

Figure 3.1: Mapping colour onto particle positions to indicate local order. a) Standard rendering of monochromatic molecules gives no additional information. However, variations of local Voronoi tessellations can quantify (b) the bond order parameter relative to the hexagonal lattice, (c) number of neighbours as defined by number of Voronoi facets, (d) the angle each molecule is orientated at relative to the x-axis, and (e) the area deviation from an expected hexagonal lattice with the same number density.

3.2 Overview of Manuscript (in Submission - 2017)

Observers may perceive that two separate images look the same but have quantifiably different intermolecular morphology. This is due to our limited ability to differentiate deviations when two images have similar densities of particles. The manuscript that follows outlines how we can quantify the internal structures of planar arrangements of particles simply by knowing their centroid positions relative to each other. The goal of this manuscript was to concatenate the tools that would best be able to quantify flat planar dispersions of particles and to implement them into an easily recognizable format where only a basic understanding of the metric will be sufficient to interpret the results.

The resulting outcome of this goal is an open source Mathematica package which focuses on the visualization of translational, entropic, and angular order metrics. In this publication, we outline how to use and interpret these the structure metrics. The manuscript also describes a way to rank disorder of molecules between similarly dense patterns by using the local descriptions for each particles to obtain a statistical mean and variation. This benefits experimentalists by providing information on how changes to sample preparation impacts the intermolecular separation and arrangement of particles. This is meant to improve experimental techniques and methods which can direct self-assemble into specific desired patterns.

The sections below highlight portions of my research that did not appear in the manuscript and/or were part of the supporting information associated with this publication. Chapter 3 expands on the interpretation and implementation of the "disLocate" tool set. The importance of visualizing the local order metrics is discussed in section 3.3. Background for each metric is in section 3.4 while also presenting the expected order metric values for the highly ordered states from which disordered patters can be gauged against. Section 3.5 discusses the influence of varying the boundary definition before applying the metrics and the influence it produces. The chapter finishes with the manuscript (in review).

3.3 The importance of visualization: mapping physics onto molecules by using colour schemes

The power of mapping physical information onto particles is really the ability to highlight exactly the regions that deviate from the expected norm. A single picture or graph can be powerful enough to prove or disprove an entire scientific conclusion [34]. The quality for well thought-out picture or graph should be its ability to quickly and effectively convey the exact information the user is

querying. For planar morphologies, additional information can be added to configurational renderings by overlaying physical information onto molecules by colouring them with a colour scheme that highlights structural deviations. This need for colourful visualization has been emphasized in a review of modern techniques for analyzing dislocations of deformed crystal structures, which found that all twelve existing methods presented structural information with some kind of colour overlay [78]. To maximize the utility of this mapping technique, the choices of colour schemes should relate to the physical interpretation of physical properties being explored and should naturally express the bounds and limitations of analysis metric.

Defining appropriate colour mappings is not a trivial task, as not only the physical parameters themselves must be considered, but also the possible range in expected variation. This concept is outlined in Figure 3.1 that shows different analysis metrics mapped onto a configuration of pentagonal molecules using different colour schemes. In Figure 3.1 a), a monochromatic grey colour is assigned to each particle and leaves all information regarding intermolecular structure up to observer interpretation. For example, the physical order metric, the bond order parameter, is a scalar quantity that ranges from zero to one (i.e. complete disorder to maximum order) [123]. Parameters with a continuous values should make use of gradient colour transitions as visual cues. The localized bond order of each particle can be represented easily with a grayscale mapping, having the colour dark if it has little to no order while white represents when a molecule is in the ordered expectation state. In Figure 3.1 b), the value of the bond order parameter is overlaid onto each molecule by converting the numerical value into a gradient scale. This quickly highlights regions where localized disorder occurs allowing for easy visual recognition of disclination lines. The gradient colour scheme provides contrast between disordered darker coloured particles from the more ordered lighter coloured particles with grain boundaries of the polycrystalline sites becoming visually distinguished from the bulk phase particles.

