Nanostructure control of materials

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2.1 Introduction

A common paradigm in science tends to assume that things are naturally inclined to pursue order and perfection. When the atomic structure of materials is concerned, such a paradigmatic order is achieved by the endless periodic repetition of local motifs in perfect crystals. Such an assumption has a quite solid background. Indeed, there are several good reasons to choose order as a constitutive paradigm. Order is convenient, the complete information about a crystalline structure can be encoded in a very compact way by retaining only the information about a single fundamental cell plus some translational symmetry operations. Order is efficient, often the most efficient structures have high degrees of symmetry and result in crystalline arrangements. But, on the contrary, disorder is everywhere; in nature order is more the exception than the rule. This is in particular the case when complex structures are concerned as, for instance, in several nanomaterials or in other systems such as polymers, biological systems and glasses. The actual driving mechanisms that lead to such disordered structures are very diverse and range from fast out-of-equilibrium cooling (metal glasses) to evolution (biological systems). In the context of the present book, one should remark that in small systems such as nano-assemblies, the competition between the contribution from the surface with respect to the contribution from the bulk becomes extremely important and there exists a critical size below which an organized disorder is more effective than order, making in this way non-crystalline structures favorite.

It must be first clarified that disorder is not necessarily randomness; we often encounter systems that are highly organized both at the local and global scale but nevertheless do not reveal any periodic (or quasi-periodic) pattern. The study of such organized but disordered structures is very challenging and the available investigation tools appear to be inadequate to capture the essential features of these structures. Indeed, a complete description of the structure of a disordered system requires information about the exact position, orientation, shape and connectivity of each element. However, part of such information is redundant or irrelevant and several degenerate states with different microscopic realizations can share the same macroscopic properties. To determine which are the accessible configurations at the local level, and to understand which are the possible combinations which generate the global packing is of fundamental importance. In particular, finding measures for local, and global, organization is the essential starting point for understanding the basic mechanisms which form these structures. It is also an essential step in the development of technologies which enable us to control and tune the structure of amorphous materials.

In this chapter we focus on disordered sphere packings as an archetypal example. We review and discuss the most suitable paradigms and tools to investigate and classify the structure of such systems. We examine the 'typical' local configurations, their relative occurrences, their correlations, their organization and the resulting overall hierarchical structure. We show that these systems are disordered but nonetheless they are highly organized. Through several examples we show that such an organization can yield to amorphous packings which are more efficient than crystalline aggregates. We show that in small-scale systems, where small numbers of atoms in nano-sized clusters are involved, such disordered configurations can have relatively large packing fractions, large particle interconnectivity and small surface-to-volume ratio.

Our study is based on the analysis of the largest empirical dataset on disordered structures presently available in the literature. Such a dataset records the positions of more than 385,000 sphere centers in six different packings of equally sized spheres. It should be noted that, although these studies are specific to the case of equal spheres, the methodology that we use is based on the analysis of the properties and constraints resulting from the inescapable rules dictated by geometry and packings. Therefore the results are rather universal.

Each section in this chapter is organized to be as self-contained as possible with cross-references to other sections when necessary. Section 2.2 describes the empirical dataset and the sample preparation. In section 2.3 we discuss the structural organization of equal spheres packings by analyzing the radial distribution function. In section 2.4 we measure the local orientational symmetry and the occurrence of known crystalline configurations showing that no crystalline or poly-crystalline order is present – even at atomic level. The study of non-crystalline structures is pursued in further details in section 2.5 where several techniques to analyze local geometrical correlations between more than two particles are discussed and applied. We find that these systems can be conveniently described in terms of packings of (irregular) tetrahedra. The volume distribution of these tetrahedra, studied in section 2.6, indicates that these packings are formed by maximizing the configurational entropy under the geometrical constraints dictated by the non-overlapping condition.
In section 2.7 we discuss the local topological properties by measuring the number of bounds between neighboring particles. We point out that there is a bijective relation between the packing density and the system’s topological organization. The hierarchical organization beyond first neighbors is analyzed in section 2.8 where the interconnectivity of the contact network is investigated. In section 2.9 we show that disorder can be efficient and these systems can pack more tightly and effectively than several ordered crystalline systems. Conclusions, in section 2.10, summarize the main results and perspectives.

2.2 Equal spheres packings

A static stack of particles in a container can minimize its potential energy (under gravity) by maximizing the packing fraction. Such a pursuit of maximum compaction is common to several other physical systems. Notably, at atomic level this is a feature associated with metallic bonding. From a purely geometrical perspective, it is known that the largest attainable packing fraction in a system of equal spheres is \( \rho = \pi \sqrt{1/8} \approx 0.74 \) (Conway and Sloane 1997, Aste and Weaire 2000) which corresponds to a disposition of the spheres in an ordered stack of parallel hexagonal layers (forming the so-called Barlow packings). On the other hand, when equal spheres are poured in a container they spontaneously arrange in a disorderly fashion occupying a fraction of the total volume (called packing fraction or packing density \( \rho \)) between 0.55 and 0.64. As mentioned above, here we are discussing a paradigmatic example of a system where the most efficient global structure is ordered but, on the other hand, it spontaneously forms disordered arrangements. It is very interesting to note that such a disordered state is rather robust and resilient; operations such as gentle shaking or compression might change the packing fraction (within a range 0.61–0.64) but no spontaneous generation of configurations with packing fraction above ~0.64 has ever been reported. Such a packing fraction appears therefore to be an (empirical) upper limit and it is often referred to in the literature as the ‘random close packing’ limit. Larger densities can be obtained only by externally inducing (partial) crystalization.

