Electronic Supplementary Information for:

Surface composition and ordering of binary nanoparticle mixtures in spherical confinement

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†Electronic supplementary information (ESI) available.

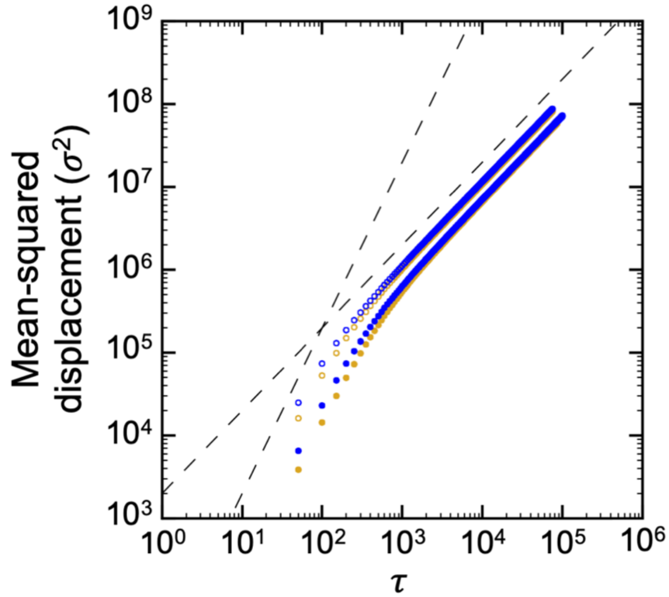

Figure S1*: Log-log plot of particle mean-squared displacement as a function of dimensionless simulation time, τ, for single-component simulations of 130 nm SP (goldenrod open circles), 130 nm SMP (blue open circles), 220 nm SP (goldenrod closed circles), and 220 nm SMP (blue closed circles). Dashed black lines of slope 2 and 1 are also included to guide the eye and demonstrate the transition to the diffusive regime. We perform these mean-squared displacement simulations at T^* = 1.0 in periodic cubic simulation boxes with total occupied volume fraction η = 0.03, and we obtain the diffusion constant D^*_i by fitting the Stokes-Einstein relation to all data $\tau \geq 10^4$.*