However, different parameters might benefit from a different colouring scheme if these values are discrete or multidimensional. The local coordination number takes on discrete values, allowing for each value to be represented by a unique colour and is shown in in Figure 3.1 c). Each particle has a unique colour that is distinct and easily differentiated from the other possible values. The downside is that this colour scheme may not be as useful when there are too many discrete values to map distinguishable colours onto. These two mappings have been creatively combined by assigning Voronoi tessellations to the gradient bond order parameter then overlaying the discrete mapping of the coordination number as coloured centroids [70]. This presents the two metrics together on a single figure, allowing for regions of angular disorder and disclination lines to become visually correlated. In another example, local properties of Voronoi area fraction, bond order, and particle displacement have been used with binned colours to indicate their local values are within certain physical bounds [71].

In some cases, the calculated metric might be continuous but a preselected discrete number of colouring bins are chosen for practical reasons. The angular orientation of each molecule and the local Voronoi area deviation were both chosen to bin specific amounts of deviation together into a single colour. In Figure 3.1 d), molecules are coloured by their the angular orientation. The angle at which each pentagon is pointing relative to the box is a continuous function, but is chosen to be represented as discrete bins. The use of four colours represents set of perpendicular reference vectors that bins angles into quadrants. This provides the distinction between neighbouring up-down pentagon pairs (seen as stripes of Red-Green/Yellow-Blue lines) which are associated with its crystal structure of the pentagonal molecules [33].

The Voronoi tessellations produced from dilute or disordered configurations will have local area partitions that are distributed around the expected Voronoi area of a hexagonal lattice with the same global number density [73]. A parameter that can have both negative or positive deviation from a mean should not use a gradient scale but instead use a colour metric that incorporate both possibilities. In Figure 3.1 e) shows molecules coloured by the amount of area deviation of the local Voronoi tessellation with respect to a hexagonal lattice with the same number density. In this case, the colour scheme of Blue to Red was selected due to its physical interpretation from

granular statistical mechanics, which utilizes the use of local volume as a proxy for local temperature [117, 52]. This is a reasonable metric to use since these steric particles do not move on noticeable timescales similar to heated molecules. High area deviation from the hexagonal pattern allows the local molecule more room to move and therefore seem more susceptible to particle displacement (more movement = "hotter") whereas molecules with this local area are expected to be in the closed-packed phase and unable to move (i.e. colder). The colour Blue is commonly interpreted with cold systems, which subconsciously links the behaviour of freezing liquids to the crystalline arrangement of the molecules into a solid. As objects heat up, they change colour via black body radiation and eventually emit into the visible spectrum with red being the first colour seen. Dark Blue sections describe local densities close to the expected result of a hexagonal lattice with the same number density. Any small deviations are likely local density frustration and not a physically different type of disorder, thus these are coloured as a lighter shade of blue (more thermal agitation, not as "cold"). Particles in a non-hexagonal non-disordered state, such as the square lattice, binned with colours of Green and Yellow with this particular arrangement having an expected value for the Voronoi area deviation of 15.47%. The sections of higher density-disorder appear in Orange and Red, colours which naturally stand out as being hotter from higher entropic movement.

Naturally, these colour schemes are subjective and highly dependent on common human experience, however, they provide a stepping point in which artistic interpretation can be fused with investigation of physical phenomena. The next section outlines how these analysis metrics are calculated before colour mapping is applied.

