

Supplementary Information for: “**Dynamics of Confined Depletion Mixtures of Polymers and Bidispersed Colloids**”, by Rahul Pandey and Jacinta C. Conrad

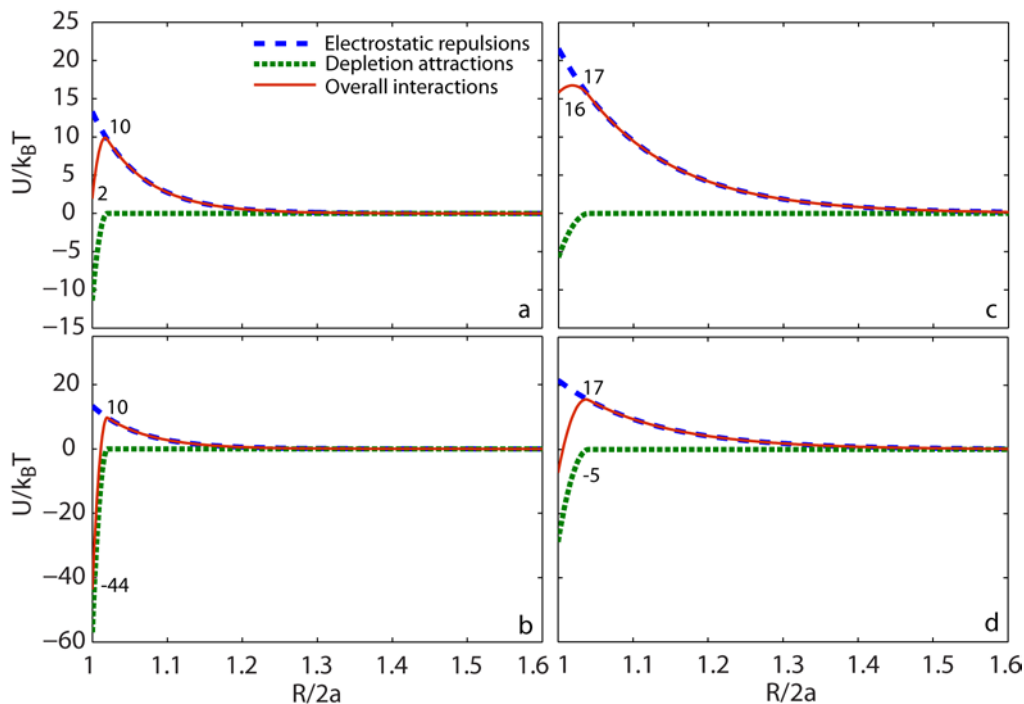


Figure S1. Dimensionless electrostatic (---)^{1,2,3}, depletion (---)^{4,5}, and overall interaction potential (—) between spherical particles as a function of normalized interparticle distance $R/2a$ for polymer concentration $c_p = 5$ mg/ml (a,c) or $c_p = 25$ mg/ml (b,d), and particle diameter $2a_L = 1.48$ μm (a,b) or $2a_S = 0.73$ μm (c,d). The numbers in each panel indicate the maximum repulsive barrier and the value at contact ($R/2a = 1$).

The electrostatic and depletion potentials were estimated as below:

1) Electrostatic Potential:

Particle charge: The rule of thumb given in Royall *et al.*³ was used to estimate particle charge given the diameter of the particle $2a$ and the Bjerrum length λ_B .

$$Z = \frac{12a}{\lambda_B} \quad (1)$$

The Bjerrum length (λ_B) was calculated as

$$\lambda_B = \frac{\beta e^2}{4\pi\epsilon_0\epsilon_r} \approx 10 \text{ nm} \quad (2)$$

where $\epsilon_r \approx 5.53$ is the dielectric constant of the solvent mixture⁶. The charge of the small and large particles were calculated as $Z_S = 183$ and $Z_L = 370$, respectively.

Screening Length: The Debye screening length ($\kappa^{-1}=100 \text{ nm}$) was taken from literature measurements of PMMA particles in CXB-DHN solvents³.

Contact Potential: The normalized contact potential ($\epsilon/k_B T$) was estimated for each population of particles as

$$\frac{\epsilon}{k_B T} = \frac{Z^2 \lambda_B}{2a(1 + \kappa a)^2} \quad (3)$$

where a is the appropriate radius for each particle population¹.