Until now the empirical investigation of the geometrical structure of these systems has been limited by the very sparse availability of accurate experimental or numerical data. Indeed, after the seminal works of Bernal, Mason and Scott (Bernal and Mason 1960, Scott 1962, Mason 1968), only very recently the use of tomography has allowed us to ‘see’ three-dimensional structures and explore their geometry from the sphere level up to the whole packing.

2.2.1 Six samples

All the structures discussed in this chapter refer to a database constructed from the empirical analysis, by means of X-ray computed tomography, of several large samples of disorderly packed monosized spheres. The experimental technique and some of the empirical results were presented in a preliminary form in Aste et al. (2004) and in a more complete form in Aste et al. (2005b). These studies are the largest and the most accurate empirical analysis of disordered packings ever performed. The entire database collects the coordinates (with precision better than 0.1% of their diameters) of more than 385,000 spheres from six samples of monosized acrylic spheres prepared in a cylindrical container. In this chapter we refer to these samples as samples A, B, C, D, E and F. The geometrical investigation of the packing structure was performed over a central region \( G \) at 4 sphere-diameters away from the sample boundaries. (Note that spheres outside \( G \) are considered when computing the neighboring environment of spheres in \( G \).) The total number of spheres in each sample, the respective numbers in \( G \) and the sample densities are reported in Table 2.1.

<table>
<thead>
<tr>
<th>Density ( \rho )</th>
<th>N</th>
<th>( N_0 )</th>
<th>( n_c )</th>
<th>( n_1 )</th>
<th>( n_1(0.2) )</th>
<th>( n_1(0.5) )</th>
<th>( n_1(1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 0.586 ± 0.005</td>
<td>102897</td>
<td>54719</td>
<td>5.81 ± 0.3</td>
<td>3.0</td>
<td>5.5</td>
<td>6.7</td>
<td>7.5</td>
</tr>
<tr>
<td>B 0.596 ± 0.006</td>
<td>34016</td>
<td>15013</td>
<td>5.91 ± 0.2</td>
<td>2.9</td>
<td>5.9</td>
<td>6.8</td>
<td>7.7</td>
</tr>
<tr>
<td>C 0.619 ± 0.005</td>
<td>142919</td>
<td>91984</td>
<td>6.77 ± 0.2</td>
<td>3.5</td>
<td>6.4</td>
<td>7.5</td>
<td>8.4</td>
</tr>
<tr>
<td>D 0.628 ± 0.008</td>
<td>35511</td>
<td>15725</td>
<td>6.78 ± 0.2</td>
<td>3.3</td>
<td>6.0</td>
<td>7.5</td>
<td>8.4</td>
</tr>
<tr>
<td>E 0.630 ± 0.01</td>
<td>35881</td>
<td>15852</td>
<td>6.99 ± 0.2</td>
<td>3.4</td>
<td>6.3</td>
<td>7.6</td>
<td>8.6</td>
</tr>
<tr>
<td>F 0.640 ± 0.005</td>
<td>36461</td>
<td>16247</td>
<td>6.97 ± 0.2</td>
<td>3.3</td>
<td>6.9</td>
<td>7.9</td>
<td>8.9</td>
</tr>
</tbody>
</table>

2.3 Searching for structure: the radial distribution function

The radial distribution function is the probability distribution to find the center of a particle in a given position at a radial distance \( r \) from the center of a reference sphere. This measurement is widely used to characterize packing structures and contains information about long-range interparticle correlations and their organization (Scott 1962, Mason 1968, Bideau and Hansen 1993).

Figure 2.1 shows the normalized radial distribution functions \( g(r) \) for the six samples A–F (Aste et al. 2004, Aste et al. 2005b). In this figure a large peak is clearly visible at \( r/d = 1 \) which is due to the contribution from the spheres in contact. The presence of other peaks after this first peak at \( r/d = 1\) also shows the changes in the packing structures.

1. Additional material is available at: http://wwwrsphysse.anu.edu.au/ granularmatter/
1 is a clear indication that the system is organized. A structure with distinct local patterns and characteristic lengths is present. For instance, it is easy to verify that a radial distance \( r/d \sim \sqrt{3} \) is consistent with configurations made by placing the centers of four touching spheres on the vertices of two in-plane equilateral triangles which share an edge. Whereas, the peak at \( r/d = 2 \) is due to three or more spheres which are lying along a (rather) straight line.

The detail of the secondary peaks (Fig. 2.1b) shows that both the peaks at \( r/d = \sqrt{3} \) and \( r/d = 2 \) increase in height with the packing density (although with different rates (see Fig. 2.1(c)). The presence of secondary peaks is a clear indication of structural organization and the fact that these peaks sharpen

with the packing fraction certainly indicates an increasing organization. On the other hand, no signs of crystallization are detected. This is discussed in the next section.

### 2.4 Local motifs and orientation symmetry

We have seen in the previous section that the radial distribution function clearly reveals the existence of a structural organization; some typical lengths (associated with special local configurations) appear repeatedly in the packing. However, the fact that there are typical local configurations which often repeat in space does not necessarily imply that there is any long-range order or (poly)crystalline regions. In this section we discuss a method to classify and quantify the type of local orientational order. Revealing and quantifying orientational order is a key issue in establishing the type of internal organization and in particular in determining whether there exists a ‘typical’ disordered state and identifying possible tendencies towards hidden symmetries.

