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Hierarchical amorphous ordering in colloidal gelation

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Supplementary Information for
"Hierarchical amorphous ordering in colloidal gelation"

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Supplementary Methods: Identifying symmetric structural elements in a three-dimensional colloidal gel

Here we explain a detailed procedure with which we identify symmetric structural elements (e.g., a pentagonal bipyramid) in this study. This identification procedure requires information of all particles' coordinates and bonds.

I. Identifying regular pentagons

The basic concept is illustrated in Fig. 1c. We simultaneously impose the topological, planar, and angular criteria to identify a regular pentagon. Below, we describe how we built the analytic code and set the threshold parameters of these criteria.

A. Topological criteria of a regular pentagon

A regular pentagon should consist of five particles. We label the five particles A, B, C, D, and E. The bonds between the five particles should form only one closed loop. We formulate the topological criteria as T1 - T10.

T1: A-B is bonded.

T2: B-C is bonded.

T3: C-D is bonded.

T4: D-E is bonded.

T5: E-A is bonded.

T6: A-C is not bonded.

T7: A-D is not bonded.

T8: B-D is not bonded.

T9: B-E is not bonded.

T10: C-E is not bonded.

The topological criteria are checked using the list of the bonds.

B. Angular criteria of a regular pentagon

For every loop of ABCDE, the edge and rotation angles are computed. Each edge angle should be around 108° to satisfy the five-fold symmetry. Each rotation angle should also be around 72°. In our experiments, the bond length is temporarily fluctuating (see Fig. 4g) and the colloids have a polydispersity of $\sim 5\%$ (see Methods). Thus, we allow the edge and rotation angles to have some finite fluctuations. The threshold parameters, $\delta\theta_{\mathrm{edge}}$ and

$\delta\theta_{\mathrm{rot}}$, are optimised, using the experimental data. Then, we formulate the angular criteria as A1-A10 as follows. Here we define point M as the centre of mass of ABCDE.

A1: $108° - \delta\theta_{\mathrm{edge}} < \angle ABC < 108° + \delta\theta_{\mathrm{edge}}$

A2: $108° - \delta\theta_{\mathrm{edge}} < \angle BCD < 108° + \delta\theta_{\mathrm{edge}}$

A3: $108° - \delta\theta_{\mathrm{edge}} < \angle CDE < 108° + \delta\theta_{\mathrm{edge}}$

A4: $108° - \delta\theta_{\mathrm{edge}} < \angle DEA < 108° + \delta\theta_{\mathrm{edge}}$

A5: $108° - \delta\theta_{\mathrm{edge}} < \angle EAB < 108° + \delta\theta_{\mathrm{edge}}$

A6: $72° - \delta\theta_{\mathrm{rot}} < \angle AMB < 72° + \delta\theta_{\mathrm{rot}}$

A7: $72° - \delta\theta_{\mathrm{rot}} < \angle BMC < 72° + \delta\theta_{\mathrm{rot}}$

A8: $72° - \delta\theta_{\mathrm{rot}} < \angle CMD < 72° + \delta\theta_{\mathrm{rot}}$

A9: $72° - \delta\theta_{\mathrm{rot}} < \angle DME < 72° + \delta\theta_{\mathrm{rot}}$

A10: $72° - \delta\theta_{\mathrm{rot}} < \angle EMA < 72° + \delta\theta_{\mathrm{rot}}$

C. Planar criteria of a regular pentagon

A regular pentagon should be a planar object in a 3D system. The orientation of the plane is randomly distributed. Because we are interested in the symmetry plane, we exclude bent pentagons from the list of pentagons detected. We design the planar criteria that can quantify the partial flatness of a candidate pentagon as follows.

First, we define the planar orientation by $\vec{n}_i$ for every particle i in the pentagon. Suppose that particles j and k are the two neighbours of particle i. Then, the orientation vector $\vec{n}_i$ is defined as follows.

$\vec{n}_i = \vec{r}_{ij} \times \vec{r}_{ik}/|\vec{r}_{ij} \times \vec{r}_{ik}|$, where $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$ and $\vec{r}_i$ is the 3D coordinates of the centre of particle i. We calculate five vectors, $\vec{n}_A, \vec{n}_B, \vec{n}_C, \vec{n}_D, \vec{n}_E$ from the positions of A, B, C, D, and E. Second, we define θ_{plane} for every pentagon. θ_{plane} is the angle between $\vec{n}_i$ and $\vec{n}_j$ such that i is bonded with j. If ABCDE has a perfect flatness, $\theta_{\mathrm{plane}} = 0$. We set the upper threshold of θ_{plane} as $\delta\theta_{\mathrm{plane}}$. Then, the planar criteria of a regular pentagon are formulated as follows.