Finally, the pair potential form¹ used to calculate the electrostatic interaction potential ($U(r)$) as a function of the separation r between particles is given by:

$$\frac{U(r)}{k_B T} = \begin{cases} \frac{\epsilon}{k_B T} \frac{\exp[-2a\kappa(\frac{r}{2a} - 1)]}{r/2a} & r > 2a \\ \infty & r < 2a \end{cases}$$

(2) Depletion Potential:

The depletion potential was calculated using the $U_{depletion}$ form given in Reference 3:

$$U_{depletion} = \begin{cases} +\infty & \text{for } r \leq 2a \\ -\Pi_p V_{overlap} & \text{for } 2a < r \leq 2a + 2r_g \\ 0 & \text{for } r > 2a + 2r_g \end{cases} \quad (5)$$

$$\Pi_p = n_p k_B T \quad (6)$$

where Π_p is the osmotic pressure of the polymer, $V_{overlap}$ is the volume of the overlapping depletion zone between two particles (calculated to account for free volume

as given in Reference 3), n_p is the polymer number density in the free volume in the sample and r_g is radius of gyration of a polymer molecule (≈ 15 nm).

- [1] A. Hynninen *et al.*, *Phys. Rev. E*, **68**, 021407 (2003)
- [2] M. F. Hsu *et al.*, *Langmuir* **21**, 4881-4887 (2005)
- [3] C. P. Royall *et al.*, *Soft Matter*, **9**, 17 (2013)
- [4] S. M. Ilett *et al.*, *Phys. Rev. Lett.* **51**, 1344-1352 (1995)
- [5] H. N. W. Lekkerkerker *et al.*, *Europhys. Lett.*, **20** (6), 559-564 (1992)
- [6] P. Wang and A. Anderko, *Fluid Phase Equilib.*, **186**, 103-122 (2001)

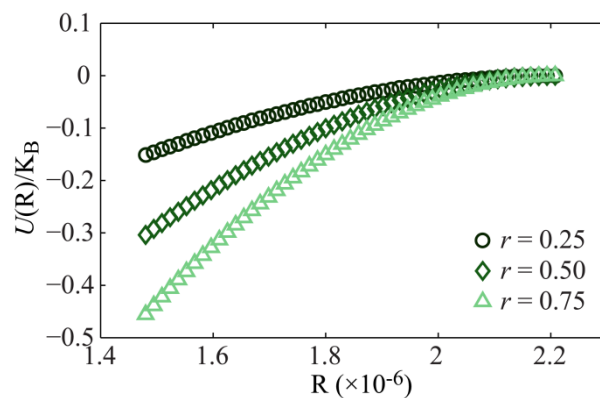


Figure S2. Dimensionless pair interaction potential from modified AO model⁶ between spherical large and small particles as a function of interparticle distance R (in m), for varying ratio of volume fraction of small particles to the total volume fraction r .

Modified AO Form⁶:

$$U_{AO} = \frac{k_B T \phi_S^*}{(2a_S^*)^3} (2a_S^* + 2a_L^* - r)^2 \left(2a_S^* + 2a_L^* + \frac{r}{2} \right) \quad (7)$$

where $a_S^* = a_S + \delta a_S$ and $\phi_S^* = \phi_S (1 + \delta a_S/a_S)$ are the effective small sphere radius and volume fraction, respectively. a_S and a_L are the bare radii of the small and large particles, ϕ_S is the volume fraction of small particles, and r is the interparticle distance.

[6] J. C. Crocker *et al.*, *Phys. Rev. Lett.* **82**, 4352-4355 (1999)

