

Supporting information for

Topological phases in nanoparticle monolayers: can crystalline, hexatic, and isotropic-fluid phase coexist in the same monolayer?

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SC1. Calculation of particle density in solution from ICP-AES:

To determine the number of particles in the as synthesized Au-DDA dispersion, we have digested it in aqueous aqua regia solution for 24 h and performed the ICP AES analysis for gold. Actual gold concentration in the as synthesised Au-DDA solution was back calculated from the experimental ICP-AES data, to be 0.009 M. Knowing the gold atom concentration and the average radius of the particles, we have calculated the average number of gold particles per mL.

For this we first found out the number of atoms per sphere. This can be obtained by calculating how many unit cells can be fitted within a single NP considering spherical shape of particle with radius, $R = 2.7$ nm.

No. of unit cell = particle vol./unit cell vol. = $4/3\pi R^3 / 0.068$

Now each unit cell of Au contains 4 gold atoms

So, a single NP of radius of R, contains $4/3\pi R^3 / 0.068 \times 4 = 4848$ gold atoms,

Next, the no of spheres in original dispersion was calculated as,

0.009 M Au-DDA solution contains $\sim 5 \times 10^{21}$ Au atoms per mL,

So, 0.009 M Au-DDA solution contains total, $5 \times 6.023 \times 10^{21} / 4848 \approx 10^{18}$ spheres per mL,

Therefore, the average number of gold particles per mL of as synthesized Au-DDA dispersion is $\sim 10^{18}$ particles/mL.

Determining the number of particles in the experimental nanofluid droplet, was then straight forward. We performed 100 times dilution of this 0.009 M Au-DDA solution for TEM imaging. Therefore, the particle density in the droplet used for TEM analysis is $\sim 10^{16}$ particles per mL.

SC2: Detailed chart of different characteristics that were determined from TEM images. The image details can be found in the following pages.

Phase	Image name	Number	Density	Ψ^{global}	p_{25}
Crystalline	a1	1631	0.0079	0.805	0.0153
	a2	657	0.0081	0.871	0.0213
Hexatic	b1	983	0.0099	0.762	0.0406
	b2	1955	0.0094	0.65	0.045
	b3	4050	0.0084	0.665	0.219
	b4	3217	0.0093	0.694	0.1041
	b5	1959	0.0094	0.66	0.0607
	b6	3443	0.0069	0.623	0.0296
	b7	2166	0.0176	0.782	0.147
	b8	2433	0.0198	0.726	0.116
	b9	2214	0.0106	0.782	0.072
Isotropic	c1	1790	0.0087	0.55	0.1016
	c2	2471	0.0075	0.534	0.163
	c3	3281	0.0072	0.54	0.159

