Supporting Information to "Depletion-Induced Encapsulation by Dumbbell-Shaped Patchy Colloids Stabilize Microspheres against Aggregation"

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1 Synthesis

1.1 Synthesis of Rough-Smooth Dumbbells

Synthesis of Spherical Polystyrene Seed Particles by Dispersion Polymerization

Non cross-linked spherical polystyrene particles of approximately 1 µm in diameter were used as seed particles for the synthesis of dumbbell-shaped particles and as a control in the encapsulation experiments. These particles were synthesized using dispersion polymerization with polyvinylpyrrolidone (PVP, M_w = 40 kg mol^{-1}, Sigma-Aldrich) as steric stabilizer. For this synthesis, 10 mL styrene (Sigma-Aldrich, $\geq$ 99%), 5.0 g PVP and 0.136 g azobisiobutyronitrile (AIBN, Sigma-Aldrich) were dissolved in 126 mL ethanol (p.a., Merck) and 14 mL water (Millipore) in a 250 mL round bottom flask. The flask was flushed with N_2 and sealed tightly with a stopper and Teflon tape. Polymerization was carried out by immersing the flask in an oil bath of 70 ℃ at an angle of 60° and rotating it at $\sim$100 rpm for 24 hours. The resulting dispersion was washed by centrifugation and redispersion in methanol to remove remaining reactant and transferred to water for further processing.

Cross-Linking of Polystyrene Spheres by Seeded Emulsion Polymerization

The rough, cross-linked seed particles were synthesized by seeded emulsion polymerization. For this synthesis, a monomer mixture was prepared consisting of styrene (distilled) with 10% v/v 3-(Trimethoxysilyl)propylacrylate (TMSPA, Alfa, 95%, stab. with 100 ppm BHT) as co-monomer, 1.5% v/v divinylbenzene (DVB, 55% tech. Aldrich) as a cross-linker and 2% wt 2,2'-azobis(2,4-dimethylvaleronitrile) (V-65, Wako chemicals GmbH) as an initiator.

A swelling emulsion was prepared by adding 1 part of this apolar monomer solution to 4 parts of aqueous phase containing 0.8% wt poly(vinyl alcohol) (PVA, M_w = 85-124 kg mol^{-1}, 87-89% hydrolyzed, Sigma-Aldrich) and 0.2% wt PVP to stabilize the emulsion. A total of 10 mL of this mixture was added to an elongated 25 mL vial. The content of the vial was then emulsified for 5 minutes at 8 krpm using an IKA T-25 Ultra Turrax with an S25N 10G dispersing tool.

This swelling emulsion was added to a 20% v/v dispersion of the seed particles made by dispersion polymerization to a swelling ratio of $S = m_\mathrm{monomer}/m_\mathrm{polymer\ seeds}$ equals 4. This vial was flushed with N_2 for $\sim$30 s, sealed with Parafilm and put on a RM5-80V tube roller (50 rpm) for 18 hours to allow for the particles to take up the monomer. After this, polymerization was carried out by immersing the vial in a 70 ℃ oil bath at an angle of 60° and rotating it at ~100 rpm for 24 hours. After polymerization, the particles were washed several times by centrifugation and redispersion in water to get rid of any free secondary nucleation particles.

Protrusion Formation

In the next step a protrusion is formed on these rough, cross-linked particles. For this, a 20% v/v aqueous dispersion of cross-linked particles was added to 10 mL of swelling emulsion with 1 part apolar phase consisting of styrene, 1.3% v/v DVB and 2% wt V-65 in 9 parts of aqueous phase containing 1% wt PVA, to achieve a swelling ratio of $S = 2$. After swelling and polymerization in the same way as described for the second step, the particles were again washed several times by centrifugation and redispersion in water.

1.2 Synthesis of Template Microspheres

The larger template microspheres were synthesized by first synthesizing smaller polystyrene spheres by dispersion polymerization and subsequently increasing their size in a seeded emulsion polymerization step.

