

Patterning symmetry in the rational design of colloidal crystals
Supplementary Material

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SUPPLEMENTARY FIGURES

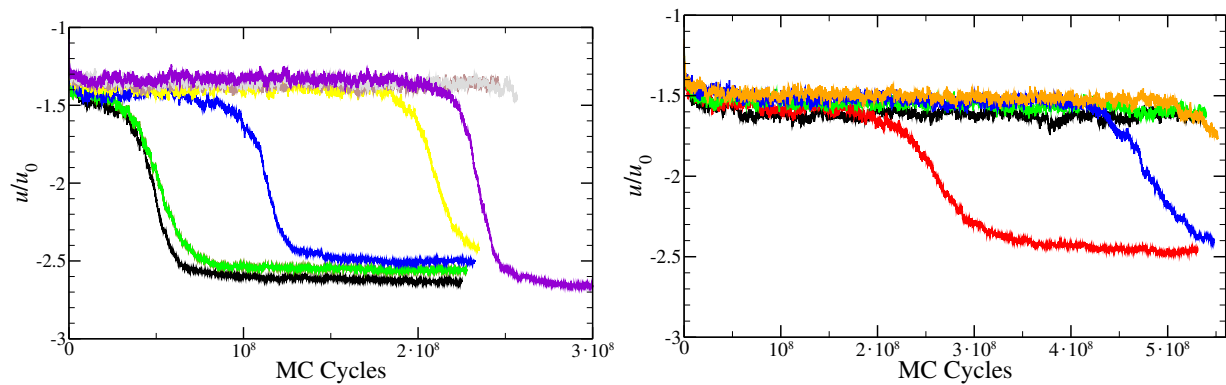


FIG. S1. **Crystallisation with disorder in the patch size.** Crystallisation runs at temperatures close to the nucleation temperature for particles with patches disordered in size. Top: $\sigma_\theta = 0.02$, bottom: $\sigma_\theta = 0.04$. Here the number density ρ is fixed to 0.65 and $N = 1000$. Nucleation of a single cluster happens in both cases at comparable temperatures.

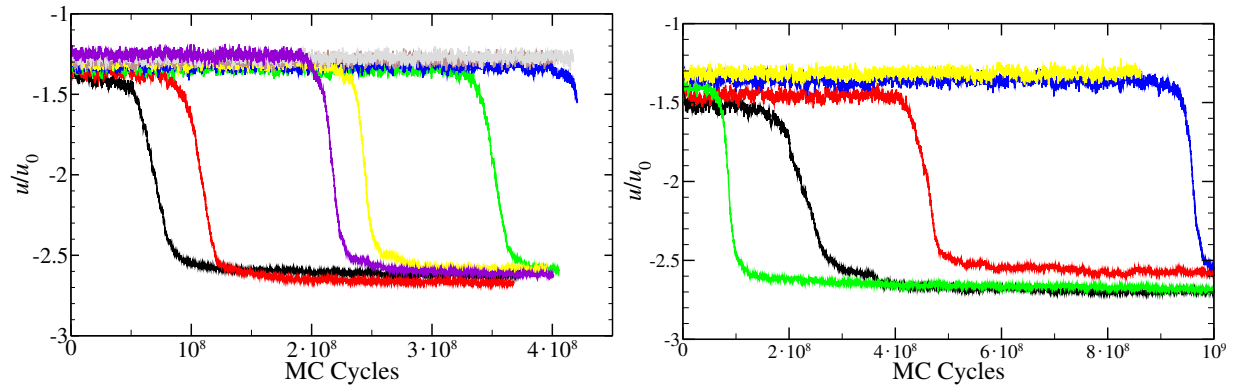


FIG. S2. **Crystallisation with disorder in the patch shape.** Crystallisation runs for patches disordered in position. The number density ρ is fixed to 0.65 and $N = 1000$. Also here nucleation of a single cluster happens in both cases at comparable temperatures.