#### 2.4.1 Two-dimensional packings and geometrical frustration

In two dimensions, when equal disks are poured in a container, they tend to organize themselves locally into close packing configurations but, at first, such a local organization is limited to very short distances yielding to an overall disordered assembly. Some shaking can increase the density leading gradually to an overall ordered configuration. It has been argued that a similar mechanism could take place in three dimensions as well. It is, however, clear from several empirical observations that the tendency towards a crystalline order (even if short-ranged) is much less spontaneous in three dimensions than in the two-dimensional case. Such a resistance to become ordered has often been associated with ‘geometrical frustration’, which is present in three dimensions but not in two dimensions. Indeed, in two dimensions six equal disks can be placed in touch with a given central disk forming the densest possible local configuration. Such a configuration is compatible with translational symmetry and it can be repeated periodically in space leading to a crystalline packing (the triangular lattice). However, in three dimensions the closest possible local configuration is an arrangement of twelve equal spheres in touch with a central sphere and with centers on the vertices of a regular icosahedron. Such a packing has local density \( \rho = 0.754 \ldots \) (which is more than 1% denser than the configurations in Barlow packings at \( \rho = 0.740\ldots \)) (Aste and Weaire 2000). But, differently from the two-dimensional case, such a compact local icosahedral configuration is not compatible with translational symmetry and therefore it cannot be repeated in space without leaving gaps; it is geometrically frustrated.
It has often been argued that competition between the tendency to form locally compact configurations and geometrical frustration, could be the key to understanding the mechanism of formation of disordered packings and glassy structures (Aste and Coniglio 2004). If this is the case, one would expect to see, at local level, configurations with rotational symmetries characteristic of icosahedral and other closely packed structures. The study of the local packing arrangements and in particular the rotational symmetry can therefore give important insights into the mechanism of formation of these structures.

2.4.2 Local rotational symmetry

A useful method to quantify and classify rotational symmetry was introduced by Steinhardt et al. (1983). This method consists of the projection, on a spherical harmonic base, of the sets of versors pointing between a sphere and its neighbors. Such an overlap between the rotational symmetry of a spherical harmonic and the local symmetry is measured by the quantity:

\[ Q_{l}^{(i)} = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} |Y_{l,m}(\theta(\vec{r}_{i,j}), \phi(\vec{r}_{i,j}))|^2 \]

with \( Y_{l,m}(\theta(\vec{r}_{i,j}), \phi(\vec{r}_{i,j})) \) the spherical harmonics. Here \( \vec{r}_{i,j} \) is the vector between the center of sphere \( i \) and the center of a neighboring sphere \( j \) and the two quantities \( \theta(\vec{r}_{i,j}) \) and \( \phi(\vec{r}_{i,j}) \) are respectively the polar and azimuthal angles. In eqn 2.1 the average \( \langle \ldots \rangle_{l} \) is restricted only over the local bonds between a sphere and its neighbors \( j \). In this way we can associate to each sphere in the system a value of \( Q_{l} \) for \( l = 4 \) and six have special significance. For instance, the simple cubic lattice has \( Q_{6}, Q_{8}^{bc} = 0.764, 0.354 \), the body centered cubic lattice has \( Q_{4}, Q_{6}^{bc} = 0.036, 0.511 \), the fcc has \( Q_{4}, Q_{6}^{fcc} = 0.191, 0.574 \), the bcc has \( Q_{4}, Q_{6}^{bcc} = 0.097, 0.485 \) and the icosahedral rotation symmetry gives \( Q_{4}, Q_{6}^{icos} = 0.663 \). Since the lowest non-zero \( Q \) common to the icosahedral, hexagonal and the cubic symmetries is for \( l = 6 \), it has been argued by several authors that the value of \( Q_{6} \) is a good indicator of the degree of order in the system and it might be used as an 'order parameter' (Richard et al. 1999a, b, Truskett et al. 2000, Torquato et al. 2000, Kansal et al. 2002). Indeed, \( Q_{6} \) is very sensitive to any kind of crystallization and it increases significantly when order appears (Richard et al. 1999a).

On the other hand, in samples A–F, we observe (Aste et al. 2004, 2005b) that a very large fraction of local configurations (between 23 and 47%) have local symmetry characterized by \( Q_{4}, Q_{8} \) with values which are rather far from any special symmetry. This analysis reveals that there are no significant fractions of local configurations with symmetry compatible with icosahedral, simple cubic, bcc, fcc or hcp. These findings exclude the existence of any crystalline order (even at local level) and also discard the ideas that a tendency towards local frustrated icosahedral order can be responsible for the resistance to crystallize for such packings. However, these findings, although intriguing, are not conclusive because the origin and nature of the most abundant configurations with \( Q_{4}, Q_{6} \approx (0.25, 0.45) \) are still elusive. In the next section we clarify this point by using different techniques to allow viewing local packing organization from a different perspective.

2.5 Understanding the structure: local geometrical organization

The radial distribution function (section 2.3) clearly shows that despite the fact that these systems are amorphous and disordered, they have a characteristic structural organization which reveals itself regularly at local level. However, the study of the local rotational symmetry, discussed in the previous section, does not disclose any known special order. In this section we focus on techniques to identify local correlations which involve more than two neighboring spheres.

