

Supporting information for "Stratification and size segregation of ternary and polydisperse colloidal suspensions during drying"

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This supporting information has four sections. In the first we present results for the scaling of the diffusion constant with diameter, for a large particle diffusing in a suspension of smaller particles. These results support our assumption in the main text that the sedimentation coefficient can be written as $K(\eta, d) = A(\eta)d^\alpha$, with α between zero and one.

In the second section, we present results that show that the finite system sizes we use are not so small that they significantly affect our results. The third section is devoted to a study that shows that the time we equilibrate our systems for, prior to starting evaporation, does not affect our results. In the final section, we show that the initial distribution of particle diameters is independent of height and is the required Gaussian.

Diffusion coefficients

We measured the diffusion coefficients D_L of tracer large particles of diameter d_L in a suspension of smaller colloidal particles of diameter d_S . The diffusion coefficient D_S of the small particles was also measured as a reference. The calculations were done using LAMMPS as

described in the main text. The values of the diffusion coefficients were calculated from the slope of the mean square displacement (MSD) as a function of simulation time. We recorded the MSD for a simulation time equal to 50 times the Brownian diffusion time of the large particles. The suspensions were initialized with a total of 15,000 small particles and 30 tracer large particles.

Figure S1 shows the ratio D_L/D_S as a function of the particle size ratio d_L/d_S . The three types of symbols correspond to three different volume fractions of small particles $\phi_s=0.006$ (circles), 0.06 (squares) and 0.3 (triangles). In the main text, in our model of colloidal diffusiophoresis, we assumed that the friction felt by the large particles $\xi(\eta, d_L) = 3\pi d_L \nu K(\eta, d_L)$. We further assumed that the sedimentation coefficient had a power law dependence on diameter: $K(\eta, d_L) = A(\eta)d_L^\alpha$, with α a volume-fraction dependent coefficient that is zero at low volume fractions, and close to one at high volume fractions. The diffusion coefficient is then $D_L = kT/\xi = kT/[3\pi d_L \nu K(\eta, d_L)]$, and so with our assumed form for K , we predict the scaling $D_L/D_S = a'(\eta)d_L^{-1-\alpha}$, with a' some function of η .

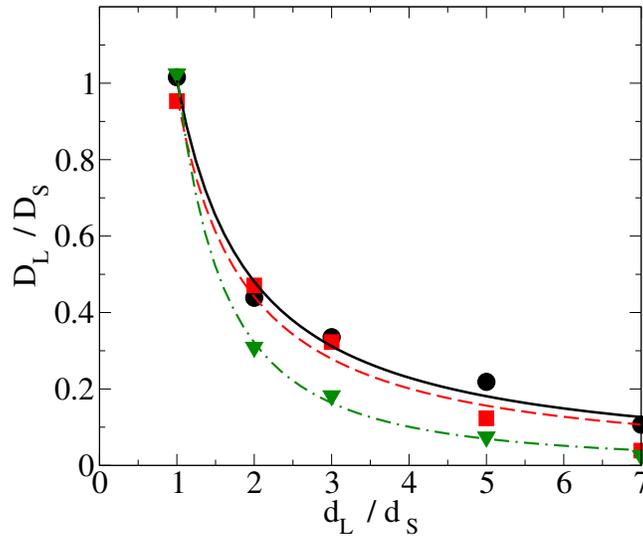


Figure S1: Diffusion coefficient D_L/D_S of tracer large particles of diameter d_L in a suspension of small colloidal particles at three different volume fractions $\phi_s=0.006$ (black circles), 0.06 (red squares) and 0.3 (green triangles). The curves are power-law fits: $D_L/D_S = a'd_L^{-1-\alpha}$.

In Figure S1 we show the calculated diffusion coefficients (points), and power law fits

(curves). We see that the power-law functions provide good fits. The best-fit exponents are $\alpha = 0.07, 0.13$, and 0.67 , at volume fractions of the small particles of $\phi_s=0.006$, 0.06 and 0.3 , respectively. As expected, we find that the coefficient α is almost zero at very low volume fraction and increases towards one at larger volume fractions. We finally note that we fixed the volume fraction of the small particles and kept the number of tracer particles constant. The finite number of large particles leads to a change of the total volume fraction of the mixture. The scaling with overall volume fraction may vary from the scaling with volume fraction of the smaller particles seen in Figure S1, but we leave calculations on that effect to future work. Even at fixed diameter and total volume fraction, the diffusion coefficient might be influenced by the composition.