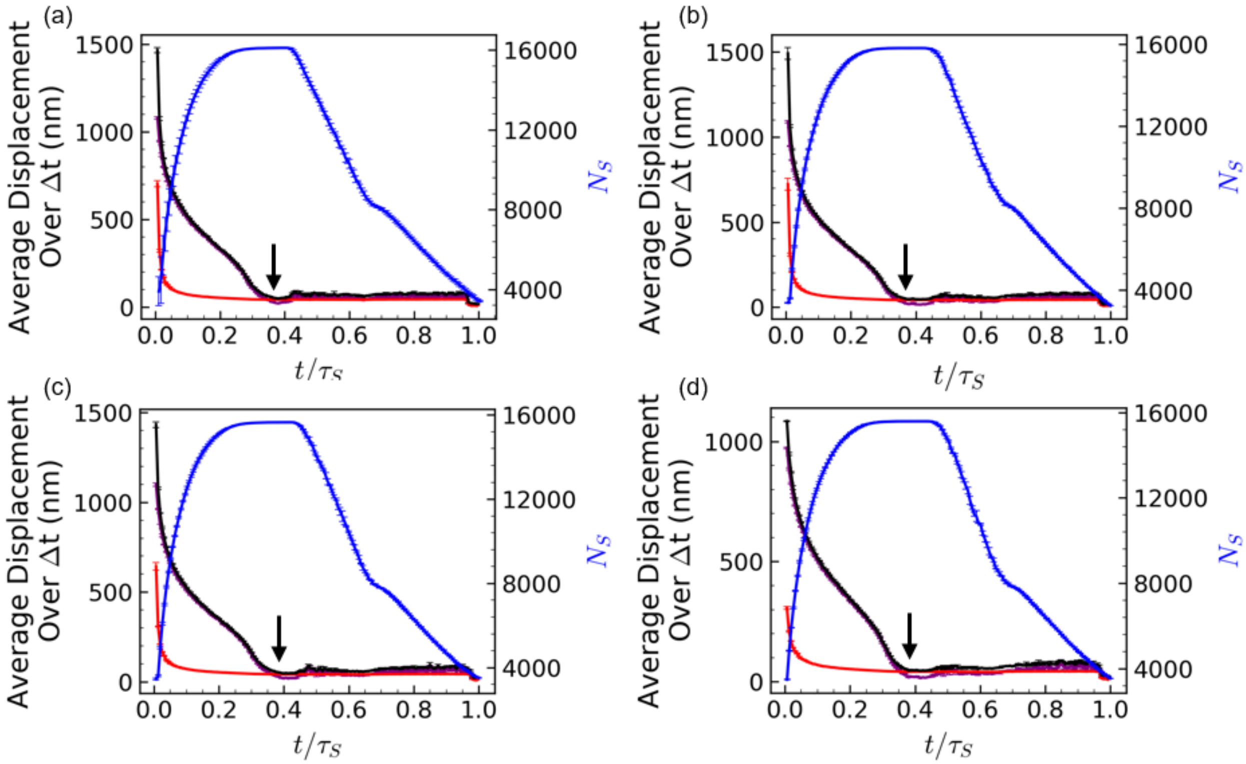

Figure S2: *Characterization of the jamming transition of surface-adsorbed particles for systems studied in Figure 4 of the main text. In all panels, black lines are the average magnitude of total particle displacement over a time period* $\Delta t = 2500\,\tau$ *for all particles on the surface of the emulsion droplet. The red and purple lines are the average magnitudes of the radial and surface tangent components of the particle displacement, respectively. For comparison, the number of particles adsorbed on the emulsion droplet surface (*N_s*) is plotted in the blue lines (right axis). The jamming transition of surface-adsorbed particles is marked with a black arrow. (a) Monodisperse* D_{SMP} *= 220 nm system with* $\phi_{SMP,\,B} = 1.0$*; (b)* D_{SMP} *= 220 nm system with 6% particle size dispersity and* $\phi_{SMP,\,B} = 1.0$*; (c) monodisperse* $D_{SP} = D_{SMP}$ *= 220 nm system with* $\phi_{SMP,\,B} = 0.8$*; (d)* $D_{SP} = D_{SMP}$ *= 220 nm system with 6% particle size dispersity and* $\phi_{SMP,\,B} = 0.8$*. All data shown is for* τ_S *= 30 s,* R_∞ *= 3.5 µm, and* $\alpha = 1.0$*.*

For each of the systems shown in Figure S2, the radial component of particle displacement (red) drops sharply in the early stages of assembly as particles diffuse and adsorb to the interface. The surface tangent component of particle displacement (purple) decreases progressively as the particle surface coverage increases until reaching zero at a jamming transition near $t/\tau_S = 0.37$ (marked with an arrow). The surface tangent component of particle displacement increases slightly in the later stages of assembly ($t/\tau_S > 0.5$) as particles are removed from the emulsion droplet surface; the progressive removal of particles from the surface frees up space for the remaining surface-adsorbed particles to slowly move/rearrange.