2.5.1 Voronoi shapes

Let us first consider the analysis of the shapes of Voronoi cells constructed around the center of each sphere. The Voronoi cell is a polyhedron the interior of which consists of all points closer to the center of the given sphere than to any other sphere center in the sample. It coincides and generalizes the Wigner-Seitz cell construction for crystalline systems. This is a powerful tool to investigate the local arrangement of packed objects in space and it can be used to classify their local organization. The advantage of such a method is that there is no arbitrary choice for the neighboring criteria. On the other hand, this is also its weakness because neighbors which are rather far from the central sphere (typically, up to distances \( r/d \approx 1.4 \)) contribute to the shape of the cell.

In (Aste et al. 2004, 2005b) we observe an average number of Voronoi faces which decreases with the density (see Table 2.2) from \( f = 14.6 \) at \( \rho = 0.586 \) (sample A) to \( f = 14.3 \) at \( \rho = 0.64 \) (sample F). Whereas the fractions of faces with 4, 5 and 6 edges (respectively \( f_{4}, f_{5} \) and \( f_{6} \)) follow mixed trends (see Table 2.2). These data give a clear indication that the internal structural organization of these systems is changing with the overall packing density. However, these measures are still not sensitive enough to define clearly a precise link between the local properties of the packing structure and the overall packing density.
Table 2.2 Average number of Voronoi faces \((f)\). Fractions of Voronoi faces with 4, 5 and 6 edges \(f_4, f_5\) and \(f_6\). Fraction of configurations with four and five common neighbors \(p_4\) and \(p_5\). Fraction of configurations with five bounded common neighbors disposed in a pentagonal ring \(555\). This configuration can be viewed as a ‘piece’ of icosahedron. (The threshold distance is 1.1d)

<table>
<thead>
<tr>
<th>(f)</th>
<th>(f_4) (%)</th>
<th>(f_5) (%)</th>
<th>(f_6) (%)</th>
<th>(p_4) (%)</th>
<th>(p_5) (%)</th>
<th>555 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>14.6</td>
<td>20.3</td>
<td>33.8</td>
<td>26.8</td>
<td>17.5</td>
<td>2.59</td>
</tr>
<tr>
<td>B</td>
<td>14.6</td>
<td>20.0</td>
<td>34.0</td>
<td>26.8</td>
<td>18.6</td>
<td>2.66</td>
</tr>
<tr>
<td>C</td>
<td>14.4</td>
<td>19.4</td>
<td>37.3</td>
<td>27.8</td>
<td>26.4</td>
<td>6.06</td>
</tr>
<tr>
<td>D</td>
<td>14.4</td>
<td>19.5</td>
<td>36.4</td>
<td>28.1</td>
<td>24.4</td>
<td>5.48</td>
</tr>
<tr>
<td>E</td>
<td>14.4</td>
<td>19.4</td>
<td>37.1</td>
<td>28.2</td>
<td>26.7</td>
<td>6.11</td>
</tr>
<tr>
<td>F</td>
<td>14.3</td>
<td>18.8</td>
<td>39.6</td>
<td>28.6</td>
<td>30.6</td>
<td>8.29</td>
</tr>
</tbody>
</table>

2.5.2 Common neighbors

An alternative interesting approach called ‘common-neighbor analysis of structure’ was introduced by Clarke and Jónsson (1993). This analysis is based on the study of local ‘bounds’ between particles. In particular, two spheres are ‘bounded’ if they stay within a given threshold radial distance. The study consists in analyzing the structure around couples of bounded particles, identifying common neighbors which are bounded to both the particles. In general, two touching equal spheres can have a number between 0 and 5 of common neighbors which are also in touch with both spheres. This number is rather sensitive to the local correlations in the packing. Indeed, in (Aste 2005) it is reported that the numbers of configurations with four or five common neighbors increase sensibly during compaction (see Table 2.2). In particular, when the threshold distance is fixed at 1.1d, the fraction of edges with four common neighbors \(p_4\) varies between 17 and 31%, whereas the configurations with five common neighbors \(p_5\) grow from less than 3% to above 8% (A to F). This is in agreement with observations in computer simulations and it suggests that these quantities could be profitably used as ‘order’ parameters to characterize the packing structure. Indeed, they are much more sensitive than the equivalent quantities obtained from the study of the shape of the Voronoi cell or the \(Q_4\) and \(Q_6\) measurements.

2.5.3 Searching for close local packings

We have previously discussed the facts that the closest local arrangement of equal spheres in three dimensions is achieved by 12 spheres in touch with a central sphere and placed on the vertices of a regular icosahedron. We have also shown in section 2.4 that in the samples A–F there are no traces of icosahedral rotational symmetry. However, this does not exclude the possibility that close packed configurations made by ‘pieces’ of icosahedron might be present in these structures. Signatures of icosahedral order can be singled out by analyzing in which way common neighbors arrange themselves around the two touching spheres. In particular a configuration of five bounded spheres arranged in a pentagonal ring around a couple of bounded spheres is a local signature of a (partial) icosahedral order. Such a configuration is indeed a ‘piece’ of icosahedron and therefore its occurrence within the samples is a good measure to understand whether icosahedral configurations might have played any significant role in the dynamic formation and in the static organization of such structures.