3.4 Expectation values for global planar structure metrics

3.4.1 Pair Correlation Function - $g(r)$

The pair correlation function is one method that can quantify the translational order of intermolecular morphology. This function describes the probability to find other particles at varying distances away from the centre of each particle. The centre of each particle is chosen as the origin to measure the distance from. A circular shell of width dr expands from the centre to a radius distance r . Any particles inside a circular shell of width Δr are counted together and binned to produce the neighbour probability $n_n(r)$ as a function of distance. This probability is then normalized by the density of the configuration ρ , which then describes its deviation from an ideal gas. Since particles of an ideal gas have equal probability to be at any distance, its pair correlation function $g(r)$ is a flat line with slope 0 with probability 1.

$$g(r) = \frac{n_n(r)}{2\pi r \Delta r \rho} \quad (3.1)$$

This function is sometimes referred to as "the radial distribution function", since it counts the distribution of neighbours over the radial dimension outwards from each particle. Short and long range translational order can be seen by the peaks in this distribution and provide probabilistic information about the relative intermolecular spacing between molecules and are commonly referred to as nearest neighbour "shells". Pair correlation functions patterns for highly ordered planar patterns are shown in Figure 3.2 a) the triangular and square lattice and a disordered hexatic state and highlights the positions of each of the first three neighbouring shells. In highly ordered states, the internal structure is evenly spaced out at specific distances meaning the pair correlation function of a periodically ordered array will produce delta functions at the specific lattice distances. The distances between particles for hexagonal and square planar lattices are shown in Table 3.1 and are normalized by the radius the particles have at the densest configuration (non-overlapping). In morphologies that are in this hexatic state (i.e. randomly jammed glass), intermolecular distances vary throughout the configuration by only small deviations away from the expected lattice positions, causing the broadening of peaks. Figure 3.2 b) shows the Fourier transform of the same morphology, showing positional ordering of the lattices with bright spots and disordered states as distributions.

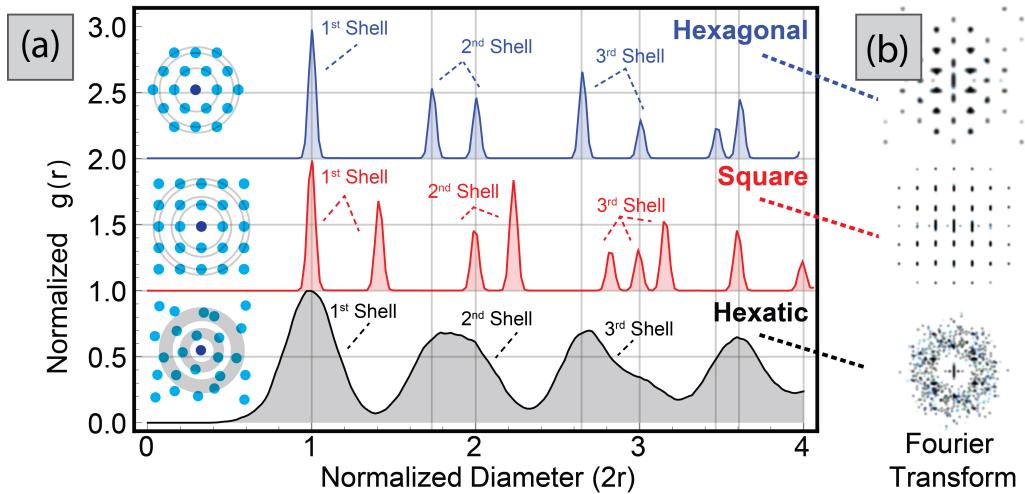


Figure 3.2: (a) Expected radial distribution functions from hexagonal lattice, square lattice, and hexatic lattice with particles displaced around the centroids of a hexagonal lattice. Insets show particles in this configuration as well as the radial width associated with the neighbour shells. (b) Fourier transforms of the particle positions which produce the associated pair correlation functions.

This equation gives exact values for the distances expected as peaks for the hexagonal lattice [87]:

$$r = (m^2 + mn + n^2)^{1/2} \quad (3.2)$$

where r is the radial distance, and m and n are integers (i.e. lattice vectors) that range from $(0, 0)$ to (m, n) . Exact values for the distances expected as peaks for the square lattice [87]:

$$r = (m^2 + n^2)^{1/2} \quad (3.3)$$

Diameter	1	2	3	4	5	6						
Lattice Hex.	1	1.732	2	2.645	3	3.461						
				4	4.358 4.582	5	5.196 5.291 5.567	6	6.082 6.245 6.557 6.928			
Square	1	1.414	2	2.236 2.828	3	3.1622 3.605	4	4.123 4.242 4.472	5	5.099 5.385 5.656	6	6.082 6.324 6.403 6.708

Table 3.1: Comparison of peak positions of the Radial Distribution Function for exact lattices (hexagonal and square) with normalized first neighbour distance as 1. This corresponds to disks with diameter equal to 1.