Supporting Figures

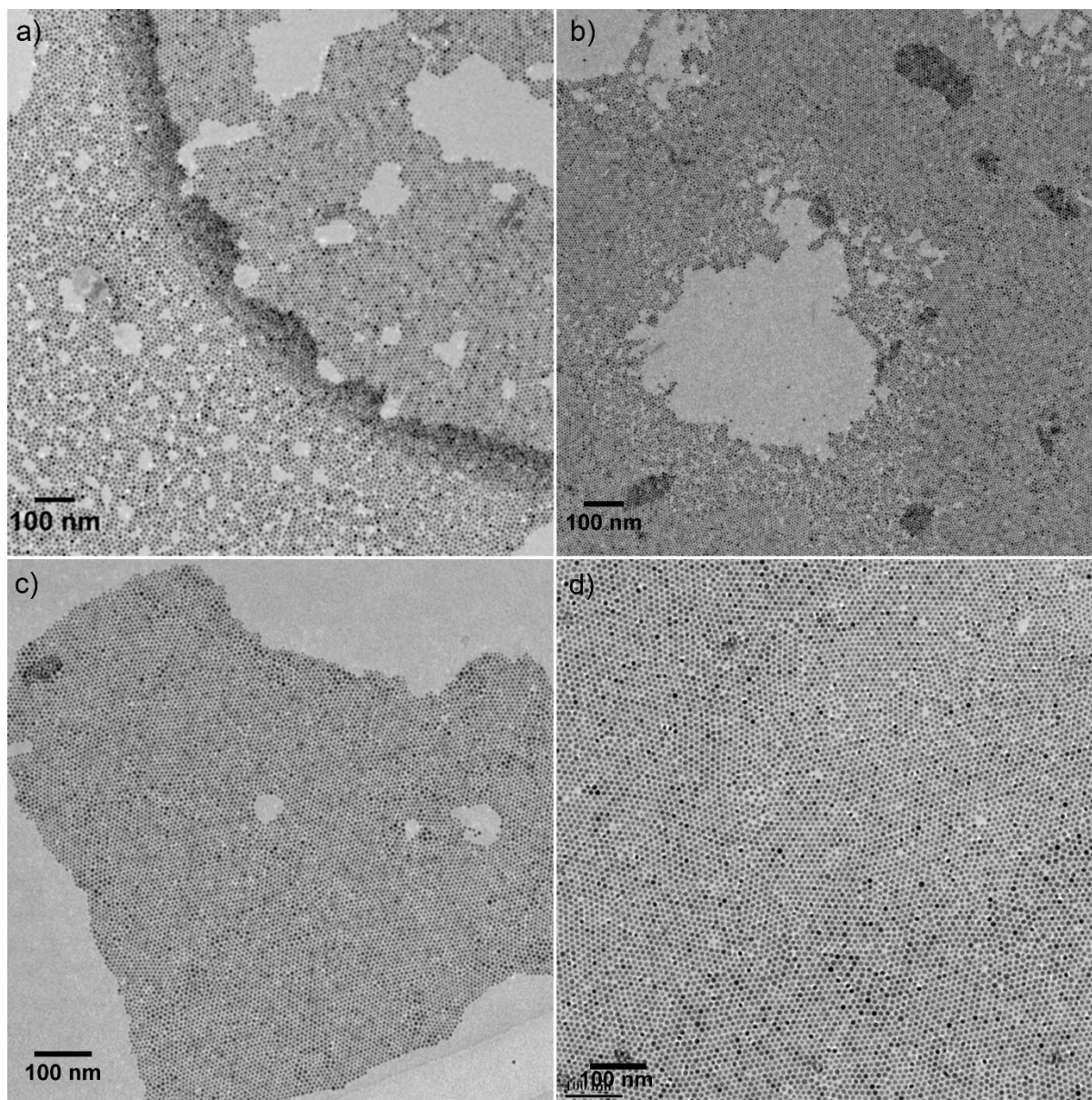
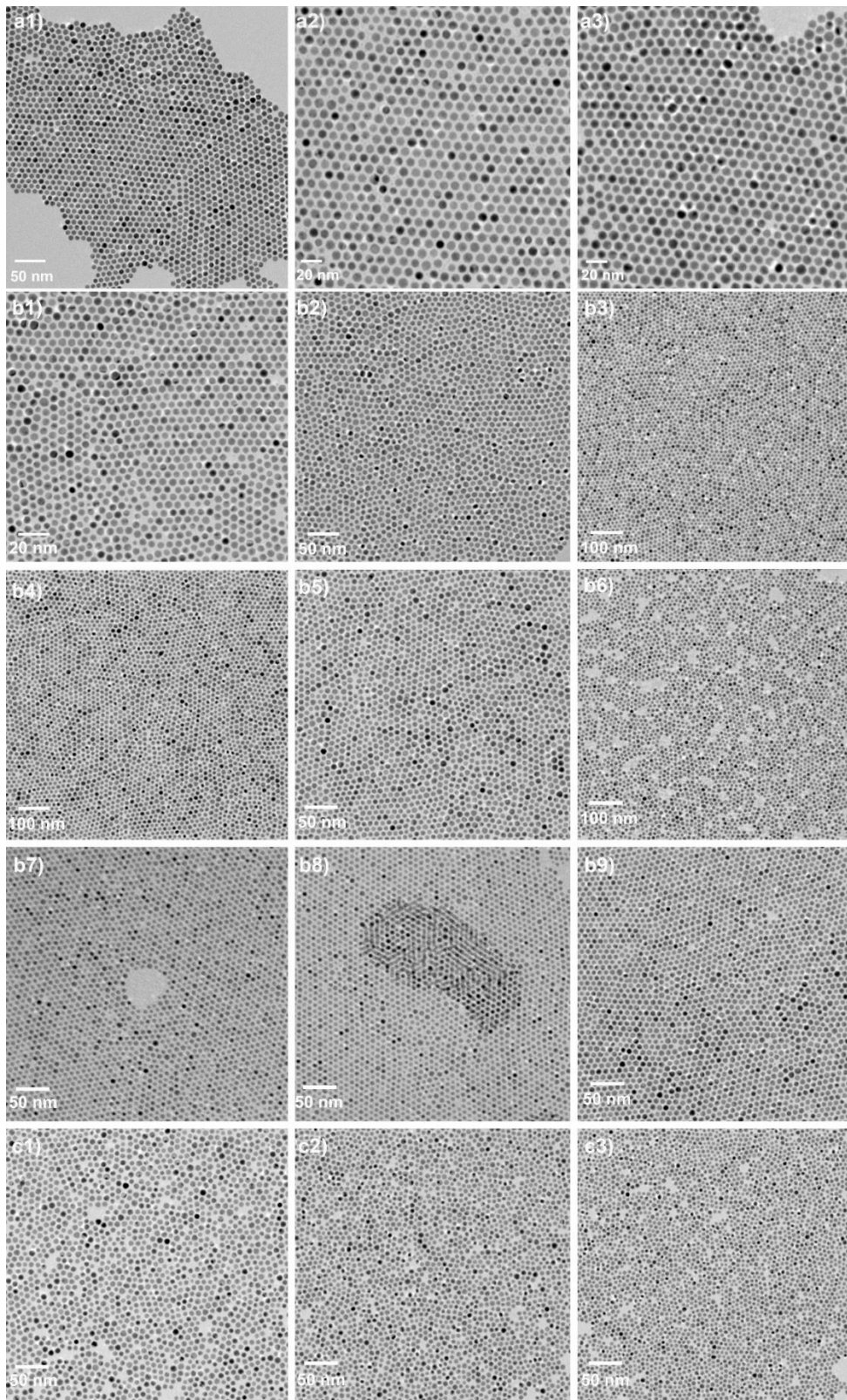
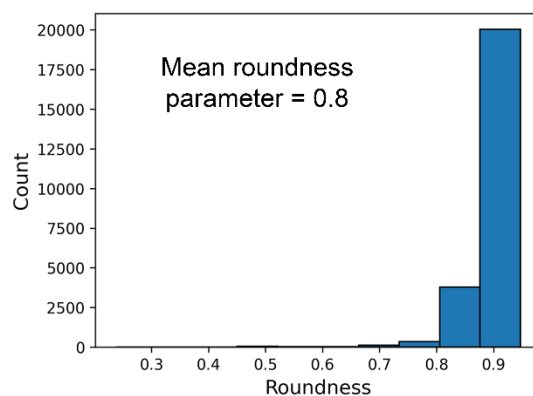
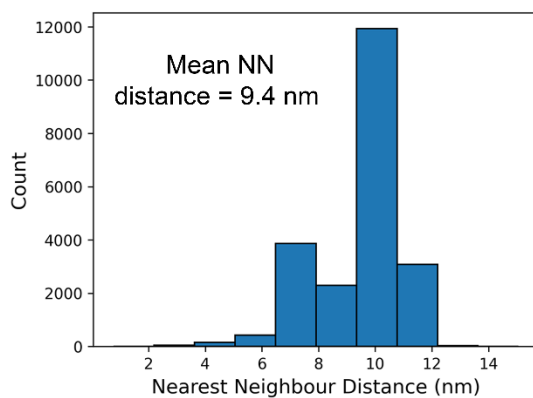
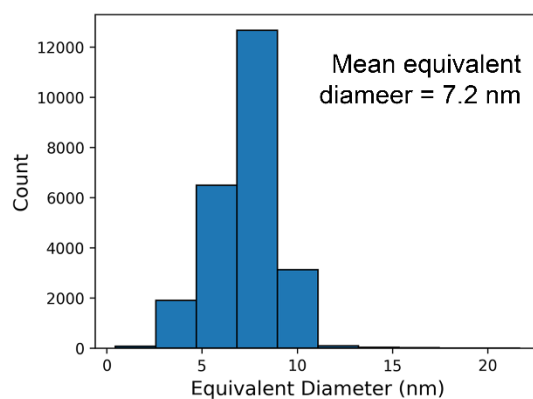