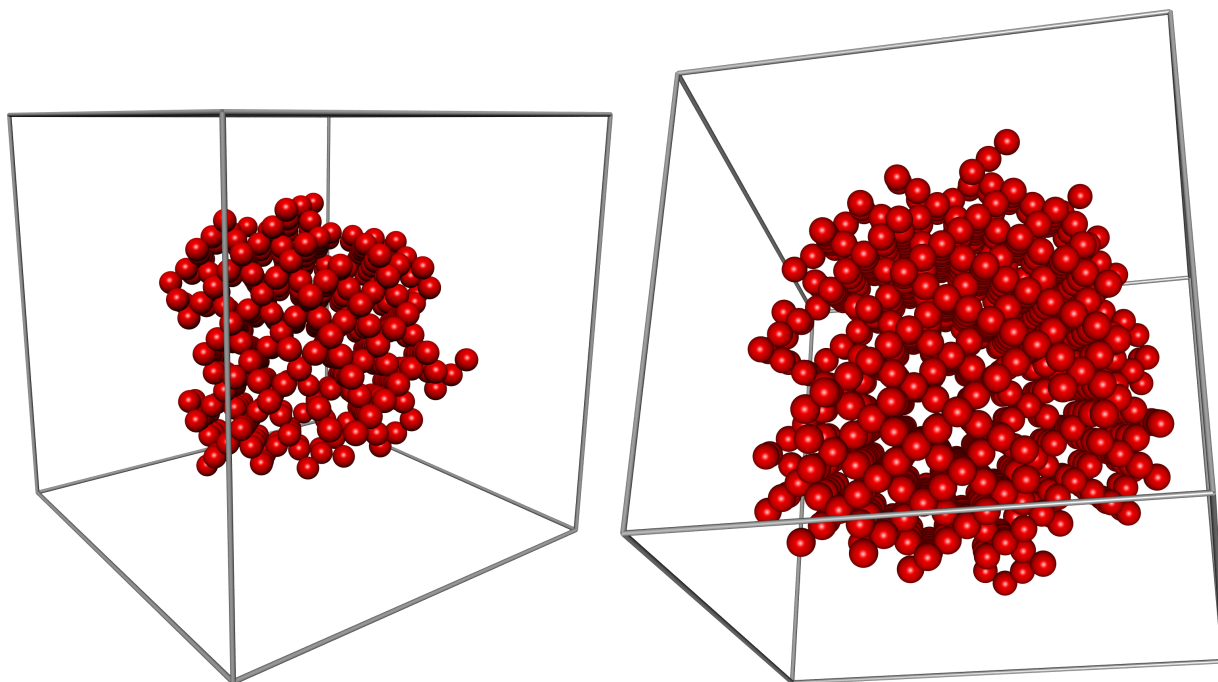


FIG. S3. **Self-assembled tetrastack clusters** Images of a growing crystal cluster of cubic tetrastack particles, when the number of cubic particles has reached the values 500 and 1000. Fluid particles have been removed for clarity. The total number of particles in the simulation is $N=4000$. Both configurations are available for inspection in a molecular viewer as Supplementary Data.