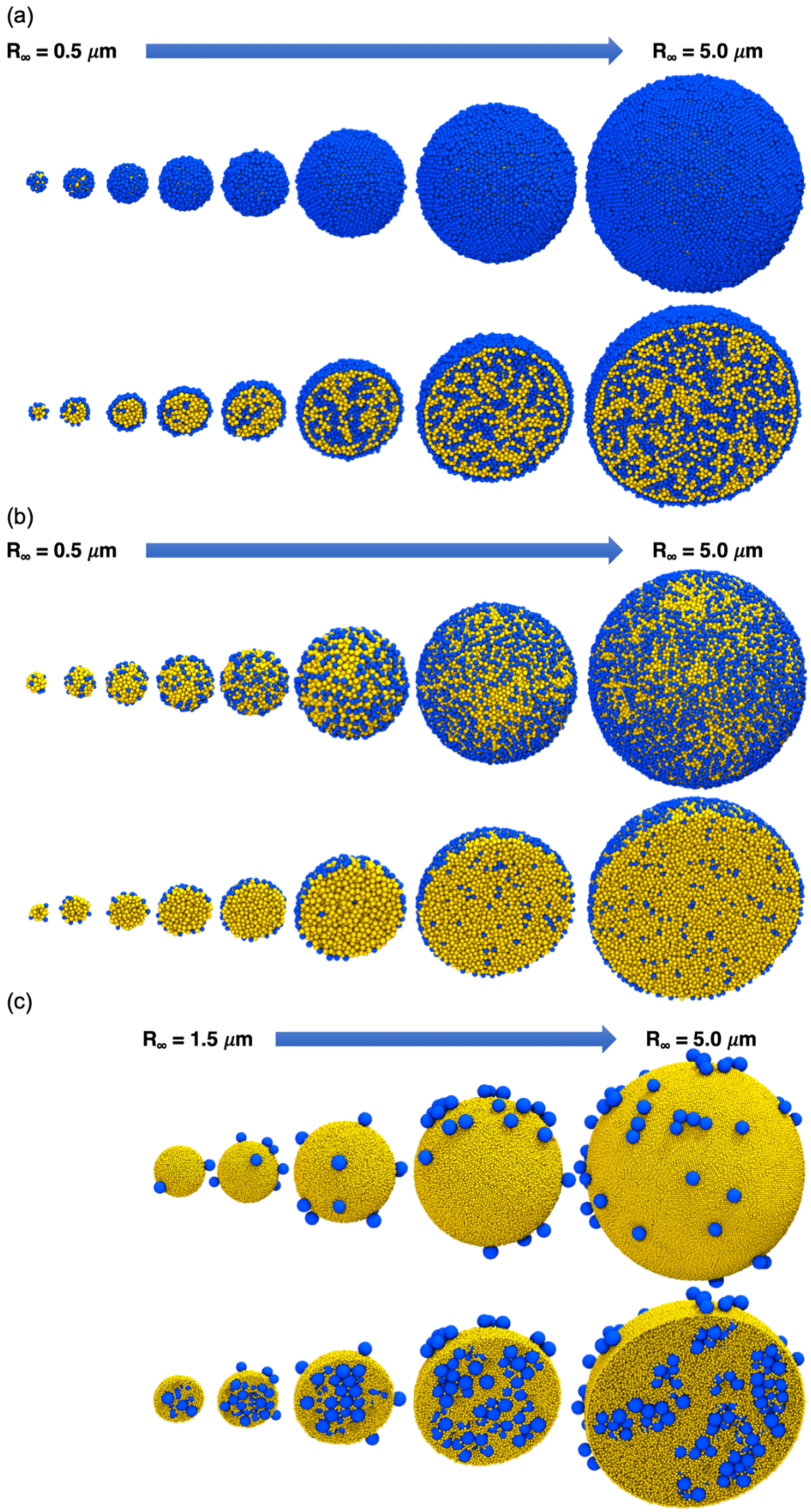

Figure S3: *Simulation snapshots of the supraball for all systems reported in main text Figure 2: (a) $D_{SP} = D_{SMP} = 220$ nm, $\phi_{SMP,\,B} = 0.5$ mixture, (b) $D_{SP} = D_{SMP} = 220$ nm, $\phi_{SMP,\,B} = 0.1$ mixture, and (c) $D_{SP} = 130$ nm, $D_{SMP} = 660$ nm, $\phi_{SMP,\,B} = 0.5$ mixture. SPs are rendered in yellow, and SMPs are rendered in blue. The upper row of each panel shows the entire supraball, and the lower row shows a cross-section of the supraball.*