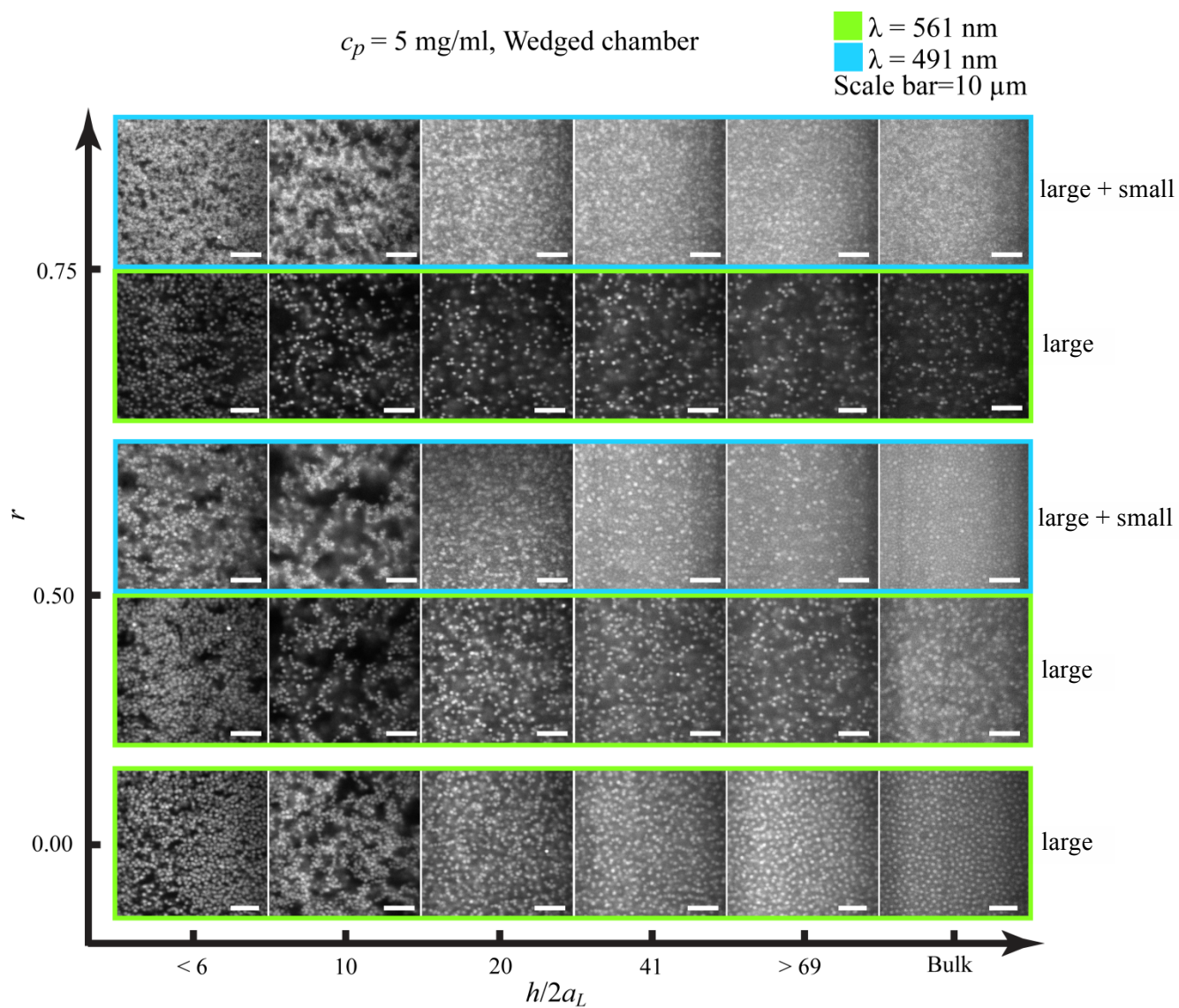


Figure S3. Confocal micrographs of small and large particles in suspensions with polymer concentrations $c_p = 5 \text{ mg/ml}$. Micrographs were acquired using a laser excitation at a wavelength $\lambda = 491 \text{ nm}$ (blue channel, both populations of particles) and $\lambda = 561 \text{ nm}$ (green channel, large particles only) at different confinements $h/2a_L$ (x -axis) including bulk samples, with varying volume percent of small particles r (y -axis).

