Supporting Information

Unraveling the impact of template geometry and confinement on template-assisted self-assembly of nanoparticles

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We calculated the radial distribution function, $g(r)$, of two sample nanoparticles in the bulk shown in Figures 3H (with 100% yield) and I (with 10% yield). The radial distribution functions are illustrated in Figure S1A and B, respectively, where the bars are $g(r)$ for the sample nanoparticle, r is the radial distance from the nanoparticle, and red curve is $g(r)$ averaged over all remaining nanoparticles in the bulk. Comparison of $g(r)$ in Figure S1A and B suggests that to achieve a high yield, nanoparticles in the bulk must be disordered. We also used $g(r)$ to calculate entropy per nanoparticle, and average entropy for all nanoparticles remaining in the bulk on the template, given by[1]

$$S = -2\pi\rho k_B \int_0^\infty \{g(r)ln[g(r)] - g(r) + 1\} r^2 dr, \quad (1)$$

where k_B is the Boltzmann constant, and ρ is the nanoparticle density. Insets in Figure S1A and B illustrate the entropy per nanoparticle color coded from red (low) to blue (high), with an average (over all remaining nanoparticles in the bulk) of -2.2 and -3.9, respectively.

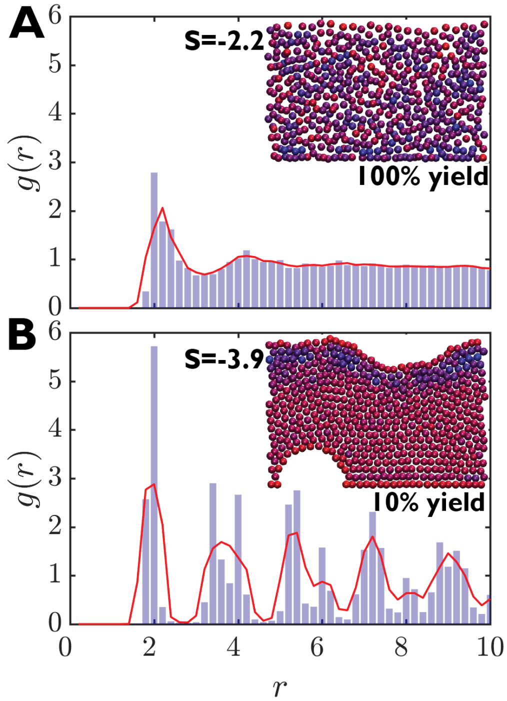

Figure S1: (A-B) Radial distribution function, $g(r)$, versus r, for state D (100% yield) and E (10% yield), respectively, on the phase diagram in Figure 2. Bars show $g(r)$ for a sample nanoparticle, and red curve illustrates $g(r)$ averaged over all remaining nanoparticles in the bulk. Entropy is color coded from low (red) to blue (high) shown in the inset, whose average is -2.2 and -3.9 for state D and E, respectively. The $g(r)$ suggests disordered (A) and ordered (B) phase, respective to state D and E on the phase diagram.

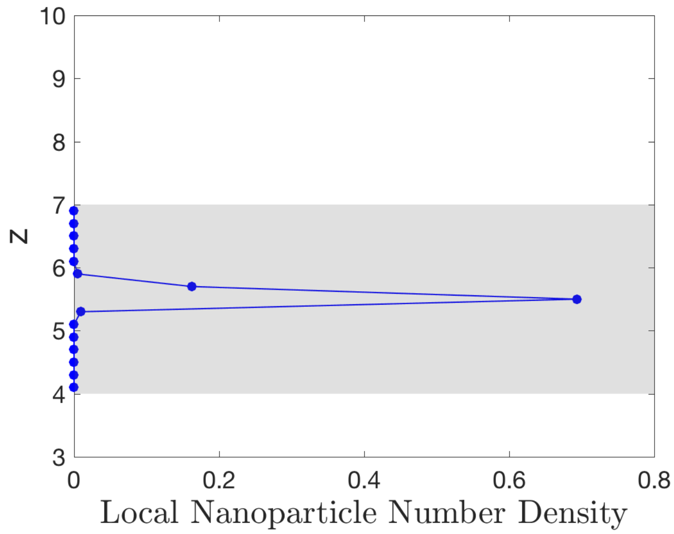

Figure S2: Variation of local nanoparticle number density in the z-direction, where overall nanoparticle number density is $\rho = 0.05$, all in nondimensionalized units. The shaded area indicates the liquid film thickness of $d = 3$. At this thickness, nanoparticles form a sheet (monolayer) within the liquid film as the density distribution is unimodal.

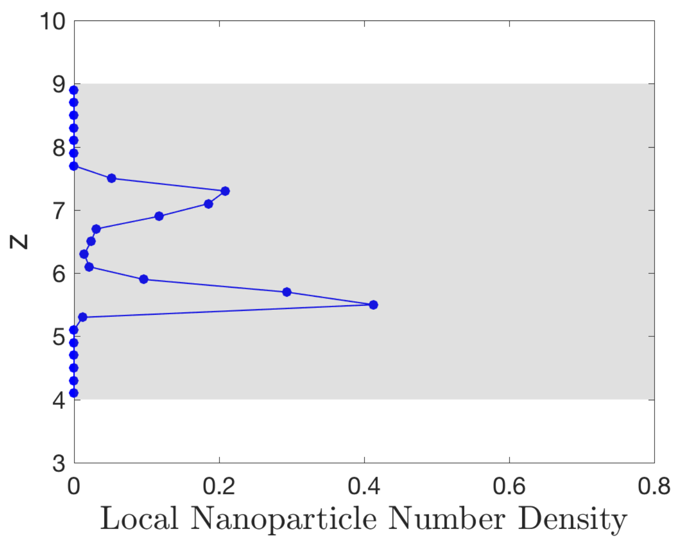

Figure S3: Variation of local nanoparticle number density in the z-direction, where overall nanoparticle number density is $\rho = 0.05$, all in nondimensionalized units. The shaded area indicates the liquid film thickness of $d = 5$. At this thickness, nanoparticles form a double layer within the liquid film as the density distribution is bimodal.

References

1. Nettleton, R. E.; Green, M. S. Expression in Terms of Molecular Distribution Functions for the Entropy Density in an Infinite System. *The Journal of Chemical Physics* **1958**, *29*, 1365–1370.