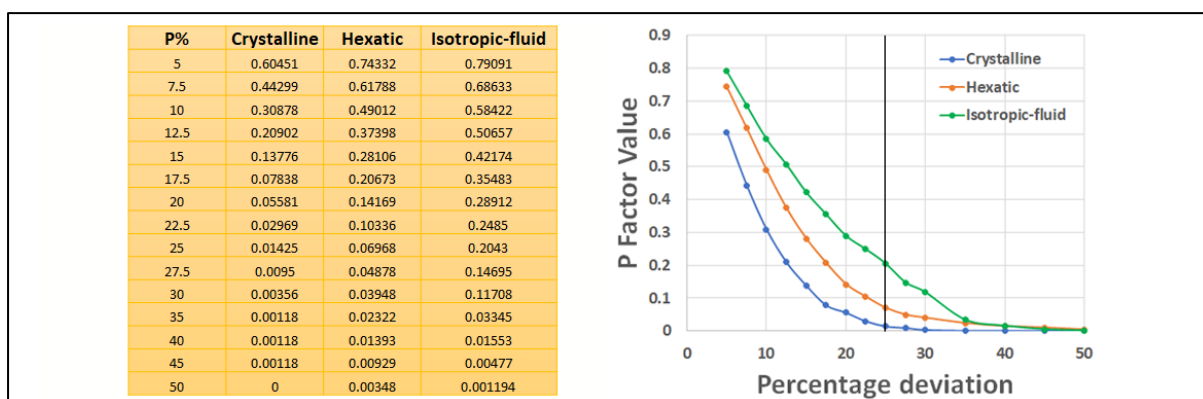
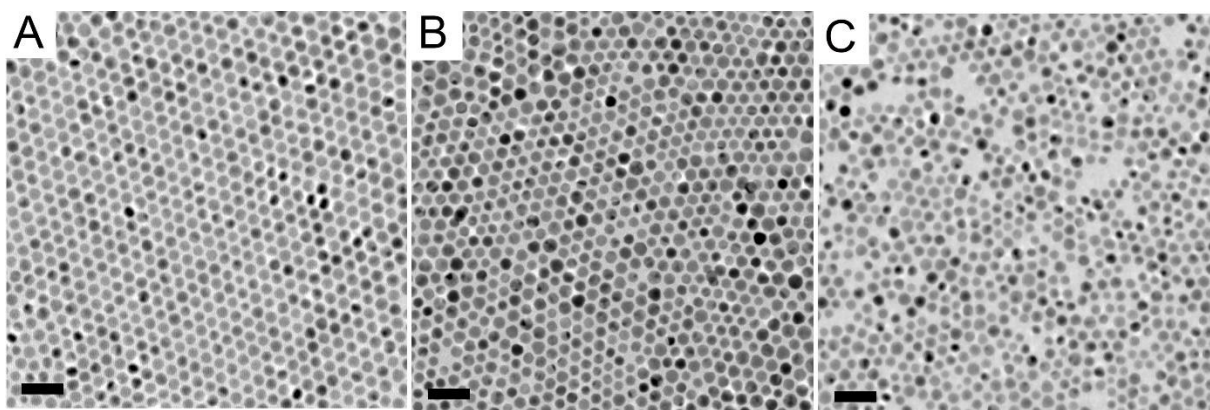
Figure SF1. Large-area NPML images taken at low magnification from different part of the TEM grid. a) Order-disorder transition across a thick particle assembly is observed. b) Particles assembly changes from ordered to disordered as we move closer to the centre of the image from the edge. c) A single NPML composed of mostly hexagonally assembled NPs. d) Dense close pack arrangement of NPs with highly ordered self-assembly of NPs.



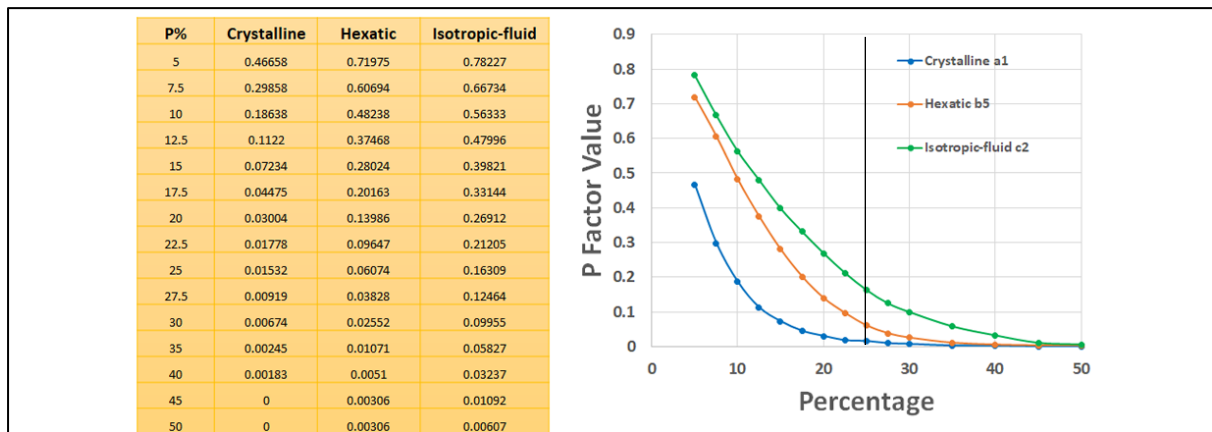
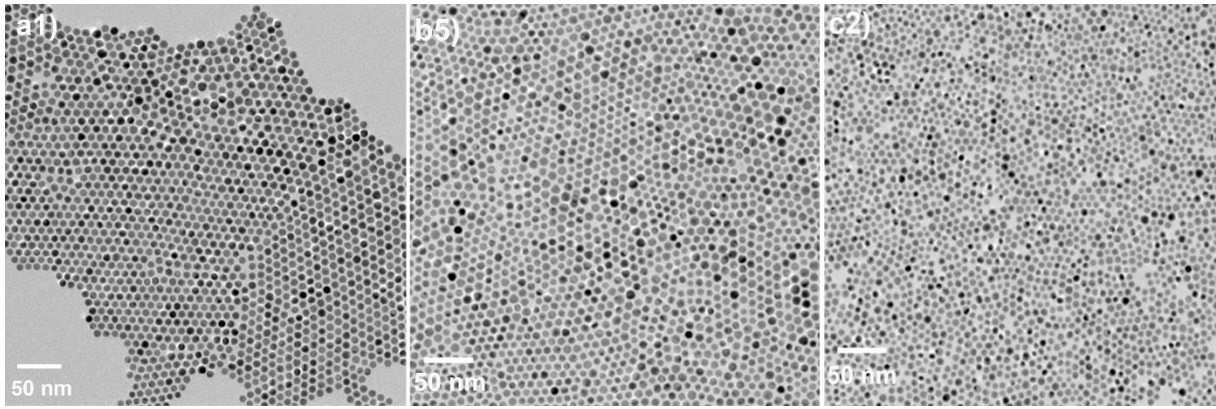
SF2 A: High-magnification TEM images of different locations of a NPML. a1-a3) Crystalline, b1-b9) Hexatic, c1-c3) Isotropic-fluid phases.