In the first synthesis step, the dispersion polymerization of polystyrene spheres, 19.7 mg PVP was dissolved in 40 mL of ethanol and 8 mL of water in a round bottom flask with a PTFE stirbar. 4.1 g of styrene (distilled) was added to the reaction vessel, after which the solution was bubbled with N_2 for 1 hour. After increasing the temperature to 70 ℃, 80.1 mg of V-65 was added to initiate the reaction. The round bottom flask was closed with a rubber septum. The polymerization was carried out for 24 hours. After the reaction, the particles were washed twice with ethanol and twice with water by centrifugation and redispersion of the sediment.

In the second step, the size of the particles was increased by swelling them with monomer from an emulsion. For this reaction, a monomer mixture was prepared by dissolving 1.5% v/v divinylbenzene (DVB, 55% tech. Aldrich) and 2% wt V-65 in styrene (distilled).

A swelling emulsion was prepared by adding 1 part of this apolar monomer solution to 9 parts of aqueous phase containing 1% wt poly(vinyl alcohol) (PVA, $M_\mathrm{w} = 31\text{-}50\ \mathrm{kg\ mol^{-1}}$, 87-89% hydrolyzed, Sigma-Aldrich) to stabilize the emulsion. A total of 8 mL of this mixture was added to an elongated 25 mL vial. The content of the vial was then emulsified for 5 minutes at 8 to 9 krpm using an IKA T-25 Ultra Turrax with an S25N 10G dispersing tool.

This swelling emulsion was added to a 20% v/v dispersion of the seed particles from the first step, so that the swelling ratio, $S = 4$. This vial was flushed with N_2, sealed with Teflon tape and put on a RM5-80V tube roller (30 rpm) to allow for the particles to take up the monomer. After 19 hours of swelling, 0.8 mL of an aqueous solution of 0.4% wt hydroquinone (Sigma-Aldrich, $\geq$ 99%) was added to prevent secondary nucleation during polymerization. The vial was then again flushed with N_2 and sealed with Teflon tape. Polymerization was carried out by immersing the vial in a 70 ℃ oil bath at an angle of 60° and rotating it at ~100 rpm for 24 hours. After polymerization, the particles were washed 4 times by centrifugation and redispersion in water.

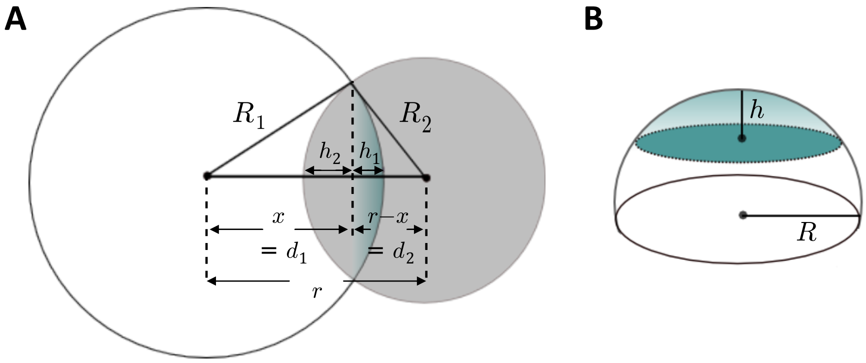

Figure S1: (A) Schematic representation of the overlap volume between two unequally sized spheres separated by a center-to-center distance r. The overlap volume is the sum of the volumes of two spherical caps with cap height h_1 and h_2, where $h_{1,2} = R_{1,2} - d_{1,2}$ and $d_1 + d_2 = r$. (B) A schematic representation of a hemisphere with radius R with a spherical cap with height h on top.

2 Size Dependent Depletion Interaction

The attractive depletion potential between two objects depends on the osmotic pressure of the depletant Π_d and the overlap between the excluded volume around each object V_overlap:[1,2]

$$u_\mathrm{depl} = -V_\mathrm{overlap}\Pi_\mathrm{d}. \tag{1}$$

In the dilute regime, where van 't Hoff's Law is valid, this can be expressed in units of $k_\mathrm{B}T$ as:

$$u_\mathrm{depl}/k_\mathrm{B}T = -\rho_\mathrm{d}V_\mathrm{overlap} \tag{2}$$

where ρ_d is the depletant concentration and $k_\mathrm{B} = 1.38 \times 10^{-23}$ JK^{-1} being Boltzmann's constant and T the temperature in Kelvin.