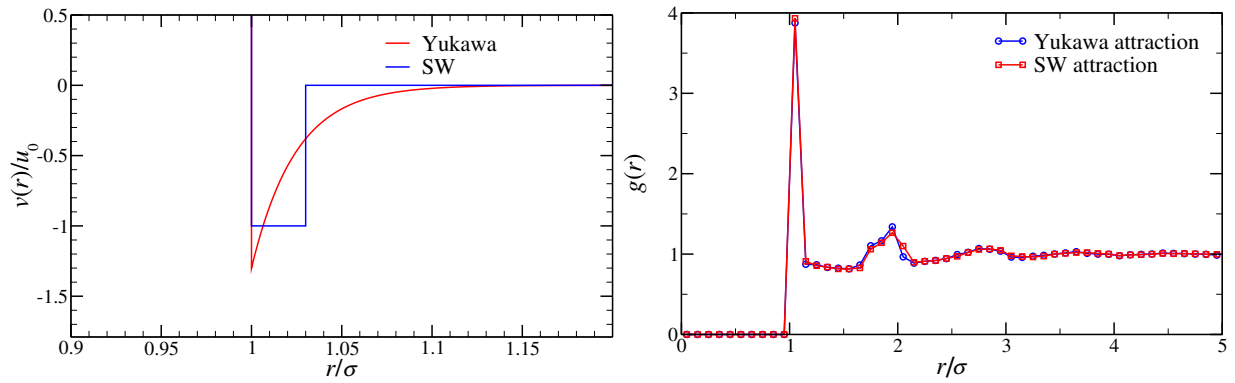


FIG. S4. **Yukawa-like attractive potential: extended law of corresponding states.** Extended law of corresponding states between a smooth short-range attraction (Yukawa) and a sharp short-range square well (SW) attraction. The two potentials (shown left) have the same reduced second virial coefficient at $k_B T/u_0 = 0.12$. The radial distribution function $g(r)$ (shown right) for the three-block Janus particles in which the attractive potential is modeled via any of the two potentials is virtually the same for the two models at that T .

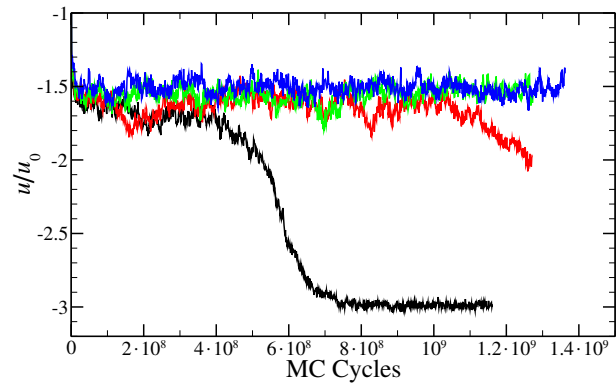


FIG. S5. **Nucleation for the smooth potential** Simulations for the smooth attraction model at temperatures close to $T = 0.12$. Nucleation is achieved at $T = 0.115$ ($\rho = 0.65$, $N = 250$).

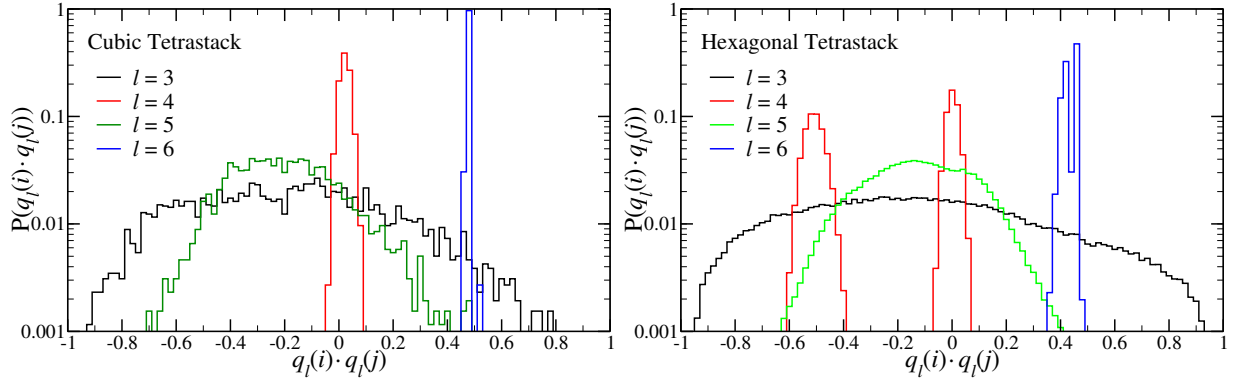


FIG. S6. **Crystallisation order parameters.** Probability distributions of the dot products $q_l(i) \cdot q_l(j)$ for the cubic (CT) and hexagonal tetrastack. The peak in the $q_4(i) \cdot q_4(j)$ centered around -0.5 allows to distinguish between cubic and hexagonal local environments. Given that we use normalised vectors, the dot product is comprised between -1 and 1 . Note the log scale on the y axis.