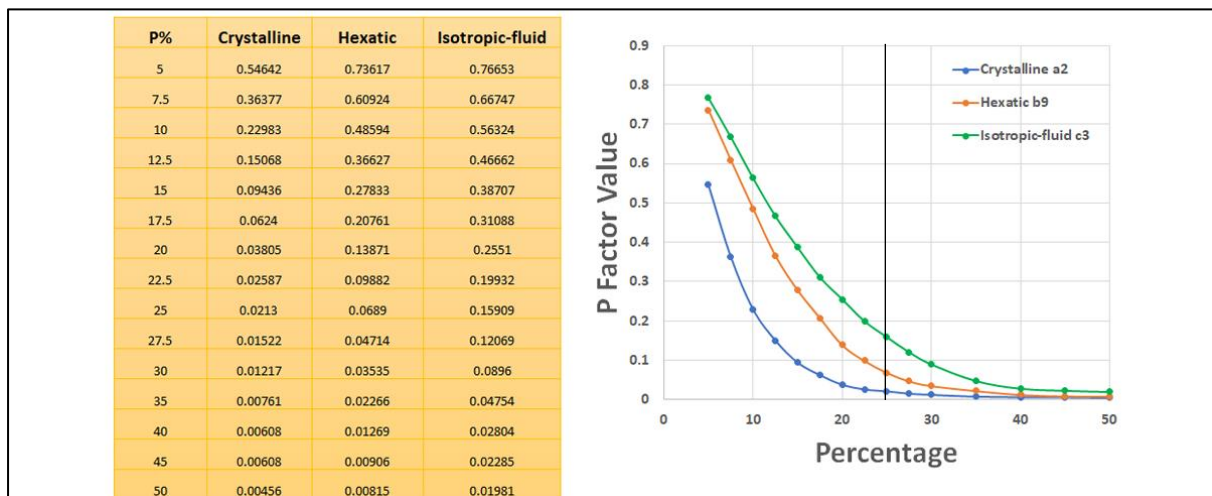
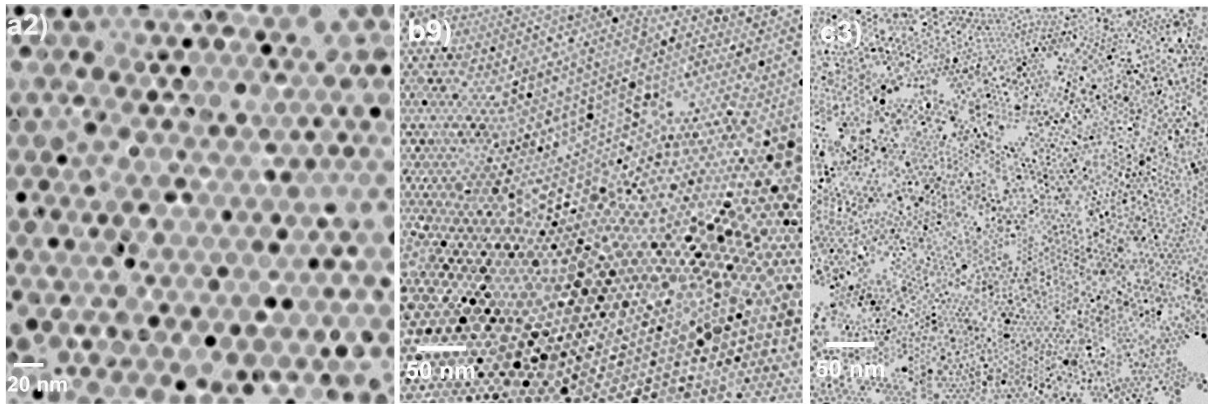
SF2 B: Histogram plot for the three different particle features counting ~24,000 particles taken from all the images in our collection as shown in fig. SF2 A. The average values are given in the inset of the graphs.



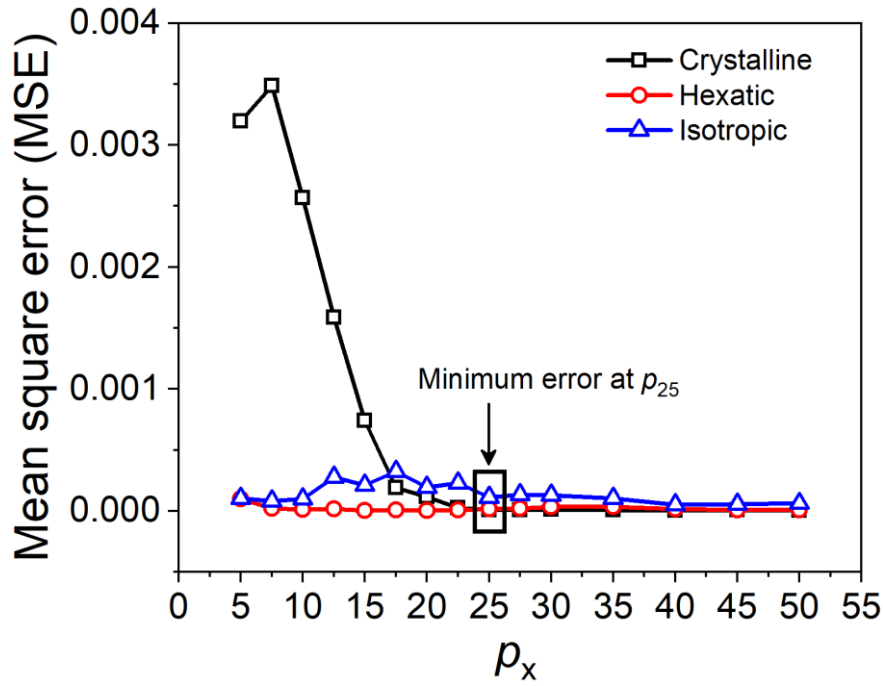
SF3 A: Screening of different p_x values, where $x = 5\text{--}50\%$. The representative images from the manuscript figure 1a were analysed and compared. All the scale bars are 20 nm. The variation in the p_x -values was plotted with percentage deviation. At the 25% deviation (p_{25}), a line is indicated as the descriptor for identifying the three different phases.