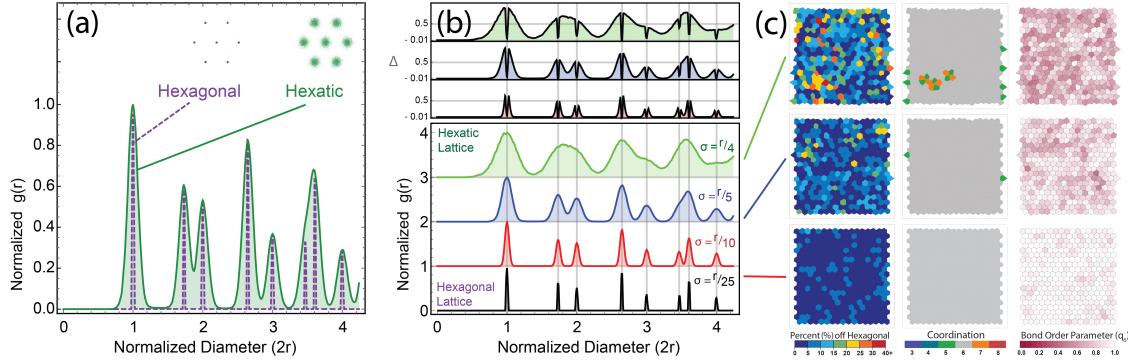


Figure 3.3: Effect of random displacements away from lattice positions. (a) Pair correlation function for hexagonal and hexatic lattice. Inset shows the relative displacement needed to broaden the $g(r)$ peaks. (b) A series of hexatic lattices with increasing mean square displacement. Lines directly connect the $g(r)$ to the (c) Voronoi tessellations of the displaced hexatic lattice positions. Tiles are colour coded (left to right): area deviation from an expected hexagonal lattice with the same number density, coordination number of neighbours as defined by number of Voronoi facets, and the bond order parameter relative to the hexagonal lattice.

3.4.2 Voronoi tessellations and local area variation

Intermolecular spacing and area fluctuation: The Voronoi tessellation partitions the substrate into sections by using the centroids of the particles. Each tile is defined by the set of perpendicular bisecting lines that defines an equal distance between objects and occurs at the midpoint of the line directly connecting the central particle to its neighbours [15]. This procedure produces localized partitions that express the maximum space each molecule can potentially possess.

Disordered systems can be analyzed by comparing the Voronoi tessellations of observed configurations to those of expected from highly ordered patterns. In disordered systems, one would expect to see a distribution in the size and shape of the local Voronoi tiles [103]. A set of closed packed circular particles will produce Voronoi tiles that are hexagonal and with an apothem equal to the twice the particle radius $2r_{\text{hex}}$ [88]. The expected mean radius of particles within the morphology $2r_\rho$ can be directly calculated generically from the global number density ρ [88]:

$$2r_\rho = \sqrt{2/(\sqrt{3}\rho)} \quad (3.4)$$

with the density ($\rho = n/A$) being the total number of objects n over the imaged area A . If the observed objects are close to this configuration, the calculated $g(r)$ should have its first peak close to the distance calculated for the lattice.

$$A^{\text{hex}} = (2\sqrt{3})(r_{\text{hex}})^2 \quad (3.5)$$

A similar radius can be calculated using the local area density of each individual particle instead. This can provide a distribution of local volume fluctuations attributed to the relative disorder away the closed-packed state. The area (A^{vor}) of a tile can be found from this radius [142].

$$2r_{\text{vor}} = \sqrt{(2/\sqrt{3})A^{\text{vor}}} \quad (3.6)$$

The hexatic lattice disorder parameter can be found through the variation of the distribution of the $2r_{\text{vor}}$ distances.

$$\Delta r^2 = \text{Var}(2r_{\text{vor}}) \quad (3.7)$$

This value describes the approximate width of the $g(r)$. The benefit of this is that the amount of hexatic disorder can be calculated as a function of local distributions in area without using the explicit center-to-center distance. This can become important when particle positions have a large approximate error from experimental observation.