P1: $\vec{n}_A \cdot \vec{n}_B > \cos(\delta\theta_{\mathrm{plane}})$

P2: $\vec{n}_B \cdot \vec{n}_C > \cos(\delta\theta_{\mathrm{plane}})$

P3: $\vec{n}_C \cdot \vec{n}_D > \cos(\delta\theta_{\mathrm{plane}})$

P4: $\vec{n}_D \cdot \vec{n}_E > \cos(\delta\theta_{\mathrm{plane}})$

P5: $\vec{n}_E \cdot \vec{n}_A > \cos(\delta\theta_{\mathrm{plane}})$

D. Implementation and its computational cost

Our method to identify a regular pentagon refers to the 10 topological, 10 angular, and 5 planar conditions. One might concern that the complex criteria explode the computational cost. Fortunately, it is not the case since we can decrease the computational cost through the effective combination of these criteria, as described below.

- First, a seed particle A is chosen arbitrarily. Then, a pair of two particles, E and B, are chosen as the two neighbours of A. At this step, T1 and T5 are automatically satisfied. In addition, T6 and A5 are tested for (A, B, E).

- If the three particles (A, B, E) have satisfied the criteria, the next particle C is explored from the neighbours of B. At this step, T2 is automatically satisfied. In addition, T9 and A1 are tested for (A, B, C, E).

- If the four particles (A, B, C, E) have satisfied the criteria, the final particle D is explored from the neighbours of C. At this step, T3 is automatically satisfied. Then, T3, T4, T7, T8, A2, A3, A4, and P1-P5 are tested.

- After the five particles (A, B, C, D, E) are given, the centre of mass, M, is calculated. Finally, the five particles are qualified by the rest of the angular criteria, A6 - A10.

The step-by-step algorithm can stop further exploration when a particle does not meet any of the criteria. This saves computational costs. We implemented the code by Python and Numpy and ran the codes on a desktop computer (using one core of Intel Core i5). The computational time was typically several minutes for detecting regular pentagons from ~ 20000 particles at one time step.

II. Identifying a pentagonal bipyramid

A. Classification of a bipyramid and a mono-pyramid

A pentagonal bipyramid is explored after a regular pentagon is detected. Here, ABCDE and XY are assumed as the regular pentagonal plane and the axis of the bipyramid, respectively. We find X (and Y) such that X (and Y) are bonded with the five particles A, B, C, D, and E. Moreover, X and Y should be bonded.

If only X satisfies the criteria and Y does not, ABCDE-X forms a regular pentagonal mono-pyramid. The fractions of pentagonal bipyramids and pentagonal mono-pyramids are compared in Extended Data Fig. 6.

B. Optimising the threshold parameters

Our algorithm requires four threshold parameters: d_{bond}, $\delta\theta_{\mathrm{plane}}$, $\delta\theta_{\mathrm{rot}}$, and $\delta\theta_{\mathrm{edge}}$. We show that our algorithm has quantitative robustness to identify five-fold symmetry with optimal parameters.

First, we evaluate the errors in our experimental system. Extended Data Fig. 4c shows the distribution of bond-bond angles. The sharp peak at $60°$ comes from rigid tetrahedra in a gel. The peak approximately ranges from $50°$ to $70°$. So, we can regard the systematic error as up to $10°$. From the experimental data, we set the thresholds of planar and rotation angles as $\delta\theta_{\mathrm{plane}} = 10°$ and $\delta\theta_{\mathrm{rot}} = 10°$.

Second, the optimisation of $\delta\theta_{\mathrm{edge}}$ needs careful investigation. In Extended Data Fig. 4c, the second peak's position deviates from $108°$. Thus, we compute the number of the detected pentagons with various $\delta\theta_{\mathrm{edge}}$. In Extended Data Figs. 4d and 4e, $\delta\theta_{\mathrm{edge}}$ is varied from $8°$ to $16°$. With $\delta\theta_{\mathrm{edge}} = 8°$, our algorithm undervalues the number of the regular pentagons. With $\delta\theta_{\mathrm{edge}} \geq 12°$, the number of the detected pentagons becomes robust. So, we set $\delta\theta_{\mathrm{edge}} = 12°$ as the optimal value.