SUPPLEMENTARY TABLES

Crystallisation results for all the models studied

	$k_B T/u_0$	N_{tot}	n_c	n_h
ideal	0.1170	1000	343 (342)	0/0
$\sigma_\theta = 0.02$	0.1170	1000	439 (439)	0/0
$\sigma_\theta = 0.04$	0.1175	1000	215 (213)	0/0
$\sigma_p = 0.02$	0.1190	1000	363 (355)	0/0
$\sigma_p = 0.04$	0.1175	1000	323 (320)	0/0
smooth attr.	0.1175	250	88 (87)	0/0

TABLE S1. Structural properties of final configurations for different studied models (disorder in the patch size, disorder in the patch position and smooth attraction) compared to the idealised Kern-Frenkel model studied in the main text. Data refer to systems a density of $\rho = 0.65$. n_s : number of crystalline particles; n_c : number of crystalline particles within a locally cubic environment; n_h : number of crystalline particles within a locally hexagonal environment. The number between parentheses are the size of the corresponding largest cluster of connected crystalline particles. Homogeneous nucleation is observed in all models, i.e., the largest cluster contains nearly all the solid particles. Note that, in simulation, crystal growth is arrested by geometric constraints and self-interaction of the cluster through periodic boundary conditions.

SUPPLEMENTARY METHODS

Crystallisation order parameters

To study nucleation of the cubic and hexagonal tetrastack we resort to the technique introduced by Steinhardt and collaborators [29] that allows to identify the local environment of each particle. To each particle i we assign a series $q_{lm}(i)$ of normalised vectors of complex numbers based on spherical harmonics defined whose components are defined as follows:

$$q_{lm}(i) = \frac{1}{\mathcal{N}} \sum_{k=1}^{N_b(i)} Y_{lm}(\mathbf{r}_{ik}) \quad (\text{S1})$$

where $N_b(i)$ is the number of first neighbours of particle i , in our case the number of particles within the attraction cutoff distance $(1 + \delta)\sigma$, \mathcal{N} is a normalisation factor, m runs from $-l$ to l and l defines the order of the complex vector. Finally, Y_{lm} is the spherical harmonic with total angular momentum l and projection m and \mathbf{r}_{ik} is the (vector) distance between the centres of particles i and k .

The probability distributions of the dot products $q_l(i) \cdot q_l(j)$, where i and j are neighboring particles, usually has well defined peaks for one or more values of l when evaluated on crystalline structures. It is thus possible to define a ‘‘crystalline bond’’ between two particles i and j if $q_l(i) \cdot q_l(j)$ falls in the interval where the probability distribution shows a peak in the lattice. Different peaks at different values of l can be combined in such definition. A particle can then be defined as solid-like if it has a minimum number of crystalline bonds. In turn, the largest collection of connected crystalline particles is the relevant order parameter for studying nucleation processes.

In Supplementary Figure S6 we show the probability distribution functions for the values of $q_l(i) \cdot q_l(j)$ with $l = 3, 4, 5$ and 6 for the cubic and hexagonal tetrastack. It is possible to unambiguously tell apart particles which belong to a cubic or hexagonal local environment as follows:

- particle i is detected as belonging to a local cubic tetrastack environment if it has at least 6 neighbours j with which $0.35 < q_6(i) \cdot q_6(j) < 0.5$ and $-0.15 < q_4(i) \cdot q_4(j) < 0.15$.
- particle i is detected as belonging to a local hexagonal tetrastack environment if it has at least 6 neighbours j such that $0.35 < q_6(i) \cdot q_6(j) < 0.5$ and at least 2 neighbours such that $-0.65 < q_4(i) \cdot q_4(j) < 0.35$.
- particle i is detected as belonging to a local tetrastack environment, without distinguishing if it is cubic or hexagonal, if it has at least 6 neighbours j with which $0.35 < q_6(i) \cdot q_6(j) < 0.5$.