Figure 3.3 a) shows the $g(r)$ from random displacements of the hexagonal lattice particles with probability to move this distance using a Gaussian probability distribution. As this distance increases, the pair correlation function spreads out into mimicking a shape of a liquid. Figure 3.3 b) shows the differences in $g(r)$ between patterns with random displacements of the hexagonal lattice particles of varying intensities. As the hexatic lattice disorder parameter rises, the broadening becomes clear in the peaks of the $g(r)$. Figure 3.3 b) shows the sequence of increasing disorder by using the visualizations for structure order parameters overlayed onto Voronoi tessellations of the configurations. The area deviation and bond order q_6 are very sensitive to the random fluctuations of points around their center, however the coordination number shows almost no change by keeping 6 neighbours throughout the fluctuations.

3.4.3 Bond order parameter - q_ℓ

The bond order parameter (q_l) is a local structure metric that describes the spatial positions of neighbours as a function of relative angular distribution between a central particle and its adjacent neighbours [123]. Classifying arc-symmetry is key for understanding melting and phase transitions of colloids [107, 100, 126] and has led to the detection of a "hexatic" phase [63].

Appropriate selection of neighbours is crucial when describing localized disorder, as the number of neighbours selected can influence the resulting analysis of the system. When selecting an appropriate distance for neighbour definition, it is possible to overshoot the closest neighbours in the first neighbour shell and take into account second-degree neighbours. One method that has been used has been to use a cutoff radius with defines neighbours as any particles within certain intermolecular distance excludes neighbours past [134, 57, 91]. This distance can be defined using a multiple of the particles diameter (usually 1.2 or 1.4 times) [123] or with the first minimum in the radial distribution function found between the first and second peaks. In submonolayer dispersions of nanoparticles, it is possible to acquire configurations where the distance between objects is much larger than the particles themselves. The use of a constant cutoff radius can provide inaccurate results by accounting for too many or too little neighbours and this would be a situation where the use of the radial distribution may not produce an accurate estimation of nearest neighbour distance. To overcome this issue, the Voronoi cell weighted definition of the bond order parameter [91] has gained our attention.

Voronoi tessellations can be used to help define the bond order parameter for very dilute systems [91]. The angle that each molecule has toward the central object can be weighted by the length of the Voronoi facet. This model allows for a continuous bond order when dealing with dilute systems. In this factor, $A(f)$ is the surface area of the Voronoi cell facet (f) separating the two neighbouring particle, and $A_{vor} = \sum_{f \in \mathcal{F}(a)} A(f)$ is the total surface area (perimeter length on 2D) of the Voronoi cell boundary $F(a)$ of particle a .

$$q'_l(a) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l \left| \sum_{f \in \mathcal{F}(a)} \frac{A(f)}{A_{vor}} Y_{l,m}(\theta_f, \phi_f) \right|^2} \quad (3.8)$$

where θ_f and ϕ_f are the spherical angles of outer normal vector \mathbf{n}_f of facet f . In this factor, $A(f)$ is the surface area of the Voronoi cell facet f separating the two neighbouring spheres that correspond to a given bond, and $A = \sum_{f \in \mathcal{F}(a)} A(f)$ is the total surface area of the Voronoi cell boundary $F(a)$ of sphere a .