Third, we evaluate the effect by the bond threshold, d_{bond}. In Extended Data Fig. 4b, the radial distribution function has its first minimum around $d_{\mathrm{bond}}/\sigma = 1.295$. However, the curve near the first minimum is almost flat. This means that the definition of d_{bond} has some arbitrariness. If the algorithm is not robust to the bond threshold, it would be difficult to compare the number of the detected pentagons between different timesteps or gel samples. So, we run our algorithm with various values of d_{bond}. Extended Data Fig. 4d shows the number of the detected pentagons as a function of d_{bond}. Near the optimal threshold of $d_{\text{bond}}/\sigma = 1.295$, the number of the detected pentagons is highly robust, where its relative error is below 1%. For detecting pentagonal bipyramids, our algorithm also shows high robustness to the bond threshold (Extended Data Fig. 4e). Hence, our method can quantitatively compare the number of five-fold symmetry between different timesteps and different gel samples.

In conclusion, the threshold parameters are optimised as follows:

$d_{\text{bond}}/\sigma = 1.295$

$\delta\theta_{\text{plane}} = 10°$

$\delta\theta_{\text{rot}} = 10°$

$\delta\theta_{\text{edge}} = 12°$

C. Comparison with topological cluster classification (TCC)

Recently, topological cluster classification (TCC) is extended to detect a pentagonal bipyramid in a colloidal glass [1]. Strictly speaking, the topology-based identification cannot discriminate between a regular pentagon and an incomplete pentagon, whose plane is partially bending or which does not have high enough five-fold rotational symmetry. So, we compare our method with TCC to clarify the impact of the angular and planar criteria on the detection of a pentagonal bipyramid. Our method disables the angular and planar criteria by setting the threshold parameters as follows: $\delta\theta_{\text{edge}} = 180°$, $\delta\theta_{\text{rot}} = 180°$, and $\delta\theta_{\text{plane}} = 180°$. Hence, we mimic the TCC analysis and evaluate the impact of the planar and angular criteria in our method.

We compare the number of detected pentagons in Extended Data Fig. 5a. TCC-like analysis overestimates the number of the detected pentagons by 3 times than our method does with $d_{\text{bond}}/\sigma = 1.295$. Similarly, TCC-like analysis overvalues the number of the detected pentagonal bipyramids by 1.7 times than our method. When using TCC-like analysis, the number of the detected pentagons (and pentagonal bipyramids) linearly depends on the bond threshold (Extended Data Figs. 5a and 5b). As shown in Extended Data Fig. 4b, the first minimum of the radial distribution function of a gel is nearly flat. The flat minimum causes the arbitrariness of setting the bond threshold, directly affecting the pentagon detection in TCC. Therefore, we may conclude that the TCC-like analysis is rather insensitive to the local symmetry.

We further investigate the role of the planar and angular criteria in detecting five-fold symmetry. Extended Data Fig. 5c compares the planar, rotation, and edge angles in the pentagonal bipyramids between the TCC-like and our methods. The distributions of the planar angle obtained by the TCC-like method contain two distinct distributions: A sharp distribution around 0° and another long-tail distribution from 10° to 40°. The sharp distribution corresponds to highly symmetric pentagons, whereas the long-tail distribution corresponds to the bent pentagons. This result shows that the TCC-like method tends to include pentagonal bipyramids with distorted pentagons.

In contrast, our method with the planar criteria cuts off the long-tail distribution (see the left panel in Extended Data Fig. 5c). For the pentagons in pentagonal bipyramids, 85% of the planar angles are less than 5° for our method, whereas only 60% of the planar angles for the TCC-like method. The planar criterion in our method provides higher sensitivity to the five-fold symmetry in a gel.

In the rotation and edge angles, both methods show similar distributions. In the distribution of the rotational angle by the TCC-like method, there is only one peak at $\theta_{\mathrm{rot}} \sim 72°$. We see no peak at $\theta_{\mathrm{rot}} = 60°$ (six-fold symmetry) nor $\theta_{\mathrm{rot}} = 90°$ (four-fold symmetry). Therefore, the TCC criteria of five-fold "topology" play an essential role in selecting the five-fold "symmetry".

These comparisons highlight the difference in single-particle-level analysis between "topological" and "symmetrical" statistics. We also note that our method has statistical robustness to the threshold parameters. Thus, our method is optimised for quantitatively analysing the five-fold symmetry in a 3D colloidal gel.

III. Identifying an octahedron

We identify an octahedron in a similar way to a pentagonal bipyramid. We identify a square, and then the bipyramid structure is analysed. Below, the square plane and the top/bottom particles are labelled as ABCD and XY, respectively.

