Supporting Information

Frustrated Crystallization Kinetics in Marginally Mismatched Binary Self-Assembly Driven by Depletion Interactions

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1. Identifying the best parameters for simulated annealing



Figure S1 a) The energy minima found in different simulation runs for various number of iterations, and two values of timesteps, and .The black dashed line shows the minimum energy value calculated by applying conjugate gradient energy minimization on LAMMPS. (b) The average hexatic order of the states with minimum energy found in different simulation runs⁰ the dashed black lines show the experimentally observed hexatic order for the monodisperse sample and the 1:1 binary mixture sample.

2. Depletion induced phase behavior of colloidal particle suspensions



Figure S2_Monodisperse colloidal particles (700 nm) suspended in water when mixed with 5 mM SDS (left) and 25 mM SDS (right). Both mixtures show stable colloidal suspensions with no evidence of self-assembly.

The number density of SDS micelles can be calculated using the following equation:¹

$$\rho = \frac{N_A}{N_{ag}} (C_S - C_{CMC})$$

where, N_{ag} : the aggregation number of SDS, N_A : Avogadro's number, C_s : the applied SDS concentration, and C_{CMC} : the critical micelle concentration.

(1)

The depletion interaction potential (Asakura-Oosawa potential) is proportional to the number density:²

$$U_{AO}(r) = -\rho k_B T V_{ov}(r) \tag{2}$$

The attractive interaction energy between the PS particles (700 nm) in 34 mM SDS was estimated to be about $5.6 k_B T$ in our prior work.³ From this reference value and the number density of the micelles at different SDS concentrations (calculated using equation 1), we can estimate the interaction strength for different SDS concentrations, as summarized in the table below:

SDS concentration	30	32	34	36.5	38	40	42
(mM)							
Number density of SDS micelles $(\rho) \ge 10^{23}$	2.22	2.39	2.56	2.77	2.90	3.06	3.22
Strength of depletion interaction $\binom{k_BT}{k_B}$	4.85	5.23	5.6	6.06	6.33	6.69	7.04



Figure S3 (a) Self-assembled polycrystal of monodisperse 700 nm particles when mixed with 34 mM SDS. (b) The distribution of center-to-center particle distance calculated from the image in (a).



Figure S4 Micrograph of an aqueous suspension of 700 nm particles (0.5% w/w) left for 18 hr. (b) Micrograph of a 1:1 binary mixture of 700 nm and 790 nm particles in water (0.5% w/w) left for 18 hr. Neither mixture had SDS added to them.



Figure S5 Micrograph of a 1:1 binary mixture of 700 nm and 790 nm at a higher particle concentration of 1% w/w. The large red structure consists of 790 nm particles, presumably formed due to the depletion force induced by the 700 nm particles. At this concentration, the binary mixture becomes unstable and not suitable for depletant (SDS) driven self-assembly.

3. Analysis of crystalline order in different binary mixture samples



Figure S6 The distribution of the hexatic order parameter found in different binary mixtures: 39:1, 19:1, and 1:1. The plots clearly show wider distributions and decline in the values for increasing fraction of impurities.



Figure S7 Images of amorphous structures in three different binary samples with different particle concentrations – 0.5%, 0.25%, and 0.125%.

4. Analysis of the simulated crystalline structures



Figure S8 Voronoi diagrams of the crystal structures calculated from the simulation for four different conditions- i, ii, iii, and iv. The results for m = 0.88 size ratio where the two particle sizes are closer (i and iii) show almost no difference in the overall hexatic order for different number ratios. In contrast, when the size ratio is m = 0.80, there is notable difference in the hexatic order (ii and iv). While the 90:1 sample remains crystalline because of the smaller number of impurities, the 1:1 sample loses its hexatic order shown by the 5- and 7- fold defects.



Figure S9 Average hexatic order vs number ratio plots for a fixed size ratio m = 0.88. Three different simulation conditions were applied: red - the range of attractive interaction σ was 4.1% of particle diameter and the final temperature of the simulation was close to zero, blue - the range of attractive interaction σ was 0.2% of particle diameter and the final temperature of the simulation was close to zero, green - the range of attractive interaction σ was 4.1% of particle diameter and the final temperature of the simulation was close to zero, green - the range of attractive interaction σ was 4.1% of particle diameter and the final temperature of the simulation was close to the room temperature.

5. <u>Two-step nucleation and growth kinetics</u>



a Monodisperse

Figure S10 (a) The two-step nucleation and growth mechanism observed in the monodisperse sample. The assembly first grows in an amorphous state (t = 0 and t = 19 min), and stable crystallites start forming in the second step (t = 41 min) resulting a polycrystalline monolayer (t = 58 min). (b) The assembly grows in the amorphous state in a binary sample from the beginning (t = 0) until the complete formation of a monolayer (t = 66 min). Since stable crystallites never form, the particles remain in an arrested state with a reduced structural order in the assembly.



Figure S11 (a) Comparison of crystal growth rates between a monodisperse sample and a 1:1 binary mixture sample (b) Voronoi diagrams of the two samples at different time points illustrating the crystallization dynamics. The monodisperse sample forms stable crystallites in the timeframe of 40 min (A) – 65 min (B). In contrast, the binary mixture shows amorphous structures both at 40 min (i) and at 80 min (ii), with a small increase in the crystalline order over a long period of time.



Figure S12 Examination of two-step nucleation events in samples with different mixture ratios - 9:1, 5:1, and 3:1. Based on the crystal images and the Voronoi diagrams, we find that the second step of nucleation that forms stable grains are rarely present in the 5:1 and 3:1 samples.



Figure S13 The number of new particles added to the surface and the average hexatic order quantified over time for a monodisperse sample (a), and for a 1:1 binary mixture (b).



Figure S14 The formation of first and second layers in a monodisperse colloidal particle suspension when mixed with 34 mM (a), 38 mM (b), and 42 mM SDS (c).

6. Spatiotemporal heterogeneity in the 1:1 binary mixture



Figure S15 Spatial heterogeneity in particle dynamics of the 1:1 binary sample, visualized using a quiver plot. The plot has been calculated by analyzing the trajectories of 3500 particles in 150 s.



Figure S16 Formation of colloidal gels in a mixture of 700 nm and 790 nm particles and 42 mM SDS (depletant). (a) The monolayer formed at the bottom wall of the sample chamber. (b) 3D gels formed above the bottom wall and in the suspension.

7. <u>Colloidal gel formation in a binary sample for stronger interaction</u>

References

- (1) Iracki, T. D.; Beltran-Villegas, D. J.; Eichmann, S. L.; Bevan, M. A. Charged Micelle Depletion Attraction and Interfacial Colloidal Phase Behavior. *Langmuir* **2010**, *26* (24), 18710–18717. https://doi.org/10.1021/la103701k.
- (2) Asakura, S.; Oosawa, F. On Interaction between Two Bodies Immersed in a Solution of Macromolecules. *The Journal of Chemical Physics* **1954**, *22* (7), 1255–1256. https://doi.org/10.1063/1.1740347.
- (3) Tanjeem, N.; Wilkin, W. H.; Beller, D. A.; Rycroft, C. H.; Manoharan, V. N. Geometrical Frustration and Defect Formation in Growth of Colloidal Nanoparticle Crystals on a Cylinder: Implications for Assembly of Chiral Nanomaterials. ACS Appl. Nano Mater. 2021, 4 (10), 10682–10691. https://doi.org/10.1021/acsanm.1c02126.