Finite size effects

We checked the finite size effects of the simulation box on the stratification of mixtures B and C2. Figure S2 shows the results for mixture B (see Table 1 of the main article). We compare the density profiles of the stratified film obtained with the original initial box size $13.9988 \times 13.9988 \times 1500 d_1^3$ (yellow dotted line) against the profiles obtained with a larger simulation box. The continuous black lines are the results for an initial simulation box size $27.998 \times 27.988 \times 1500 d_1^3$. The panels (a), (b), and (c) show the profiles for the small, intermediate and large particles, respectively. For mixture B, we find that doubling the lateral size of the simulation box has only a small quantitative effect on the stratification. For example, it has essentially no effect on the depletion of the largest species from a layer at the top of the final film.

Figure S3 shows the comparison between density profiles for mixture C2 (see Table 1 of the main article) with the original initial box size $55.08 \times 55.08 \times 1500 d_1^3$ (yellow dotted line) and the results of the new simulations with initial simulation box size $103.55 \times 103.55 \times 1500 d_1^3$. For mixture C2, we find that almost doubling the lateral size of the simulation box has

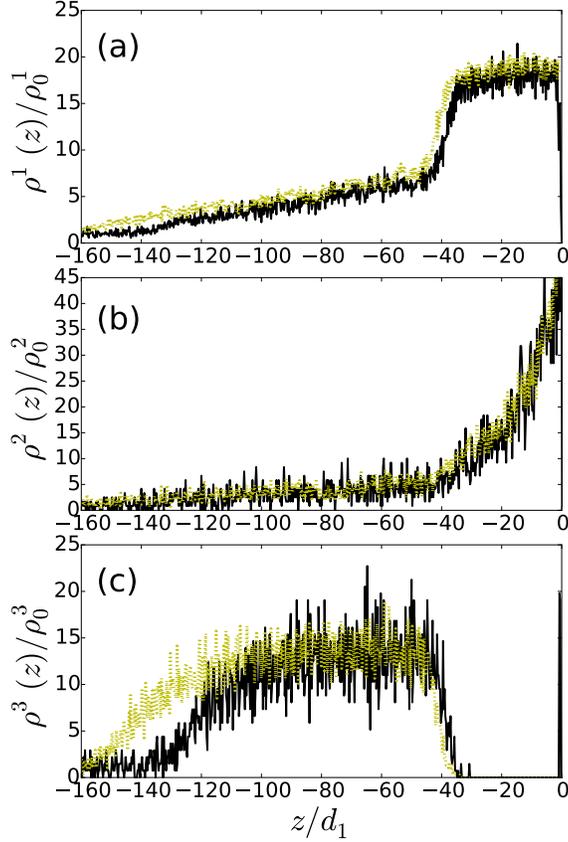


Figure S2: Density profiles for the ternary mixture B, where $d_2/d_1=0.7$ and $d_3/d_1=2.0$. The yellow dotted lines are the final profiles for runs that started with the initial simulation box size $13.9988 \times 13.9988 \times 1500 d_1^3$. The thick black lines are the final profiles for the initial simulation box size $27.998 \times 27.988 \times 1500 d_1^3$. The panels a), b) and c) are for the species 1, 2 and 3, respectively.

only a small quantitative effect on the stratification, shown by the density profiles.

Equilibration time before evaporation

In experiments, evaporation starts immediately after the preparation of the sample. In the simulation reported in the main paper, the interface downward movement was started $20t_0$ after the initial preparation of the random non-overlapping configuration of particles, equivalent to $8 \tau_B^1$, where τ_B^1 is the Brownian time of particles with diameter d_1 . Here we compare the stratification profiles of system whose evaporation was started after $2 \tau_b^L$ and

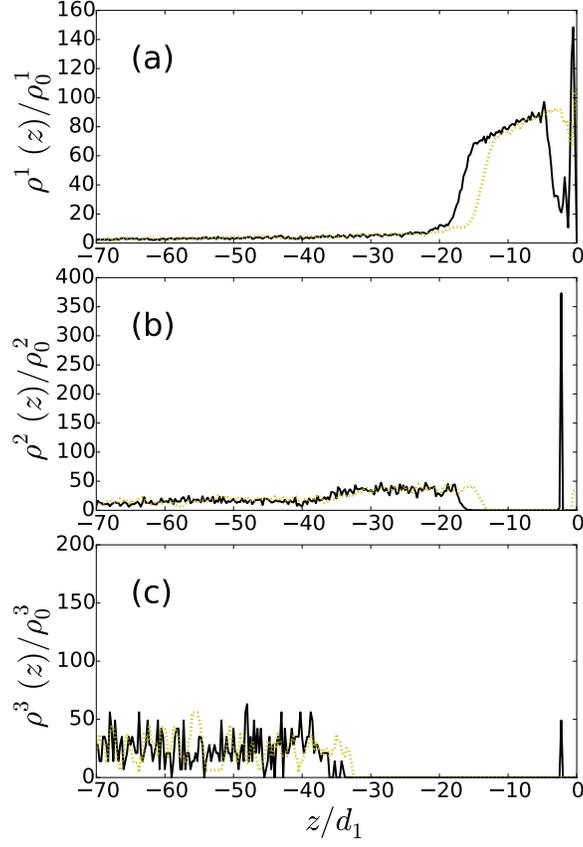


Figure S3: Density profiles for the ternary mixture C2, where $d_2/d_1=4.0$ and $d_3/d_1=8.0$. The yellow dotted lines are the final profiles for runs that started with the initial simulation box size $55.08 \times 55.08 \times 1500 d_1^3$. The thick black lines are the final profiles for the initial simulation box size $103.55 \times 103.55 \times 1500 d_1^3$. The panels a), b) and c) are for the species 1, 2 and 3, respectively.