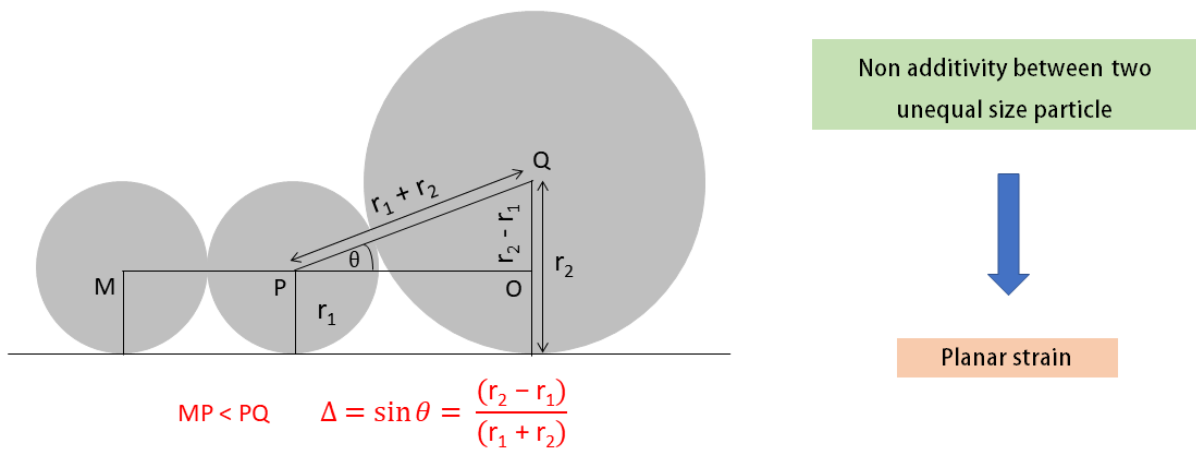
SF3 B: Screening of different p_x values, where $x = 5\text{--}50\%$. Three images taken from figure SF2 A were analysed and compared. The variation in the p-values was plotted with percentage deviation. At the 25% deviation (p_{25}), a line is indicated as the descriptor for identifying the three different phases.



SF3 C: Screening of different p_x values, where $x = 5\text{--}50\%$. Three images taken from figure SF2 A were analysed and compared. The variation in the p-values was plotted with percentage deviation. At the 25% deviation (p_{25}), a line is indicated as the descriptor for identifying the three different phases.



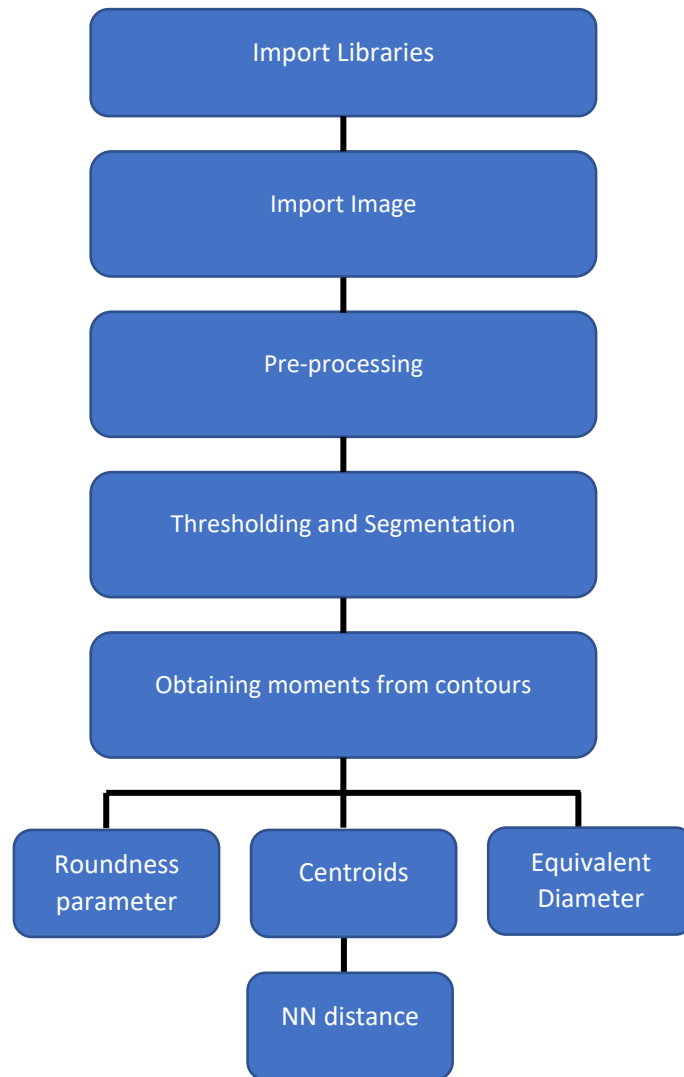
SF3D: The mean square errors (MSEs) calculated from the three repeated sets of measurements of three different sets of images for the crystalline, hexatic, and isotropic-fluid phases, as shown above (Fig. SF3 A-C). The MSE is minimum at p_{25} .



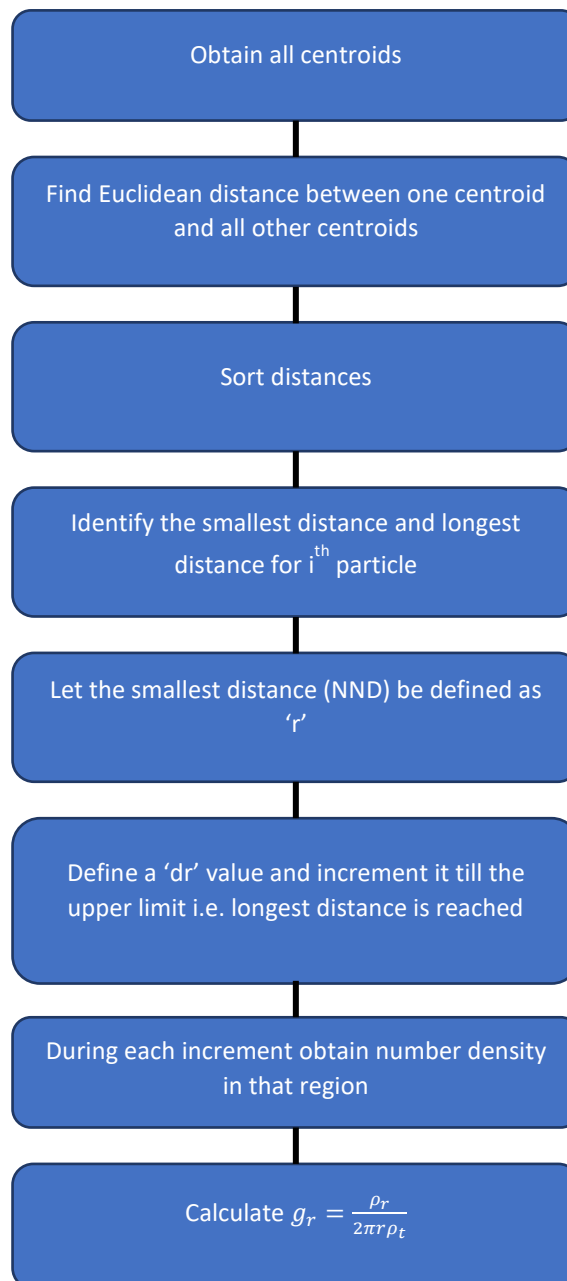
SF4: Schematic that displays the origin of non-planarity between the two unequal size particles sitting next to each other on a flat surface. The non-additivity (Δ) in the calculation of centre-to-centre distance between the two unequal size particles is given as a function of the inclined angle (θ). This inclination give rise to the planar strain in the monolayer.