To calculate the depletion interaction between two spheres with unequal radii R_sphere1 and R_sphere2 (i.e. the microspheres and the smooth lobes of the dumbbells), the overlap volume as function of their center-to-center distance $V_\mathrm{overlap}(r)$ needs to be calculated. For this calculation, radii R_1 and R_2 are defined such that $R_{1,2} = R_{\mathrm{sphere}1,2} + r_\mathrm{g}$, with r_g the radius of gyration of the depletant polymer. When the excluded volumes of both spheres start to overlap at $r < R_1 + R_2$, the total V_overlap is the sum of the two spherical caps of R_1 and R_2 with respective cap height h_1 and h_2 as indicated in Figure S1.

The height of each cap is defined as $h_{1,2} = R_{1,2} - d_{1,2}$. From Figure S1 it is clear that both spherical caps have an equal base. Using this equality and the condition that $d_1 + d_2 = r$, the following expression for d_1 is found:

$$d_1 = \frac{R_1^2 - R_2^2 + r^2}{2r}. \tag{3}$$

The volume of each spherical cap can then be found by calculating the solid of revolution by integration from d_1 (eq 3) to R_1:

$$V_\mathrm{cap}(R_i, d_i) = \pi \int_{d_i}^{R_i} (R_i^2 - x^2)\, dx = \frac{\pi}{3}(2R_i^3 - 3R_i^2 d_i + d_i^3). \tag{4}$$

The depletion interaction between the two spheres as function of their center-to-center distance in the range of $R_{\mathrm{sphere1}} + R_{\mathrm{sphere2}} < r < R_1 + R_2$ then becomes

$$u_{\mathrm{depl}}(r)/k_{\mathrm{B}}T = -\rho_{\mathrm{d}}(V_{\mathrm{cap}}(R_1, d_1) + V_{\mathrm{cap}}(R_2, d_2)) \tag{5}$$

Besides the depletion attraction, there is also a repulsive electrostatic contribution to the net interaction between the particles. To calculate the electrostatic repulsion between the dumbbells and the microspheres, the screened Coulomb interaction[3] is generalized to accommodate two spheres of unequal radius and surface potential:

$$u_{\mathrm{el}}(r)/k_{\mathrm{B}}T \ = \ \frac{(\Psi_{\mathrm{m}}R_{\mathrm{s}}/k_{\mathrm{B}}T) \times (\Psi_{\mathrm{s}}R_{\mathrm{s}}/k_{\mathrm{B}}T)}{\lambda_{\mathrm{B}}r} \exp[-\kappa(r \ - \ (R_{\mathrm{m}} \ + \ R_{\mathrm{s}})]. \tag{6}$$

where $\Psi_{\mathrm{m,s}}$ and $R_{\mathrm{m,s}}$ are the surface potentials and radii of respectively the microsphere and the smooth lobe of the dumbbells, λ_{B} is the Bjerrum length and κ is the inverse Debye length. The net interaction between two particles can be obtained by summing the attractive depletion interaction and repulsive electrostatic interaction:

$$u(r) = u_{\mathrm{depl}} + u_{\mathrm{el}}. \tag{7}$$

Due to both the small size of the depletant ($r_{\mathrm{g}} = 19 \pm 6$ nm) and the short Debye length ($\kappa^{-1} \sim 2$ nm) compared to the size of the particles (> 1 µm), this net interaction is considered very short-ranged. The minimum of the potential well defined by eq 7 is therefore considered the pair potential ε between the particles.