The densest configuration of circular particles is a hexagonal lattice which has six nearest neighbours around every particle at a regular interval of $2\pi/6$ radians, however, particles could arrange themselves into configurations with other symmetries than six-fold. Table 3.2 shows values for the

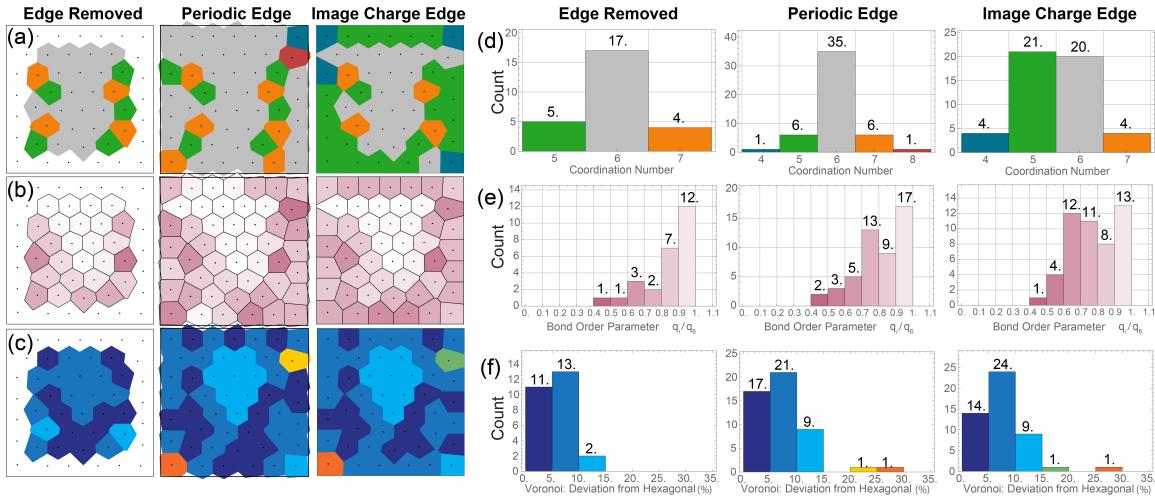


Figure 3.4: Edge definitions of virtual particles effect the statistics of disorder metrics (a) coordination number, (b) bond order q_6 (c) Voronoi area deviation

Voronoi bond order parameter q_ℓ for n neighbours spaced evenly at $2\pi/\ell$ angles. These results provide an expectation value of the maximum symmetry and can be used to normalize local particle values by to gauge the angular deviation. A particle with normalized bond order with the least deviation (closest to one), will provide information about what kind of arc-symmetry is most probable within that configuration. This normalization factor and the use of symmetries other than $\ell = 4$ and 6 is useful in separating types of arc-symmetric angular ordering of particles that can be misclassified as disordered states. I developed the use of this in for classifying relative amount of disorder of planar dispersions and explain in depth the subtle details of this normalization within the publication of section 3.6.

q_3	q_4	q_5	q_6	q_7	q_8
0.7905	0.8290	0.7015	0.7408	0.6472	0.6837

Table 3.2: Values of Voronoi bond order parameter for varying symmetry ℓ for n neighbours spaced evenly at $2\pi/\ell$ angles.

3.5 The Relation Between Edge Effects and Neighbours

3.5.1 Boundary conditions are neighbour corrections

Directing self-assembly can be done through molecular containment [31]. Larger volumes allow particles to settle into equilibrium states, whereas hard walls impose boundaries that frustrate internal particles. In many systems, the boundary conditions will influence the morphology inside the container. Analysis tools that rely on neighbour definitions, such as the bond order parameter, will provide inaccurate results when assumptions are made about objects that lay outside the boundary.

Truncated edges are ones in which objects on the boundaries are removed from the calculation. Here we make no assumptions about any unseen objects or the nature of the morphology outside the image. Figure 3.4 shows an example of how the edge particles are removed. Typically, particles are dispersed over a large area, however, only a small fraction of the morphology is actually contained within image. In this case, neighbours are calculated for all of the particles visible, however only a

subset of those are used for calculating the structural signatures. Particles with Voronoi tiles that touch or extend outside the boundary are removed from the metric statistics but still contribute as neighbours to the interior. This is done to reduce errors associated with the unknown dispersions outside the image.

