedral hole, may be the first stage towards crystal nucleation. In support of this interpretation, we refer to the remarkable lack of octahedral configuration in the bulk fluid as can be seen in table 1 and figure 23.
References