We observe (Aste, et al. 2005b) that such configurations are present only in very small fractions (from 0.01 to 0.1%, see Table 2.2), indicating therefore that this kind of close-packed local arrangement has very little statistical significance and no relevant physical importance. This observation is in agreement with the results from the \(Q_4, Q_6\) analysis in section 2.4. It appears therefore that, differently from the two-dimensional case (section 2.4), in three dimensions closed packing configurations are not present – even at the local level. A further demonstration of this comes from the study of the local volume fractions. Over a total number of more than 209,000 local Voronoi configurations, only 14 have volume fractions above 0.74 (the \(f_{cc}\) has 0.7405... and the icosahedral arrangement has 0.75...). Similar evidence can be obtained by looking at the local density associated with the Delaunay tetrahedral decomposition. Such decomposition is constructed by choosing the vertices of each tetrahedron on the centers of four neighboring spheres under the condition that no other spheres in the pack have centers within the circumsphere of the Delaunay simplex. We find that across the samples A–F only 2% of Delaunay configurations are closed tetrahedra. This is further evidence that close-packed configurations play no relevant role in the structure of these systems. This therefore also implies that geometrical frustration, resulting from local dense packing incompatible with global translational symmetry, cannot have any relevant role in the mechanism of formation of these disordered systems.

2.5.4 Dihedral angles distribution

A further step toward the understanding of which kind of local configurations are present in these systems can be undertaken by analyzing the distribution of dihedral angles between common neighbors around a given couple of bounded spheres. Previously we have calculated the number of common neighbors and shown that the most frequent configurations are the arrangements with four and five common neighbors. Let us here study how these spheres are distributed inside this common ring. To this end, we first construct the triangle between two bounded spheres and one common neighbor and then we measure the dihedral angles between such a triangle and all the other triangles formed with the other common neighbors. The resulting distribution of angles is shown in Fig. 2.2.
neighboring spheres and chosen in such a way that no other spheres in the
pack have centers within the circumsphere of each Delaunay tetrahedron.
In this section we discuss how these Delaunay tetrahedra partition space
and in particular we focus on the distribution of the Delaunay volumes. Indeed,
in a given packing some local configurations are closer and others are looser
and the whole packing is made by gluing together these local configurations
in a disordered way which is compatible with mechanical stability, geometrical
constraints and global density. The study of how space is shared among
the packed spheres is essential for understanding how efficiently the spheres
are arranged locally.

It has been observed (Aste 2005) that the volumes of the Delaunay tetrahedra
follow distributions which, at large volumes, are well described by the
exponential behavior \( P(v) \approx \exp(-\beta v/d^3) \), where the coefficients \( \beta \)
grow with the density ranging between \( \beta \approx 44 \) at \( \rho = 0.586 \) (sample A) to
\( \beta \approx 73 \) at \( \rho = 0.64 \) (sample F) (see Fig. 2.3).

In order to understand the origin of such exponential behavior, let us
consider the whole system as an ensemble of local independent cells that
freely exchange volume among each other under the constraint that the sum
over all the volumes must be a constant which characterizes the state of
the system. If we assume that: (i) cells are indistinguishable (the shapes are
ignored); (ii) there are no correlations among cells; (iii) the geometrical
constraints on the packing (stability, kissing number, etc.) have no relevance,
then the probability of finding a cell with a volume \( v \) must be given by:
\( P(v) \approx \exp(-\beta v/d^3) \), with \( \beta = d^3/\langle v \rangle \) (Aste 2005). However, this simple argument
predicts coefficients which are not satisfactory; we obtain \( \beta = 36\rho/\pi \)
which gives values for the coefficients which are one order of magnitude lower
than the empirical coefficients. On the other hand, it is also evident from Fig.
2.3 that these distributions are not pure exponentials. Indeed, they have an
exponential tail at large volumes but the exponential behavior ceases at
smaller volumes.

Looking in detail at Fig. 2.3 we observe that the exponential trend starts at
values of \( v/d^3 \) around 0.125 = 1/8. Such a critical volume is very meaningful;
it is the maximum volume for a tetrahedron made from the centers of four
spheres with two spheres in touch and the other two common touching neighbors.
A configuration which corresponds to a tetrahedron with five edges with
length equal to \( d \) and one edge with length \( \sqrt{3}/2d \). The fact that the exponential
ceases around this volume indicates that the Delaunay tetrahedra can arrange
freely in space only up to the limit when spheres get in contact and geometrical
constraints begin to be relevant. We can therefore view these systems as
comprising two phases: (i) a ‘solid’ phase made by compact tetrahedra (\( v/d^3 \)
\leq 1/8) which are geometrically constrained and are responsible for the
mechanical stability; (ii) a ‘fluid’ phase made by loose tetrahedra
(\( v/d > 1/8 \)) which are geometrically unconstrained and take volumes accordingly

2.6 A packing of tetrahedra

In the previous section, we discussed that these amorphous structures can be
conveniently viewed as the result of a packing of tetrahedra. A natural way
to study such a system of tetrahedra is the Delaunay decomposition where
space is divided into minimal tetrahedra (with vertices on the centers of

This figure shows a distribution which is symmetric in \( \theta \) and 360-\( \theta \). In
such a distribution, the largest peak is at \( \theta = \arccos(1/3) \approx 70.5^\circ \) (and 360-
\( \arccos(1/3) \approx 289.4^\circ \)) which is the dihedral angle of a regular tetrahedron.
Another (smaller) peak is visible at \( \theta = 2\arccos(1/3) \approx 141.0^\circ \) (and 218.9\ldots
\)) which corresponds to a configuration with two touching tetrahedra. This
clearly indicates that the common neighbors tend to gather together in the

The dashed lines are at the angles \( \theta = n \frac{360}{5} \) (\( n = 1, 2, 3, 4 \)), which
will correspond to icosahedral configurations.
with the distribution which maximizes entropy. We verified that, by assuming that the exponential behavior is followed only above \( \nu d^2 = 1/8 \), one can calculate analytically the coefficients at the exponent
\[
\beta^{-1} = \frac{\langle \nu \rangle}{d^3} - \frac{1}{8} = \frac{\pi}{36} - \frac{1}{8}
\]
which returns values rather close to the ones measured empirically.