A. Identifying a square

The topological criteria of a square are modified as follows.

T1: A-B is bonded.

T2: B-C is bonded.

T3: C-D is bonded.

T4: D-A is bonded.

T5: A-C is not bonded.

T6: B-D is not bonded.

The angular criteria of a square are modified as follows. Note that M is the centre of mass of ABCD.

A1: $90^\circ - \delta\theta_{\mathrm{edge}} < \angle ABC < 90^\circ + \delta\theta_{\mathrm{edge}}$

A2: $90^\circ - \delta\theta_{\mathrm{edge}} < \angle BCD < 90^\circ + \delta\theta_{\mathrm{edge}}$

A3: $90^\circ - \delta\theta_{\mathrm{edge}} < \angle CDA < 90^\circ + \delta\theta_{\mathrm{edge}}$

A4: $90^\circ - \delta\theta_{\mathrm{edge}} < \angle DAB < 90^\circ + \delta\theta_{\mathrm{edge}}$

A5: $90^\circ - \delta\theta_{\mathrm{rot}} < \angle AMB < 90^\circ + \delta\theta_{\mathrm{rot}}$

A6: $90^\circ - \delta\theta_{\mathrm{rot}} < \angle BMC < 90^\circ + \delta\theta_{\mathrm{rot}}$

A7: $90^\circ - \delta\theta_{\mathrm{rot}} < \angle CMD < 90^\circ + \delta\theta_{\mathrm{rot}}$

A8: $90^\circ - \delta\theta_{\mathrm{rot}} < \angle DMA < 90^\circ + \delta\theta_{\mathrm{rot}}$

The planar criteria of a square are modified as follows.

P1: $\vec{n}_A \cdot \vec{n}_B > \cos(\delta\theta_{\mathrm{plane}})$

P2: $\vec{n}_B \cdot \vec{n}_C > \cos(\delta\theta_{\mathrm{plane}})$

P3: $\vec{n}_C \cdot \vec{n}_D > \cos(\delta\theta_{\mathrm{plane}})$

P4: $\vec{n}_D \cdot \vec{n}_A > \cos(\delta\theta_{\mathrm{plane}})$

B. Identifying an octahedron

Particles X and Y are topologically searched as the common neighbours of ABCD. The position of O is recalculated as the centre of mass of ABCDXY. Then, the rotational angles are calculated and filtered to meet the angular criteria. Below, we describe the full description of the angular criteria in the final qualification of regular octahedra.

A9: $90° - \delta\theta_{\mathrm{rot}} < \angle AOB < 90° + \delta\theta_{\mathrm{rot}}$

A10: $90° - \delta\theta_{\mathrm{rot}} < \angle BOC < 90° + \delta\theta_{\mathrm{rot}}$

A11: $90° - \delta\theta_{\mathrm{rot}} < \angle COD < 90° + \delta\theta_{\mathrm{rot}}$

A12: $90° - \delta\theta_{\mathrm{rot}} < \angle DOA < 90° + \delta\theta_{\mathrm{rot}}$

A13: $90° - \delta\theta_{\mathrm{rot}} < \angle AOX < 90° + \delta\theta_{\mathrm{rot}}$

A14: $90° - \delta\theta_{\mathrm{rot}} < \angle XOC < 90° + \delta\theta_{\mathrm{rot}}$

A15: $90° - \delta\theta_{\mathrm{rot}} < \angle COY < 90° + \delta\theta_{\mathrm{rot}}$

A16: $90° - \delta\theta_{\mathrm{rot}} < \angle YOA < 90° + \delta\theta_{\mathrm{rot}}$

A17: $90° - \delta\theta_{\mathrm{rot}} < \angle BOX < 90° + \delta\theta_{\mathrm{rot}}$

A18: $90° - \delta\theta_{\mathrm{rot}} < \angle XOD < 90° + \delta\theta_{\mathrm{rot}}$

A19: $90° - \delta\theta_{\mathrm{rot}} < \angle DOY < 90° + \delta\theta_{\mathrm{rot}}$

A20: $90° - \delta\theta_{\mathrm{rot}} < \angle YOB < 90° + \delta\theta_{\mathrm{rot}}$

[1] Hallett, J. E., Turci, F. & Royall, C. P. The devil is in the details: Pentagonal bipyramids and dynamic arrest. *J. Stat. Mech.: Theory Exp.* **2020**, 014001 (2020).