Supporting Algorithms

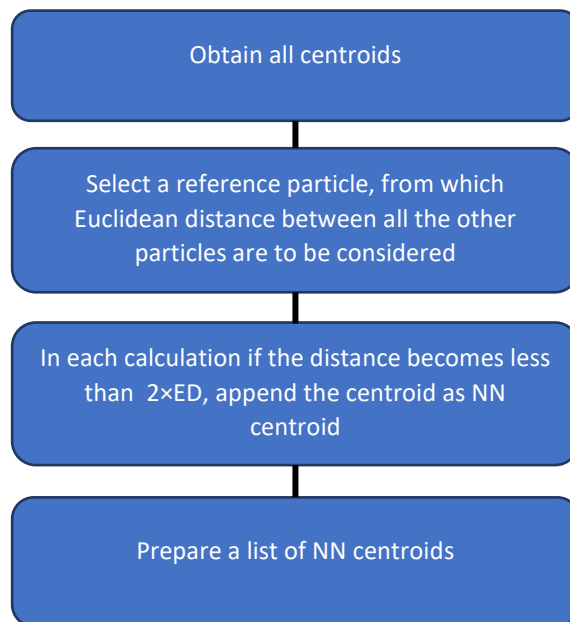
SA1: Algorithm for obtaining geometrical properties of the NPs



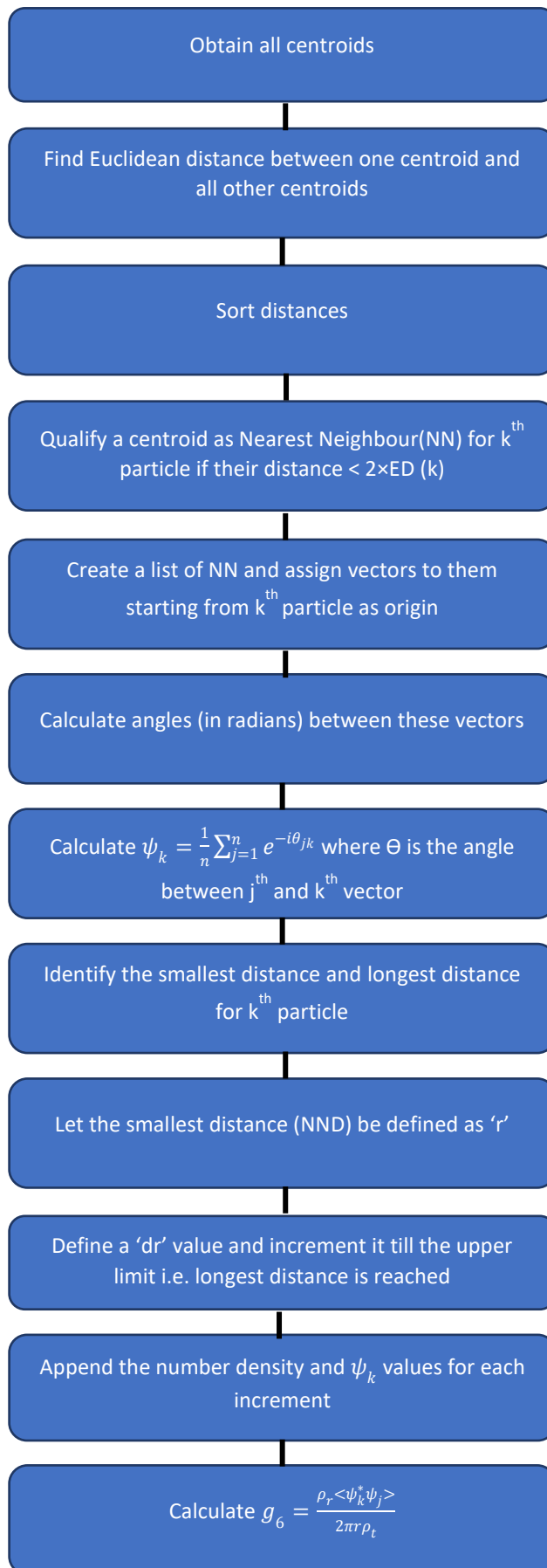
SA2: Algorithm for calculating Radial Distribution Function (RDF)