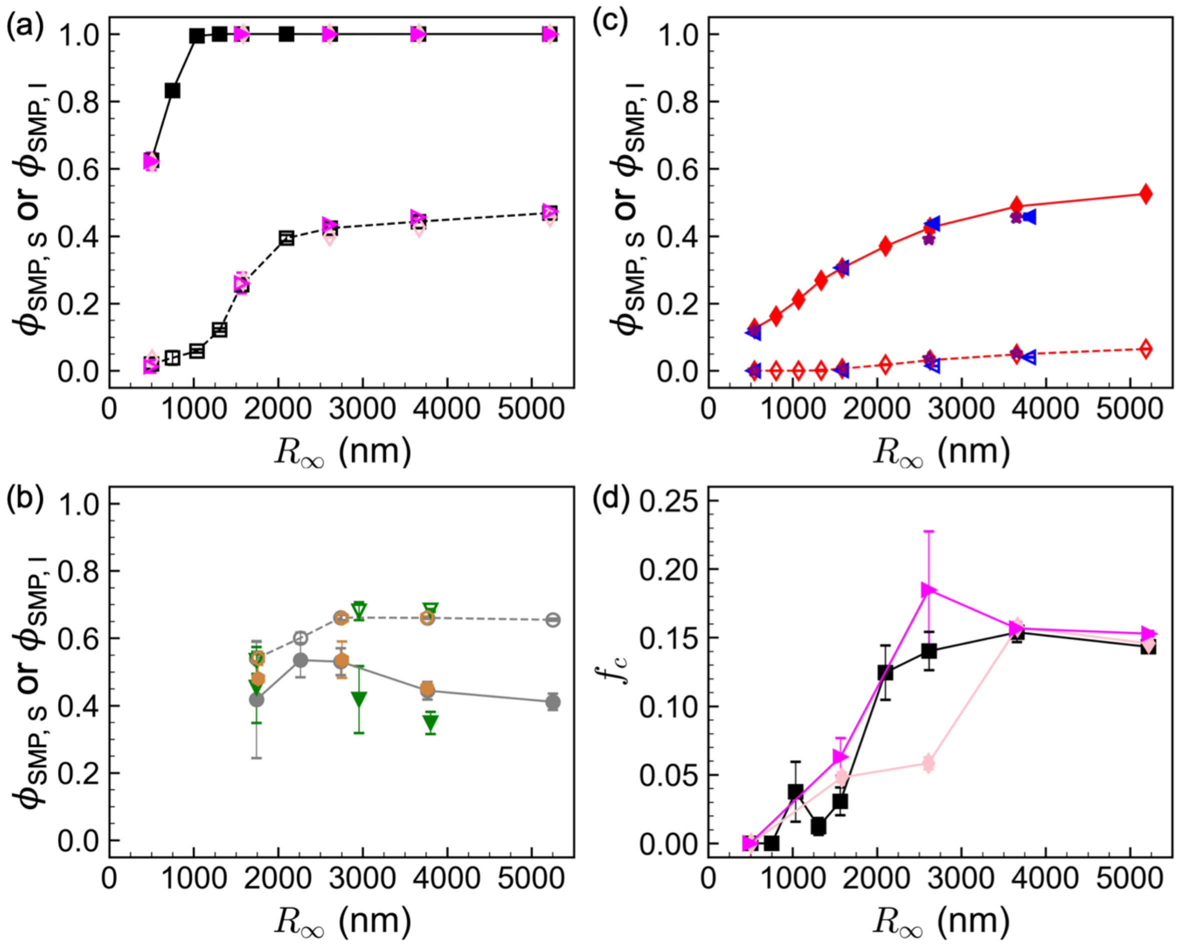

***Figure S4**: Impact of altering R_∞ on (a), (b), (c) $\phi_{SMP, S}$ (solid symbols and solid lines) and $\phi_{SMP, I}$ (open symbols and dashed lines) and (d) f_c. Black squares in (a) & (d) are a $D_{SP} = D_{SMP} = 220$ nm (SMP/SP size ratio = 1.0), $\phi_{SMP, B} = 0.5$ mixture, $\alpha = 1.0$, pink diamonds in (a) & (d) are a $D_{SP} = D_{SMP} = 220$ nm (SMP/SP size ratio = 1.0), $\phi_{SMP, B} = 0.5$ mixture, $\alpha = 0.5$, and magenta arrows in (a) & (d) are a $D_{SP} = D_{SMP} = 220$ nm (SMP/SP size ratio = 1.0), $\phi_{SMP, B} = 0.5$ mixture, $\alpha = 2$. Grey circles in (b) are a $D_{SP} = 130$ nm, $D_{SMP} = 660$ nm (SMP/SP size ratio = 5.1), $\phi_{SMP, B} = 0.5$ mixture, $\alpha = 1.0$, green downward triangles in (b) are a $D_{SP} = 130$ nm, $D_{SMP} = 660$ nm (SMP/SP size ratio = 5.1), $\phi_{SMP, B} = 0.5$ mixture, $\alpha = 0.5$, and goldenrod hexagons in (b) are a $D_{SP} = 130$ nm, $D_{SMP} = 660$ nm (SMP/SP size ratio = 5.1), $\phi_{SMP, B} = 0.5$ mixture, $\alpha = 2.0$. Red diamonds in (c) are a $D_{SP} = D_{SMP} = 220$ nm (SMP/SP size ratio = 1.0), $\phi_{SMP, B} = 0.1$ mixture, $\alpha = 1.0$, blue arrows in (c) are a $D_{SP} = D_{SMP} = 220$ nm (SMP/SP size ratio = 1.0), $\phi_{SMP, B} = 0.1$ mixture, $\alpha = 0.5$, and purple stars in (c) are a $D_{SP} = D_{SMP} = 220$ nm (SMP/SP size ratio = 1.0), $\phi_{SMP, B} = 0.1$ mixture, $\alpha = 2.0$. All data shown is for polydisperse systems with 6% particle size dispersity and $\tau_S = 30$ s.*