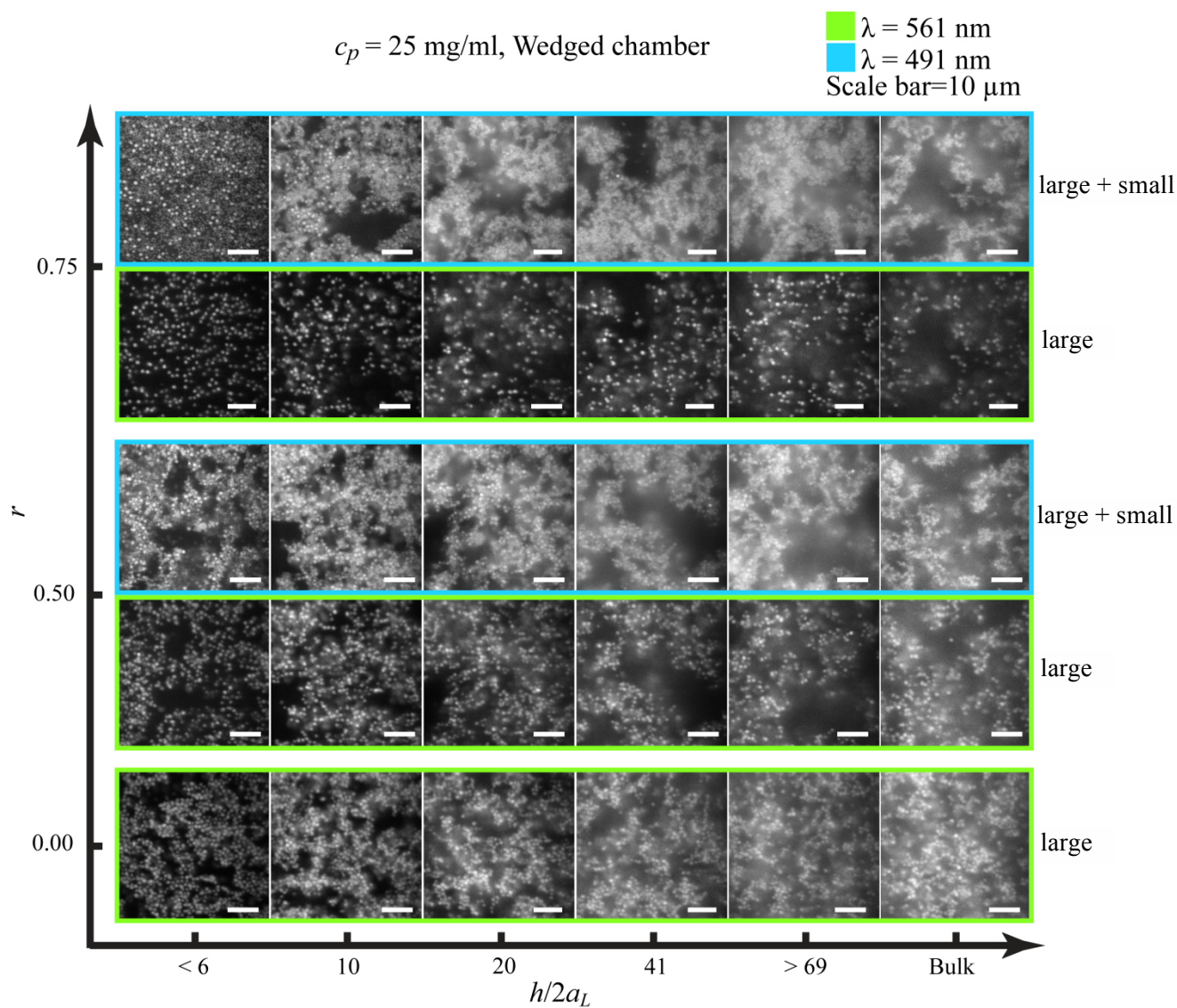


Figure S4. Confocal micrographs of small and large particles in suspensions with polymer concentrations $c_p = 25$ mg/ml. Micrographs were acquired using a laser excitation at a wavelength $\lambda = 491$ nm (blue channel, both populations of particles) and $\lambda = 561$ nm (green channel, large particles only) at different confinements $h/2a_L$ (x -axis) including bulk samples, with varying volume percent of small particles r (y -axis).