### 2.7 Structural organization and packing fraction

In the previous sections we have observed that the sample density affects several local structural properties. Understanding if there is a uniform, bijective and reproducible relation between the packing properties and the sample density is of great importance because it will open up the possibility of classifying complex structures by using only the information concerning their density, which is a simple and scalar parameter.

#### 2.7.1 Neighbors in contact

In this section we address this question by looking at the average number of spheres in contact with a given sphere. This is probably the most investigated structural parameter in the literature of packings (Smith et al. 1929, Bernal and Mason 1960, Scott 1962, Mason and Clark 1966, Mason 1968, Steinhardt, et al. 1983, Seidler, et al. 2000, Aste and Weaire 2000, Sederman et al. 2001, Torquato and Stillinger 2001, Silbert et al. 2002, Kohonen et al. 2004). Indeed, this is a very simple topological quantity which gives important information about the local configurations and the packing stability. Moreover, historically this is the first topological quantity investigated in these systems (Smith et al. 1929, Bernal and Mason 1960, Scott 1962). Unfortunately, although simple in its definition, such a number is unavoidably an ill-defined quantity. Indeed, from a geometrical perspective, the information about the positions, and eventually the sizes of all spheres, are not sufficient to determine such a number; two spheres can be arbitrarily close but not in touch. In the literature several physical methods have been used (Smith et al. 1929, Bernal and Mason 1960, Scott 1962, Kohonen et al. 2004), but they encounter problems all essentially associated with the uncertainty on the correct threshold distance which must be used to distinguish between ‘touching’ and ‘non-touching’ spheres.

Here we discuss the results reported in Aste et al. (2004, 2005b) where the number of spheres in contact \( n_c \) and their distribution were calculated with great accuracy on the six samples A–F. Table 2.1 reports the values of the average number of neighbors \( n_i \) computed in \( G \) at the four different radial distances: \( r = d, 1.02d, 1.05d \) and \( 1.1d \). As one can see, this number ranges between 3 and 8.9 increasing with the sample density and the threshold distance. The probability distribution for the number of spheres within a radial distance 1.05d is plotted in Fig. 2.4. An estimate for the actual number of spheres in contact can be calculated by deconvoluting the behavior of \( n_i(r) \) (shown in Fig. 2.5) with a complementary error function normalized to \( n_c \). Such a deconvolution extracts the information on the number of neighbors in contact from the spread in \( n_i(r) \) due to the polydispersity in the sphere diameters (Aste et al. 2005b). The resulting values of \( n_c \) are also reported in Table 2.1.

#### 2.7.2 Connectivity and density: a rigidity percolation?

The relation between the average number of neighbors in contact and the packing density is shown in Fig. 2.6. As one can see there is a clear and
consistent increasing behavior of $n_c$ with the density. A similar increasing trend was also found in simulated packings (Clarke and Jönsson 1993, Yang et al. 2000). Interestingly, from Fig. 2.6 one can see that a linear extrapolation is consistent with a value $n_c = 4$ at the packing density $\rho = 0.555$. These two values have a special significance: the packing density $\rho = 0.555$ is the lowest empirically achieved and it coincides with the dilatancy onset (Onoda and Liniger 1990). On the other hand, $n_c = 4$ is the average number of neighbors required to exactly match the number of degrees of freedom with the number of constraints in these systems (Maxwell counting) (Lagrange 1788, Maxwell 1864, Aste 2005). When freedoms and constraints are exactly matched the system is isotropic (Moukarzel 1998, Edwards and Grinev 1999); the intergranular forces are uniquely determined by the balance of force and torque alone. On the contrary, an over-constrained structure can generate self-stress and the deformation of individual grains becomes relevant. In such an isotropic unstressed state, the system has zero elastic modulus (in the thermodynamic limit) (Thorpe and Chubynsky 2001, Chubynsky and Thorpe 2001), it is therefore marginally rigid and it can be seen as an intermediate state between fluid and solid (Ball and Blumenfeld 2002). The observation that such an isotropic state can be realized at densities $\rho = 0.55$ suggests that at such a density a rigidity percolation (Thorpe and Chubynsky 2001, Chubynsky and Thorpe 2001) takes place. Below $\rho = 0.55$ the system would be still a fluid, unable to sustain its own weight and it cannot be realized under gravity, above this density the system becomes (marginally) rigid and realizations start to be empirically observable.
2.8 Packing hierarchy: the topological structure beyond first neighbors

Any mechanical stress, any perturbation or any infinitesimal local displacement must propagate from particle to particle through the network of bounded neighbors (Aste et al. 2002). The understanding of the hierarchical organization of such a contact network beyond first neighbors is therefore crucial. However, such analysis is not trivial. Indeed, one must consider that in a disordered packing the local environment surrounding each particle is unique. The packing itself can be considered as a gigantic three-dimensional jigsaw puzzle where each local configuration interlocks precisely with the surrounding ones in a hierarchical organization which goes beyond first neighbors.