Periodic boundary conditions are ones in which objects on or near the edge are translated by a set of periodic basis vectors toward the opposite side. Figure 3.4 b) shows an example of how the Voronoi tessellations are influenced by periodic boundaries. Instead of truncation with calculating neighbours along the edge, periodic boundaries include virtual particles that outside the image and are identical to the ones on the opposite side. This causes the cells to protrude outside of the image box and is represented in Figure 3.4. One thing to note is that even though local tiles may extend outwards, change in shape does not influence to global area reduced areas, causing the sum total area of the Voronoi tiles to be exactly similar to the area of the image itself. This seems to influence the order metrics to recognize these virtual particles as having hexagonal order. This is because the periodic translations cause particles to keep their local structure and because most particles are already in the hexagonal state.

Hard boundary conditions are ones in which there is a fixed container that holds the samples. This correction changes the number of neighbours that objects on the boundary have. For some analysis methods, it is crucial that the number of neighbours is properly defined. This hard edge correction imposes a set of virtual particles outside of the boundary that are equidistant and perpendicular to the wall. Conceptually, this is similar to the method of image charges. For the electric field to be zero at the boundary of a conductor, the system can be estimated by substituting in a virtual particle with opposite charge that is equidistant from the boundary. In this case, the constraint of the container can be replaced with objects outside that would produce the same steric influence as a hard box. This neighbour definition forces the Voronoi tessellation to exactly calculate cells that are within the container. This essentially mimics clipping an unbounded Voronoi tessellation into an area but adds information about neighbours outside the image and is shown in Figure 3.4. The added information from these virtual particles provides a more accurate idea of how neighbouring particles need to be arranged such that they impose the same steric influences as the box. This seems to influence the order metrics to recognize these virtual particles as causing more disorder. This is because the reflecting translations cause particles to mirror flip their local structure, which produces a fixed shape to one side of the Voronoi polygon. This seems to remove the two facets which are expected with periodic conditions to only having 1 facet that also points in a different direction.

Defining Neighbours using Method of Image Charges

The method of image charges was borrowed from the concept developed for electromagnetic physics problems [46]. The idea is that a charge that is close to a perfectly conducting wall (metal) will induce a mirror-charge that is opposite in charge and equidistant away from the conductor boundary. This produces satisfactory boundary conditions that exactly sets the electric field to zero at the conductor interface.

This method can be extended into the excluded-volume potential. Instead of image particles inducing a charge, they induce a volume-interaction which equally and oppositely imposes the particles at the boundary. This has been a very useful concept when conceptualizing and numerically implementing hard boundary conditions. In morphologies, the container acts as the excluded-volume that opposes the internal particle pressure and thus, the virtual particles are not needed for computation. In disLocate, the boundaries are replaced with a set of virtual particles that has the exact same influence as the container, allowing for a more accurate understanding of confined morphology.

This is the proper procedure in how to generate image charge virtual particles. Any particles within one or two particle radius of a hard wall edge is moved perpendicularly and equidistant away from the edge. This cutoff is needed to reduce computational cost, but to also to reduce any errors that could come from having very complex boundary (concave polygon sections) that could move

image particles onto of each other. This accounts for most of the system, but the most important part is to include image charges that produce the sharp corners. To do this, for every corner take the absolute closest particle and apply the same procedure using the corner as the mirror edge. This will result in a Voronoi cells at the edges that are exactly similar to that of the container.

In the "dislocate.m" package, the default edge definition is to ignore particles that have Voronoi cells that extend outside the container. In this case, they still count toward metrics for particles within the bulk, but do not contribute their error associated with the unknown neighbours outside the observation window. This is the most accurate way to quantify experimental systems. However, the inclusion of these particles within simulations is needed to fully describe the outcomes.