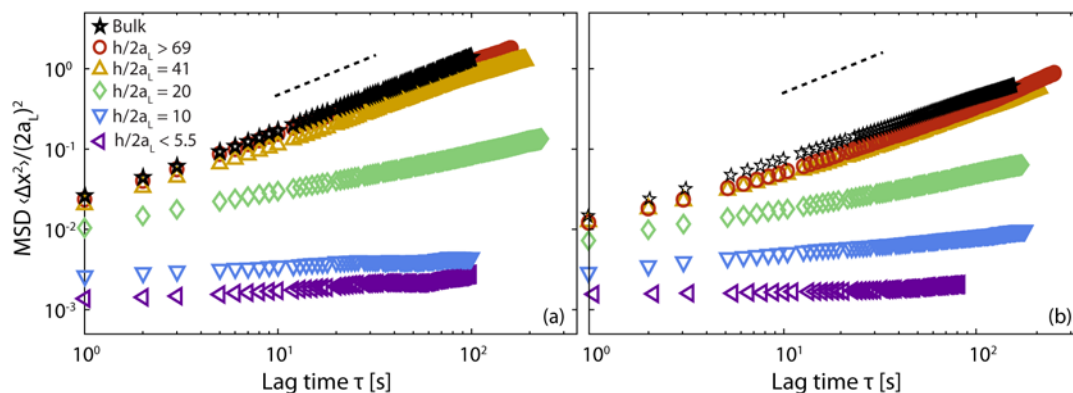


Figure S5. Mean-squared displacement (MSD) $\langle \Delta x^2 \rangle / (2a_L)^2$ as a function of lag time τ of large particles in binary suspensions with concentration of depletant polymer of $c_p = 5$ mg/ml and fixed ratio of volume of small particles to total particles volumes ($r = 0.50$) at confinement times of (a) 0.5 hours and (b) 30 days. Confinement thicknesses $h/2a_L$: bulk (\star) > 69 (O), 41 (Δ), 20 (\diamond), 10 (∇), and < 5.5 (\triangleleft). The dashed lines indicate a slope of 1.

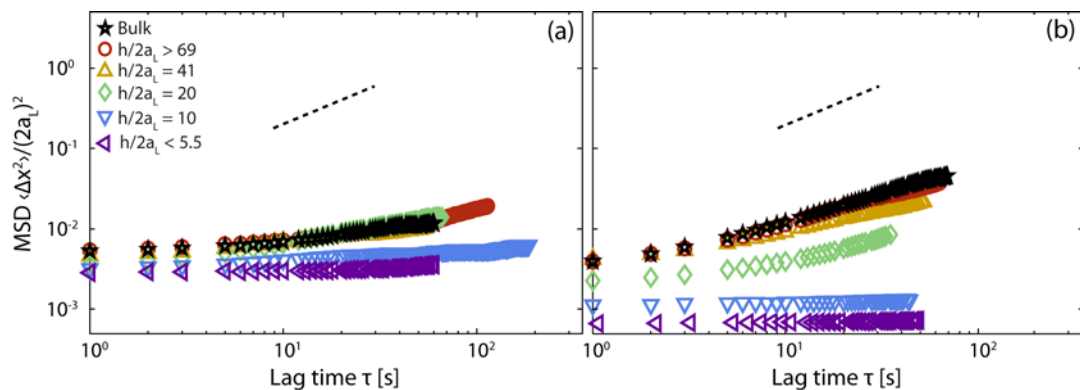


Figure S6. Normalized mean-squared displacement $\langle \Delta x^2 \rangle / (2a_L)^2$ as a function of lag time τ of large particles in binary suspensions with concentration of depletant polymer of $c_p = 25$ mg/ml and fixed volume of small particles ($r=0.50$) at confinement times of (a) 0.5 hours and (b) 30 days. Confinement thicknesses $h/2a_L$: bulk (\star) > 69 (\circ), 41 (\triangle), 20 (\diamond), 10 (∇), and < 5.5 (\triangleleft). The dashed lines indicate a slope of 1. We note that the samples in (b) were aged for one month in bulk solution before loading into wedge chambers, so that the particles swelled slightly compared to the initial measurements in (a); the increase in particle size is the primary origin in the decrease in the MSD.

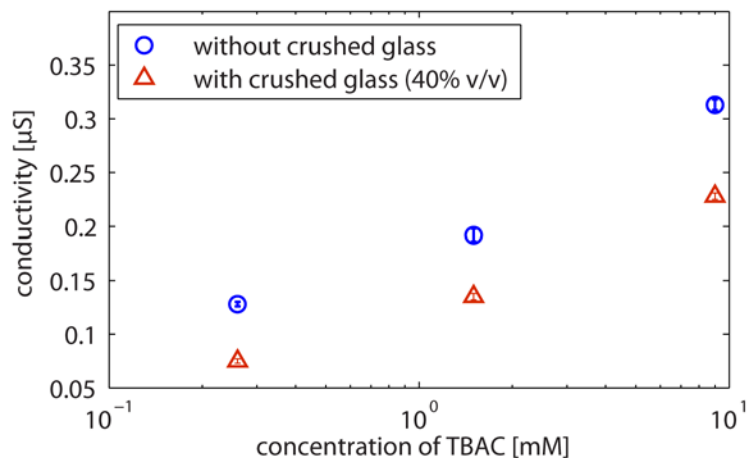


Figure S7. Conductivity as a function of concentration of TBAC (tetrabutylammonium chloride) salt in a solvent mixture of cyclohexylbromide and decahydronaphthalene (weight ratio of 3.1:1), for bulk solvent (○) and for a solvent containing 40 volume % crushed glass (△), which mimicked the “confined” solvent. The error bars indicate the standard deviation over five measurements.