2.8.1 Shell analysis

In this section we apply to disordered matter an approach which was originally developed for the study of crystalline systems (Brunner and Laves 1971, O’Keeffe 1991b, Conway and Sloane 1997) and disordered foams (Aste et al. 1996a, Aste 1997). The topological structure of crystalline frameworks has been intensely studied in terms of the number of atoms that are $j$ bonds away from a given atom. If we start from a given ‘central’ atom, the first ‘shell’ (distance $j = 1$) is made by all the atoms in contact with the central one. The second shell (distance $j = 2$) consists of all atoms which are neighbors to the atoms in the first shell, excluding the central one. Moving outward, the atoms at shell $j + 1$ are all the ones which are bonded to atoms in shell $j$ and which have not been counted previously.

In the ideal case of infinite, periodic, crystalline structures with no boundaries, the number of atoms per shell should increase with the topological distance and it has been shown that, in several three-dimensional crystalline structures, the law of growth for the number of atoms ($K_j$) at shell $j$ can be described with: $K_j = a j^2 + b j + c$ (where $a$, $b$ and $c$ coefficients might vary with $j$ but only within a bounded finite interval) (Brunner and Laves 1971, O’Keeffe 1991b, Conway and Sloane 1997, Grosse-Kunstleve et al. 1996). Following the definition of O’Keeffe (1991a), the asymptotic behavior of $K_j$ can be characterized in terms of an ‘exact topological density’: $TD = (a_j)/3$ (Grosse-Kunstleve et al. 1996). It has been noted that such a topological density is interestingly related with the geometrical density of the corresponding crystalline structure and it is a powerful instrument to characterize such systems. For instance, it is easy to compute $K_j$ for the cubic lattice: $K_j = 4 j^2 + 2$. Whereas spheres packed in a bcc (body centered cubic) crystalline arrangement have $K_j = 6 j^2 + 2$ ($j > 0$). On the other hand, it has been shown (Conway and Sloane 1997) that for Barlow packings of spheres, $K_j$ are always in a narrow range with $a_j$ within 10 and 11.5. More generally, it has been observed by O’Keeffe and Hyde (1996) that for lattice sphere packings with coordination number $n$, the general rule holds, $K_j = (n - 2) j^2 + 2$, implying therefore $a = n - 2$.

Beyond perfect crystalline order very few results are known either from theoretical, empirical or numerical points of view. One can argue that $K_j$ must grow with a law comparable with the law for a spherical shell, $K_j \sim a j^2 - 4 \pi j^2$. However, it is also clear that the shape of the growing shell and its roughness can drastically influence the value of the coefficient $a$ (as observed in two-dimensional cases) (Aste et al. 1996b). Moreover, it can be shown (Aste et al. 2005a) that in some topological networks the law of growth can follow an intrinsic dimension which is different from the dimension of the embedding space (three in our case). This mechanism can produce a power law growth with exponents different from 2, or different behaviors such as exponential – or even faster – laws of growth. By applying such analysis to the six empirical samples (A–F) we observe that the number of spheres at a given topological distance $j$ from a central one follows the quadratic law

$$K_j = a j^2 + b j + c$$

up to a critical distance $\tilde{j}$, above which the shells hit the sample boundaries and $K_j$ begin to decrease (see Fig. 2.7).
2.8.2 Network interconnection

We have observed that the coefficient ‘a’ in the polynomial growth described by eqn 2.2 depends on the criterion of the threshold distance which defines bounded neighbors. Indeed, changes in the threshold distances are unavoidably associated with changes in the contact network. Such a threshold affects also the average coordination number \( n \) in the contact network (Fig. 2.5). In Fig. 2.8 we show that these two quantities are positively correlated; the coefficient \( a \) increases monotonically with \( n \). Interestingly, these disordered systems have values of the coefficient \( a \) which are consistently larger than \( a = n - 2 \) observed in lattice sphere packings. Such larger values indicate that the contact network in disordered packing is more densely inter-connected than in the analogous lattices. A topologically more compact network must correspond to structures which are more stable and robust. It appears therefore – for the first time – that disorder can, in some cases, be more efficient than order. This will be explored in further detail in the next section.

2.9 Can disorder be more efficient?

In the previous section we have observed that the contact network of a disordered sphere packing is consistently more interconnected than the equivalent network in lattice sphere packings, suggesting that disordered structures might be more stable or robust in comparison with the equivalent crystalline structures. In this section we show that disordered packings might indeed be more efficient than ordered, crystalline structures. In particular, we investigate the geometrical organization in a spherical shell within a given radial distance \( r \) from the center of a particle and we compute the number of particles, the volume and the surface of the convex hull made from the particle-centers.