after $20 \tau_b^L$, where τ_b^L is the Brownian time of the largest particles in the system. Figure S4 shows the density profiles for mixture C1, at the end of evaporation after an equilibration of $2 \tau_b^L$ or after $20 \tau_b^L$. Note that they are very similar.

Initial distributions of polydisperse mixtures

Figure S5 shows the initial diameter distributions of particles for the initial configuration of the system with polydispersity $\gamma/d_{av} = 0.24$. There are only minor statistical deviations from the expected Gaussian distribution. Therefore, the deviations from the Gaussian dis-

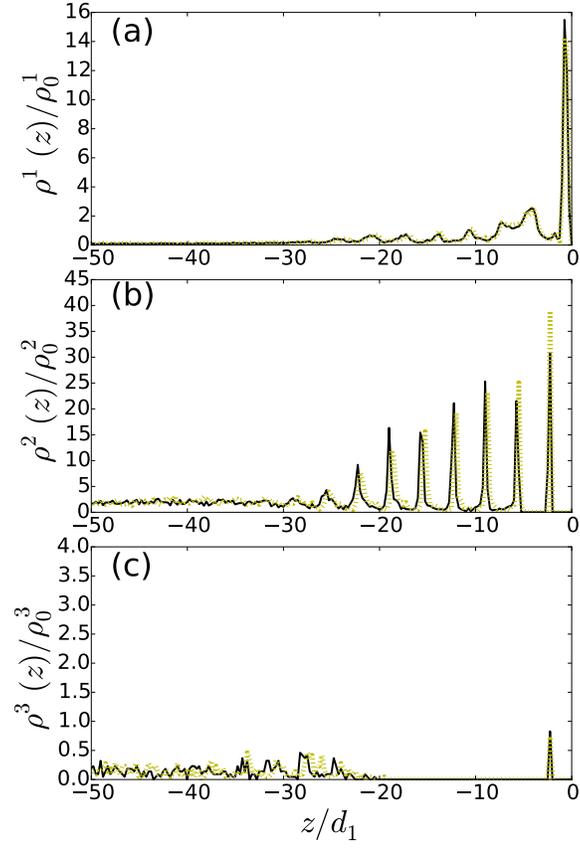


Figure S4: Density profiles for mixture C1, at the end of evaporation after an equilibration of $2 \tau_b^L$ (full line) or after $20 \tau_b^L$ (dashed yellow line).

tributions measured at the end of evaporation (Fig 5 (b),(c),(d) of the main article) are due to colloidal diffusiophoresis.

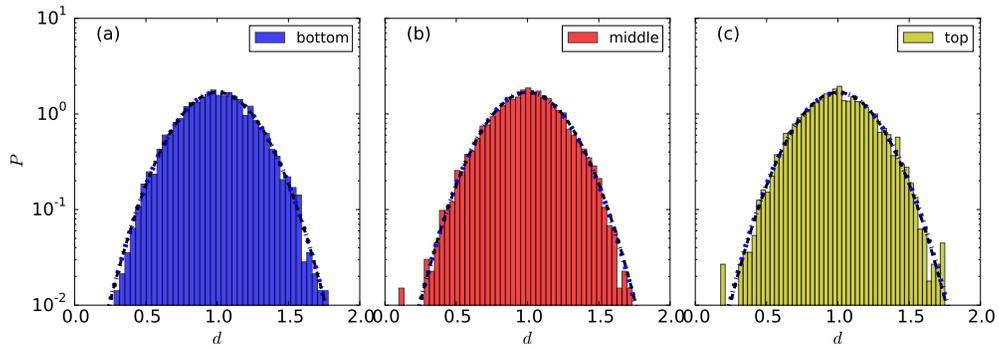


Figure S5: Initial probability density functions for the particle diameter, $P_d(d)$, for three height sections. This is for the system with polydispersity $\gamma/d_{av} = 0.24$. (a) P_d in bottom section of width $H/3$. (b) P_d in the middle part, the region of height $H/3$ and centered at $H_{fin}/2$. (c) P_d in the top part of width $H/3$. The black dashed lines are the original Gaussian distribution of diameters, and the blue dotted lines are fits of the data to a Gaussian function.