3 Supporting Figures

- Figure S2: The coverage of the template microsphere for extended simulations (up to 1.8×10^6 MC cycles) at $\varepsilon = -7\ k_{\mathrm{B}}T$ and both $\gamma\varepsilon\ = 0$ and $-2k_{\mathrm{B}}T$.
- Figure S3: Optical microscopy images of microspheres encapsulated by small spherical particles.
- Figure S4: Optical microscopy images taken in time to show that the encapsulation by small spherical particles is dynamic.

References

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2. Lekkerkerker, H. N. W. and Tuinier, R. *Colloids and the Depletion Interaction.* Springer, (2011).

3. Verwey, E. J. W. and Overbeek, J. T. G. *Theory of the Stability of Lyophobic Colloids.* Elsevier, New York, (1948).

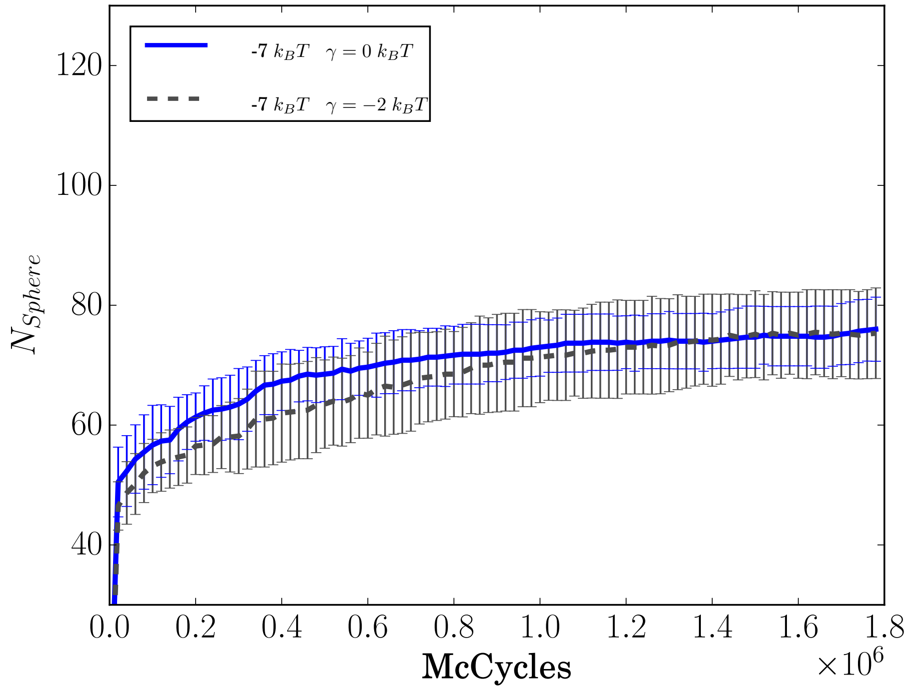

Figure S2: Coverage of a microsphere at an interaction strength of $-7\ k_{\mathrm{B}}T$ in an extended simulation (up to 1.8×10^6 MC cycles) both with (dashed) and without (solid) additional $-2\ k_{\mathrm{B}}T$ attraction on the rough lobes, showing both systems converge to a packing of $N_{\mathrm{Sphere}} \approx 70$ dumbbells on the microsphere.