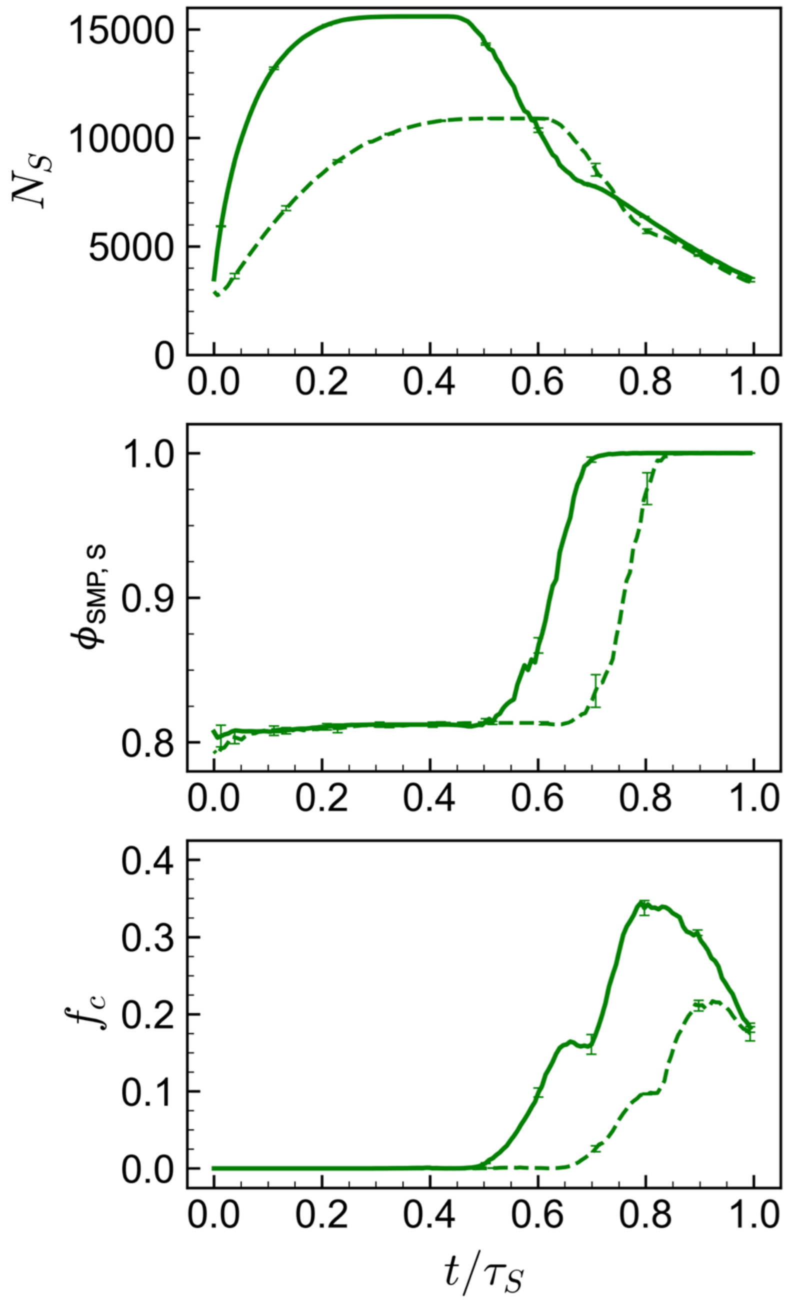

Figure S5*: Time evolution of the number of particles on the droplet surface (N_S), $\phi_{SMP,\,S}$, and f_c in a $D_{SP} = D_{SMP} = 220$ nm system with 6% particle size dispersity, $\phi_{SMP,\,B} = 0.8$, $R_\infty = 3.5$ μm, and α = 1.0. Solid lines are $\tau_S = 30$ s and dashed lines are $\tau_S = 3$ s.*