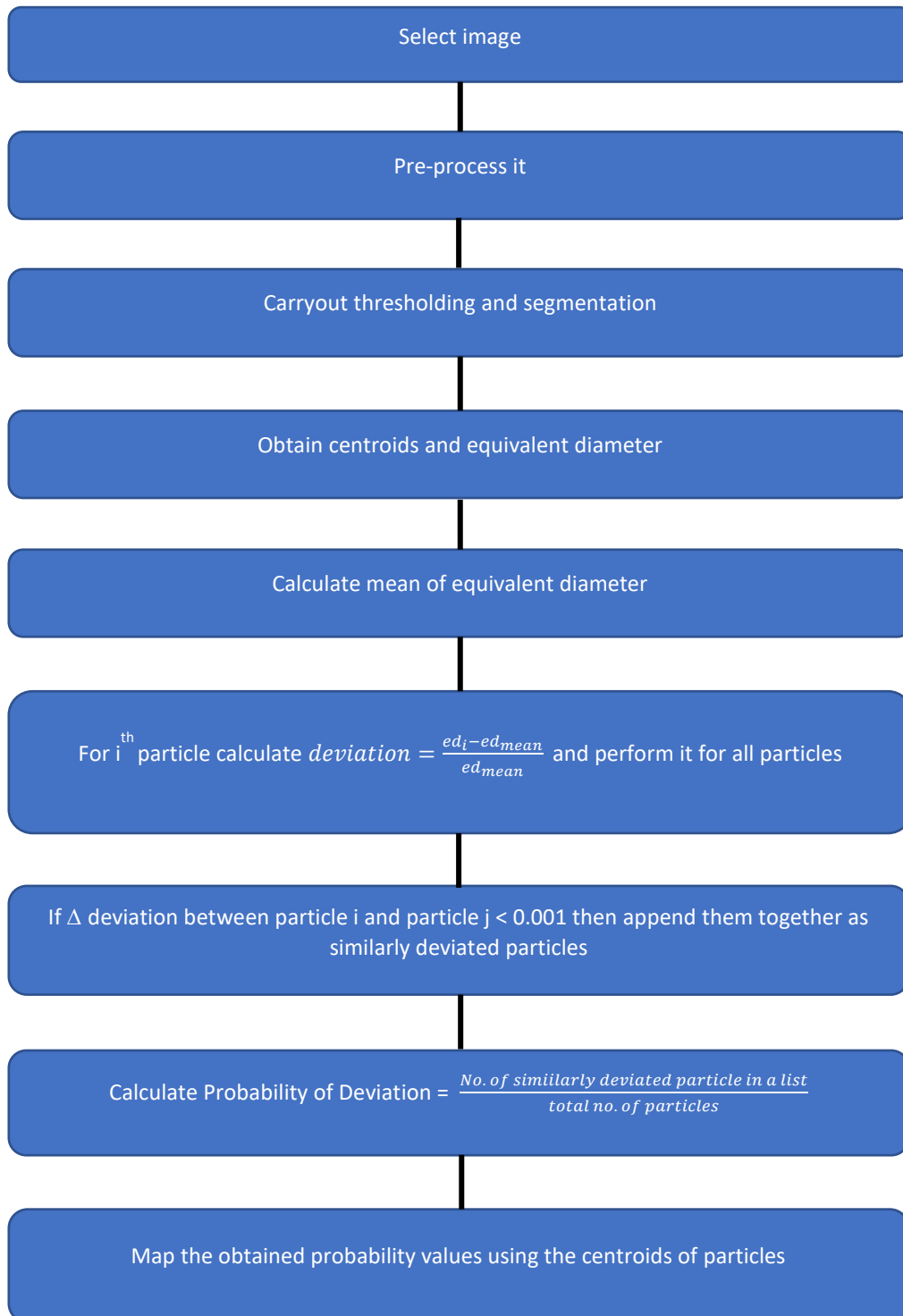
SA3: Algorithm for finding Nearest Neighbour (NN)



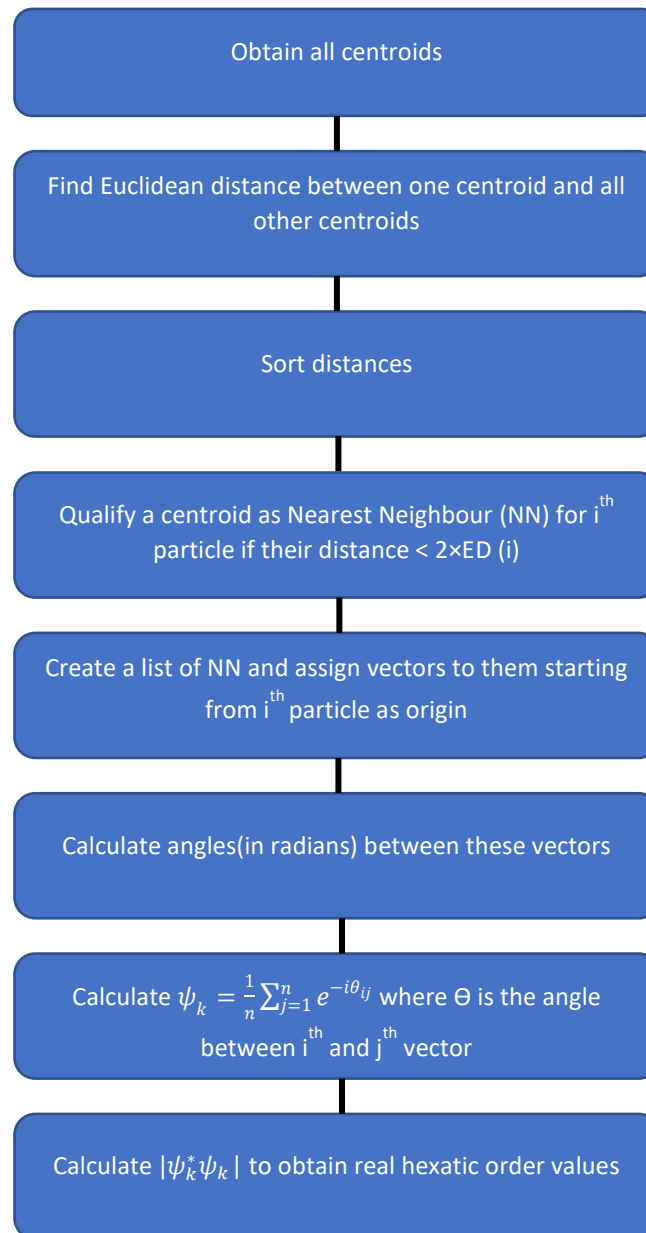
SA4: Algorithm for calculating bond order correlation function (BOCF).