Robustness regarding the shape of the attractive potential

In the case of spherically interacting particles, Noro and Frenkel [30] have shown that hard-core particles with a short range attraction (less than roughly 10% percent of the particle diameter) show a behaviour that does not depend on the details of the interaction potential. This is a general and very useful results in colloidal physics, where the attraction is typically very short-ranged. The thermodynamics properties of different models can be scaled in a universal curve if temperature is substituted by the reduced second virial coefficient, a finding known as the extended law of corresponding states. This has been later shown to apply also to anisotropically interacting particles [31] as long as the geometry of the model is preserved. As an example, results reported in Ref. [16] suggest that the Kern-Frenkel model, although it models the attractive interaction via a short-range square-well, is able to reproduce the thermodynamics and crystallisation mechanism of the experimental study reported in Ref. [8], strongly supporting the independence of the results from the actual shape of the model.

To further strengthen the results reported in the main text, we investigate here the case in which the square-well potential is replaced by a short-range Yukawa attractive potential. In this case the pair interaction can be written as:

$$v(\mathbf{r}_{ij}, \{\hat{\mathbf{p}}_i^{(n)}\}, \{\hat{\mathbf{p}}_j^{(n)}\}) = \begin{cases} \infty & \text{if } r_{ij} < \sigma \\ v_{\text{Yuk}}(r_{ij}) & \text{if } \begin{cases} \sigma < r_{ij} \leq r_c \\ \text{and} \\ \hat{\mathbf{p}}_i^k \cdot (\mathbf{r}_{ij}/r_{ij}) > \cos(\theta)_{i,k} \\ \text{for } k = 1, 2, 3 \text{ or } 4, 5, 6 \\ \text{and} \\ \hat{\mathbf{p}}_j^k \cdot (-\mathbf{r}_{ij}/r_{ij}) > \cos(\theta)_{j,k} \\ \text{for } k = 1, 2, 3 \text{ or } 4, 5, 6 \end{cases} \\ 0 & \text{otherwise} \end{cases}, \quad (\text{S2})$$

with

$$v_{\text{Yuk}}(r) = -u_0 A \frac{\exp[-(r - \sigma)/\xi]}{(r/\xi)}. \quad (\text{S3})$$

We fix $\xi = 0.025$ and set $A = 52.0312$ so that the second virial coefficient B_2 of the square well and of the Yukawa models are the same at $T = 0.12$. Supplementary Figure S4 shows a comparison between the square-well and the Yukawa attractive interactions used in this work. Supplementary Figure S4 shows the pair distribution function $g(r)$ of the two models at $T = 0.12$ and $\rho = 0.65$. Despite the different shape of the short-range attractive potential, the structure of the fluid is identical, in full agreement with the extended law of corresponding states [30,31].

To confirm our hypothesis that crystallization is unaffected by the shape of the attractive potential we investigate nucleation in the Yukawa model, finding confirmation of nucleation in the tetrastack lattice in the same condition as the square-well model. Supplementary Figure S5 shows the time dependence of the potential energy for the Yukawa model in a system of 250 particles. Crystallization proceeds via spontaneous nucleation of a single seed. The resulting number of cubic and hexagonal crystal particles in the system and the number of cubic and hexagonal particles in the largest crystalline cluster are reported in Table S1.

Visualisation of clusters

To provide a visual example of the growing cubic tetrastack we show in Supplementary Figure S3 two representative images extracted from a run in which a crystal seed grows with time. The two clusters correspond to the green points in Figure 3 of the main text. The images show that the growing clusters are very compact and no grain boundaries or defects are present in the bulk. Specifically, we show images of the crystal cluster when the number of cubic particles $n_c = 500$ and $n_c = 1000$. Corresponding files in xyz format are attached to this supplementary material.

SUPPLEMENTARY REFERENCES

- [30] Noro, M.G. & Frenkel, D. Extended corresponding-states behaviour for particles with short-range attractions. *J. Chem. Phys.* **113**, 2941–2944 (2000)
- [31] Foffi, G. & Sciortino, F. On the possibility of extending the Noro-Frenkel generalized law of corresponding states to nonisotropic patchy interactions. *J. Phys. Chem. B*, **111** 9702–9705 (2007)