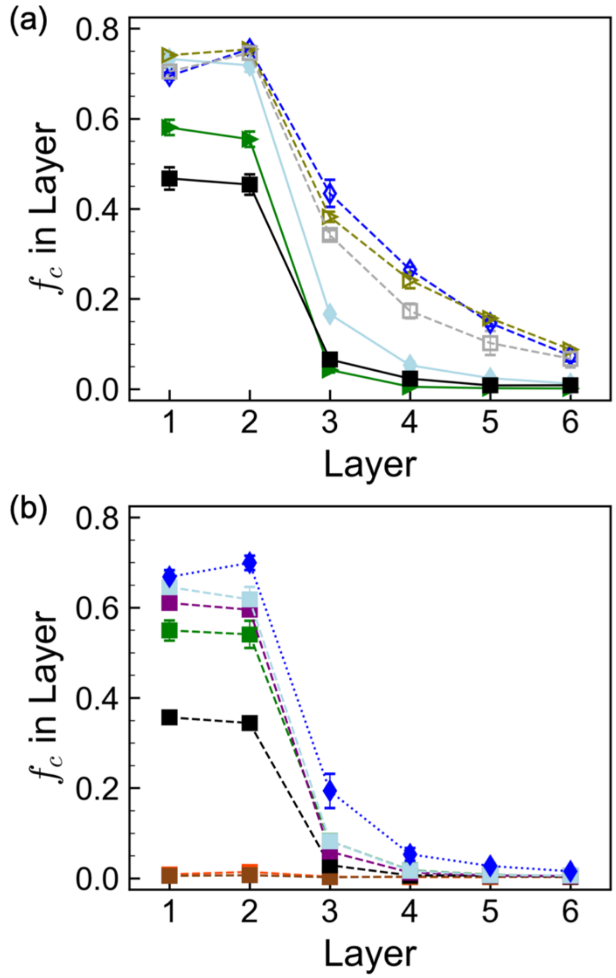

***Figure S6**: Fraction of crystalline particles within the outermost 6 layers in the supraball (1 representing the surface layer) for (a) τ_S = 30 s and (b) τ_S = 3 s. Dark blue diamonds, olive triangles, and grey squares in (a) are monodisperse $D_{SP} = D_{SMP}$ = 220 nm systems with $\phi_{SMP,\,B}$ = 1.0, 0.8, and 0.5, respectively. Light blue diamonds, green triangles, and black squares in (a) are $D_{SP} = D_{SMP}$ = 220 nm systems with 6% particle size dispersity and $\phi_{SMP,\,B}$ = 1.0, 0.8, and 0.5, respectively. Dark blue diamonds in (b) are a monodisperse D_{SMP} = 220 nm system with $\phi_{SMP,\,B}$ = 1.0 and light blue, purple, green, black, brown, and orange squares in (b) are $D_{SP} = D_{SMP}$ = 220 nm systems with 6% particle size dispersity and $\phi_{SMP,\,B}$ = 1.0, 0.9, 0.8, 0.5, 0.2, and 0.1, respectively. All data shown is for R_∞ = 3.5 µm and α = 1.0.*

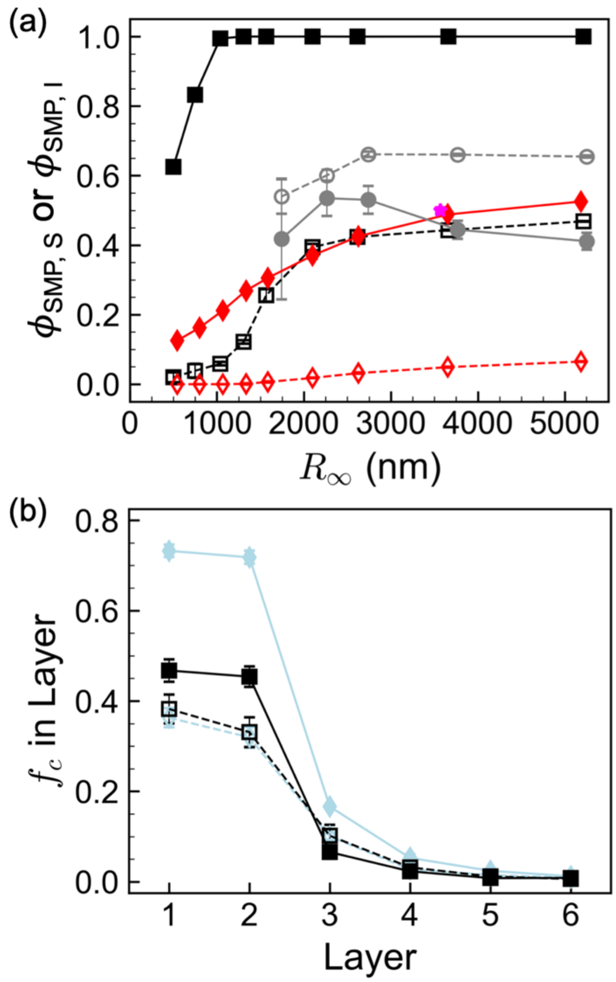

Figure S7: *(a) Impact of particle-interface interactions on $\phi_{SMP,\,S}$ (solid symbols and solid lines) and $\phi_{SMP,\,I}$ (open symbols and dashed lines). Black squares, red diamonds, and grey circles in (a) are identical to Figure 2a in the main text (attractive particle-interface interactions), and magenta stars in (a) are a D_{SP} = D_{SMP} = 220 nm, $\phi_{SMP,\,B}$ = 0.5 mixture with purely repulsive particle-interface interactions. (b) Impact of particle-interface interactions on f_c. Light blue diamonds in (b) are a D_{SMP} = 220 nm, $\phi_{SMP,\,B}$ = 1.0 system and black squares in (b) are a D_{SP} = D_{SMP} = 220 nm, $\phi_{SMP,\,B}$ = 0.5 mixture. Attractive particle-interface interactions are denoted in (b) with solid symbols and solid lines and repulsive particle-interface interactions are denoted in (b) with open symbols and dashed lines. All data shown is for τ_S = 30 s and α = 1.0, and the systems in (b) are at R_∞ = 3.5 µm.*