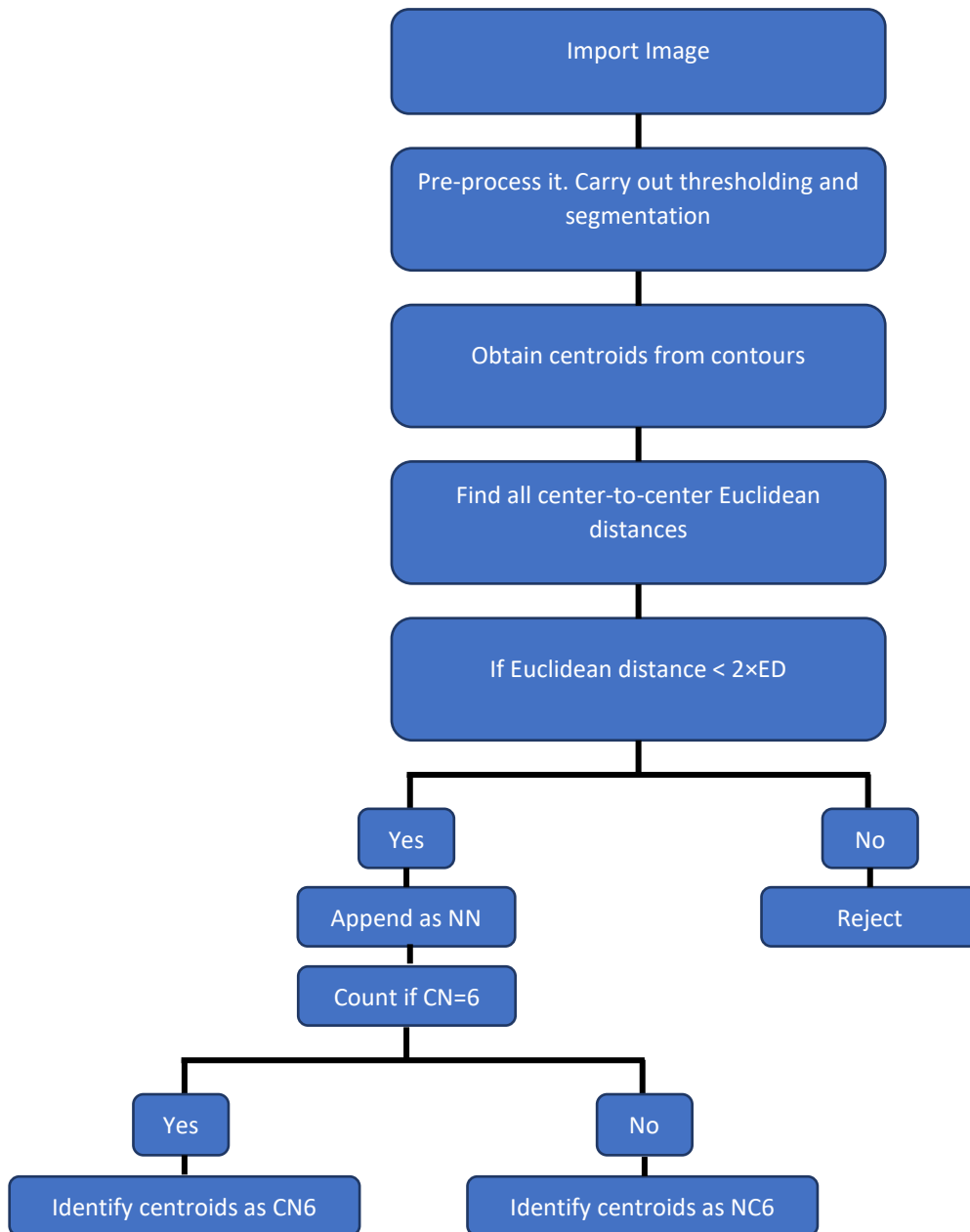
SA5: Algorithm for probability of size deviation mapping



SA6: Algorithm for calculating Hexatic Order Parameter



SA7: Algorithm for calculating Coordination Number (CN)



SA8: Algorithm for strain calculation

The following scheme was utilized: 1) *Finding deflected position*: Particle centroids (that reside within each Voronoi polygon) were first connected using a Delaunay triangulation (DT, a complementary technique to Voronoi tessellation) mesh, so that every vertex of a triangle would represent a unique centroid. In our case, the triangles are irregular in shape depending on the position of the centroids, therefore, the current centroid's locations are marked as the deflected positions where the deflection is considered to arise from a hypothetical undeflected point. 2) *Finding hypothetical undeflected position*: To find out the corresponding undeflected points for each centroid, we used a set of custom-made algorithms. First, we considered each side of a polygon (which connects two points of a triangle) to find out the hypothetical third equilibrium point. Likewise, iterating the method for all other sides of the polygon we obtained a set of points enclosed within the polygon (for example, we get six points for a hexagon). In the next step, we calculated the minimum and maximum values of x- and y- coordinate taking account of all the points obtained from the previous step. By this, we reached a centroid zone, that has the most probable location for the hypothetical undeflected point for the central particle. Finally, we considered the geometric center of the polygon by taking average of all the vertices of the polygon and subtract it one-by-one from the countable set of imaginary points present within the centroid zone. The result with minimum difference value indicates the ideal centroid position which has almost equal distances from all the vertices of the polygon. 3) *Calculating planar strain*: Once the deflected and undeflected positions for each point were determined, we apply the constant strain triangle method to obtain the planar strain elements (two planer stain and one shear strain) for each triangle (S1).

$$\begin{bmatrix} \varepsilon_x \\ \varepsilon_y \\ \gamma_{xy} \end{bmatrix} = B \begin{bmatrix} d_{1,x} \\ d_{1,y} \\ d_{2,x} \\ d_{2,y} \\ d_{3,x} \\ d_{3,y} \end{bmatrix}; B = \frac{1}{2A} \begin{bmatrix} y_2 - y_3 & 0 & y_3 - y_1 & 0 & y_1 - y_2 & 0 \\ 0 & x_3 - x_2 & 0 & x_1 - x_3 & 0 & x_2 - x_1 \\ x_3 - x_2 & y_2 - y_3 & x_3 - x_2 & y_3 - y_1 & x_3 - x_2 & y_1 - y_2 \end{bmatrix}$$

where, [x], [y] are the coordinates, and [d] is the displacement vector of the three vertices of the triangle, A is the triangle area, $\varepsilon_x, \varepsilon_y$ are the isotropic components (compression/dilation) and γ_{xy} is the shear part. The three-element strain vector was then utilized to calculate the mean principal strain ($\varepsilon_{max,min}$) and the torsion angle (θ) using the following transformations,^{S1}

$\varepsilon_{max,min} = \frac{\varepsilon_x \varepsilon_y}{2} \pm \sqrt{\left(\frac{\varepsilon_x \varepsilon_y}{2}\right)^2 + \gamma_{xy}^2}$ and $\tan 2\theta = \frac{2\gamma_{xy}}{\varepsilon_x - \varepsilon_y}$, From the mean principal strain of the constituting triangles, the average planar strain of each Voronoi cell is calculated.

Reference

S1. R. D. Cook, D. S. Malkus, M. E. Plesha, R. J. Witt, Concepts and Applications of Finite Element Analysis, 4th ed., Wiley, New York, 1974.