2.9.1 Packing efficiency

The number of sphere centers within a radial distance \( r \) from the center of a given sphere (\( n(r) \)) can be viewed as a measure of how efficiently locally dense agglomerates of spheres are formed. We call this quantity the packing efficiency (Aste et al. 2004). It is well known that no more than 12 spheres can be found in contact with one sphere (the ‘Kissing number’) (Aste and Weaire 2000), but the upper limit for the number of spheres within a given radial distance is, in general, unknown. Figure 2.9 shows the average, the maximum and the minimum numbers of neighbors within a given radial distance from any sphere in \( G \). Clearly, there are no neighbors up to distances close to \( r = d \), when suddenly the number of neighbors increases very steeply and then, after this jump, it increases with the distance following a less steep trend with very comparable behaviors between all six samples A–F. It is of

![Graph showing the coefficient 'a' plotted as a function of the average coordination number of the contact network (n), showing that disordered packings have larger topological densities in comparison with lattice sphere packings.](image)

![Graph showing the total number of sphere centers in a cluster made by all the spheres with centers within a given radial distance r from a given sphere. The thick lines are the average cluster sizes in (G) for samples A–F. The thin lines are the clusters with maximum/minimum number of spheres at a given distance. The filled area is bounded at the top by the most efficient (largest numbers of spheres) packings among the Mackay icosahedron (Mkly) and the lattices fcc, hcp, bcc, sc.](image)
some interest to compare the empirical values of $n_i(r)$ obtained for these disordered samples with the known values in crystalline and other ordered structures.

We observe that in a large range of radial distances between $1d$ and $2d$ there are some local configurations with packing efficiencies which are above the ordered ones. Moreover, in the region around $r \sim 1.6d$, disordered packings show better average packing efficiencies than all ordered ones (Mackay icosahedron (Mkly), face centered cubic (fcc), hexagonal closed packed (hcp), body centered cubic (bcc) and simple cubic (sc)). This is rather surprising if we consider that the fcc and hcp packings are more than 15% denser than the disordered packings. Such a high efficiency is counter-intuitive; disordered systems have a lower global density therefore, inside a given volume, there must be on average a lower number of sphere-centers than in the crystalline aggregate. On the other hand, we find that in disordered packings there are spherical regions which contain on average a larger number of spheres than the equivalent ordered packings. This, although being counter-intuitive, is not a contradiction; indeed one can observe from Figs 2.9 and 2.10 that at larger distances the crystalline packings are more efficient (sc excepted) than the disordered ones. A careful analysis of Fig. 2.10 shows that disordered packings have values of the efficiency which are comparable with the crystalline close packings up to radial distances of about three sphere diameters corresponding to clusters made of about 100 spheres. In other words, small aggregates of the order of 100 spheres can spontaneously pack into disordered configurations, achieving densities comparable with the Barlow packings.

### 2.9.2 Isoperimetric quotient

When assemblies of relatively small numbers of spheres are concerned, the surface starts playing a very relevant role in determining the efficiency of the packing. Indeed, many physical systems such as atoms in metals can reduce their configurational energy by both increasing the packing fraction and decreasing the surface area. It is therefore interesting to calculate the surface area associated with the clusters of spheres within a radial distance $r$ from a central sphere. A good measure of the relative weight between surface area and volume in a cluster is the ‘isoperimetric quotient’ which measures the ratio: $36\pi (\text{volume})^2/(\text{surface area})^3$, a quantity which is always smaller or equal to 1 and reaches this maximum value for a spherical shape. Figure 2.11 shows the isoperimetric quotients for the clusters resulting from all the spheres within a given radial distance from a central sphere in the samples A–F. Such a quantity is obtained by generating the convex hull from the set of sphere centers and then calculating the volume and surface area of such convex domain. From Fig. 2.11 one observes that the isoperimetric quotient of disordered clusters can be larger than the values for crystalline clusters with the same sizes, showing therefore that, also in this respect, disorder can be more efficient than order.

![Graph showing isoperimetric quotient vs cluster size](image-url)

2.11 Average isoperimetric quotients ($36\pi (\text{volume})^2/(\text{surface area})^3$) vs number of particles in the clusters formed by all the spheres within a radial distance from a given central sphere. The empty square symbols correspond to ordered and crystalline packings (Mkly, fcc, bcc, hcp, bcc, sc).
2.10 Conclusions

In this chapter the structural properties of disordered packings of equally sized spheres have been investigated. Our efforts have been devoted to discuss and uncover several specific features that are relevant for the understanding of the structure of amorphous systems. The most important concepts and the principal findings can be schematically summarized in the following points: (i) _disorder_ is not _randomness_, characteristic lengths and similar local motifs are repeated (non-periodically) all over the systems; (ii) _amorphous systems are organized_ and such organization can be detected and quantified with several techniques; (iii) such a structural organization _extends hierarchically_ beyond first neighbors; (iv) there are no _signatures of (poly)-crystalline arrangements_ – even at local level; (v) the contact network reveals a _higher degree of connectivity_ than the equivalent crystalline structures, showing that disorder can be efficient and robust; (vi) the _local density_ in small amorphous clusters, made by all the particles within a radial distance from a central particle, can be _higher_ than in crystals and other ordered structures; (vii) such clusters can have _smaller surface extensions_ (larger isoperimetric quotient) than the equivalent ordered structures.

The analyses and discussions presented in this chapter concern packings of monosized spheres. Such packings have been considered as the archetypal form for amorphous arrangements of particles in space. On the other hand, different physical systems have distinct properties that are consequences of different interactions between particles and/or are the outcomes of different dynamics. However, in this chapter we focused on some structural properties which are the results of geometrical and topological constraints only. Therefore, the laws and properties that we have uncovered are mostly determined by the rules governing the packing of objects in space. In the quest for universality, such laws and rules should be valid and applicable to a very broad range of systems.

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2.12 References


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