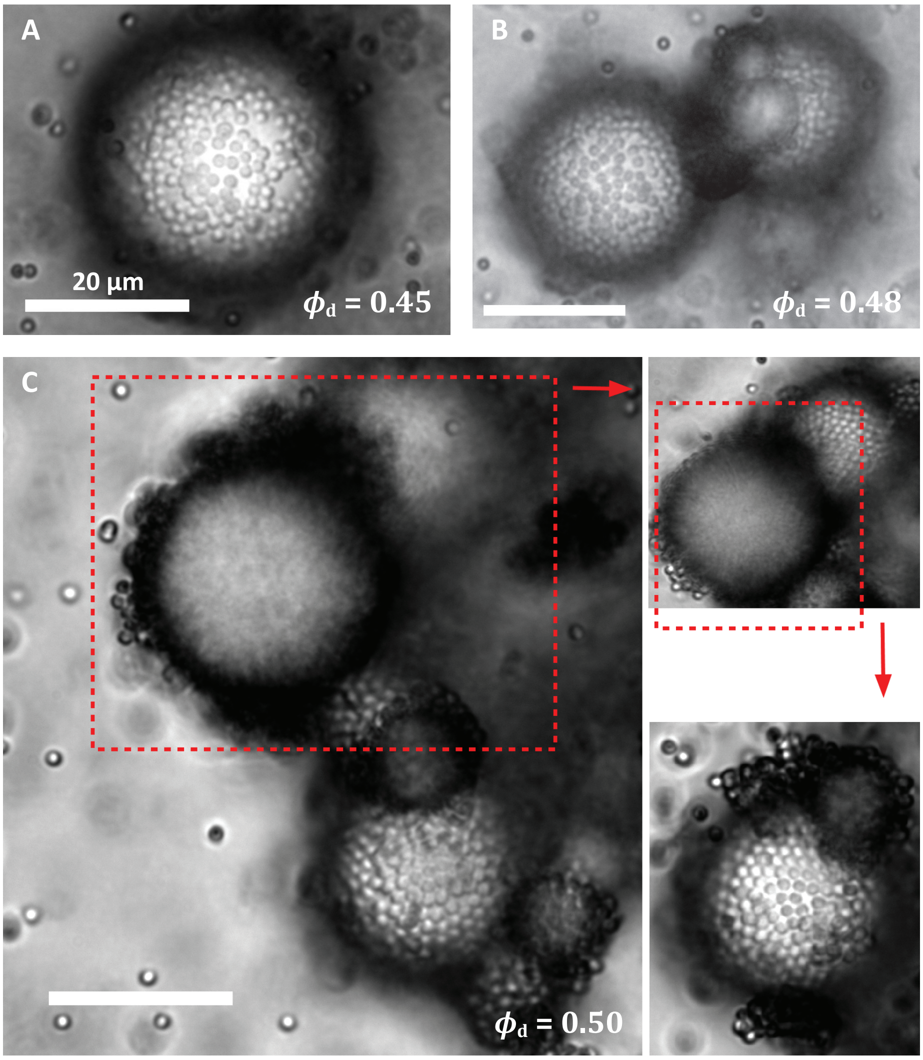

Figure S3: Optical microscopy images of the encapsulation of microspheres by small spherical polystyrene particles at increasing dextran concentrations. The coverage of the microspheres increases with increasing polymer concentration to the formation of multiple layers at $\phi_\mathrm{d} = 0.50$. The insets in (C), of which the positions are indicated by the red boxes, show the clustered microspheres at a different focal plane. All images are taken 3 days after sample preparation. The scalebars represent 20 µm.

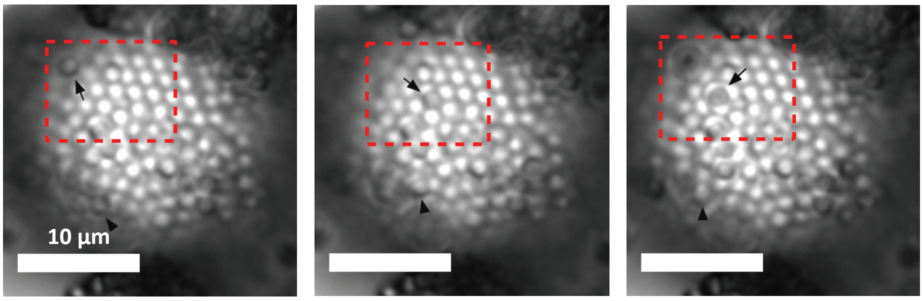

Figure S4: Small polystyrene particles attach and detach from a microsphere in time ($\phi_\mathrm{d} = 0.50$). The particle indicated by the black arrow inside the red box has an escape time of $\tau = 127$ s. On top of the first layer of bound small spheres, multiple layers start to form. The triangle ▲ indicates a small sphere that is hopping over the first layer of polystyrene particles. The scalebars represent 10 µm.