Supplementary material to Dynamic stratification in drying films of colloidal mixtures

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EVOLUTION OF DENSITY PROFILES

The evolution of the stratified structure during evaporation and of the related density profiles is shown in Fig. 1.

STRATIFICATION AT DIFFERENT SIZE RATIOS AND INITIAL VOLUME FRACTIONS

Snapshots of the final configuration obtained in simulations of binary mixtures with size ratio \(d_1/d_s=2\), and 14 are shown in Figure 2. The formation of a top layer depleted of large particles is clearly visible in both cases.

In Fig. 3 we show snapshots of the top regions of the final configurations for initial volume fractions \(\eta_0=0.1\) (a) \(\eta_0=0.2\) (b), and \(\eta_0=0.4\) (c), obtained with an evaporation velocity \(v_{ev}=0.1\). The layer with only small particles is visible in the final film layer regardless of the initial volume fraction, but as the initial particle density increase, the segregation mechanism becomes less efficient.

DETAILS OF THE SIMULATION METHOD

We run computer simulations of mixtures of spherical particles in a simulation box with dimensions \(L_x \times L_y \times H\). Periodic boundary conditions are used in the \(x\)- and \(y\)-direction, while in the \(z\)-direction the box is delimited at the bottom by a hard substrate, and at the top by a soft wall, which models an air-water interface. We do not explicitly simulate the solvent water molecules but describe the motion of the colloidal particles using Langevin dynamics, which includes Brownian diffusion effects and neglects hydrodynamic flow. The equation of motion for a particle \(i\) with diameter \(d_i\), mass \(m_i\) at position \(\mathbf{r}_i\) is

\[
m_i \ddot{\mathbf{r}}_i = - \sum_{j<i} \nabla U_{ij}(\mathbf{r}_i, \mathbf{r}_j) - \xi_i \dot{\mathbf{r}}_i + \delta F_i ,
\]

where \(\xi_i = 3\pi\nu d_i\) is the friction coefficient and \(\nu\) is the viscosity of the solvent. The term \(\delta F_i\) is a random force sampled from a Gaussian distribution with width \(\sqrt{k_BT} \xi_i\), where \(k_B\) is the Boltzmann constant and \(T\) the temperature. The Langevin dynamics was carried out using the LAMMPS package [1] with a time step \(dt = 0.001\)

\[
\tau_B = 0.0025 \, t_0 ,
\]

where \(\tau_B = d_i^2 / D_s\) is the Brownian time of the small particles, and \(t_0\) is the standard Lennard-Jones unit of time in LAMMPS. We also used a friction parameter \(\xi = 100 \, d_c\) and a temperature of 40, both in standard Lennard-Jones LAMMPS units.

The interaction energy models screened charged particles, i.e., the interparticle potential energy \(u_{ij}\) between particles \(i\) and \(j\), either small or large, of diameters \(d_i\) and \(d_j\) is a short range Yukawa interaction

\[
u_{ij}(r)/k_BT = \begin{cases} c \exp(-\kappa(r-\sigma)) & r < r_c \ 
0 & r \geq r_c \end{cases}
\]

where \(r\) is the centre-to-centre particle distance, \(c\) is the contact energy, and \(\kappa\) determines the steepness of the potential. These two parameters influence the overall softness of the potential. In this simulation, we choose \(c/k_BT = 25\) and \(\kappa d_s = 20\). The distance \(\sigma = (d_i + d_j)/2\) and the cut-off is \(r_c = (d_i + d_j)/2 + d_s\).

The binary mixture is modeled by small particles with diameter \(d_s = 1\) and mass \(m_s = 1\) and large particles with diameter \(d_l = 7d_s\) and mass \(m_l = d_l^3 m_s\). Because of the soft interaction between particles, it is possible to define an effective diameter of the spheres using the Barker-Henderson relation [2]

\[
d_{eff} = d + \int_{d}^{\infty} (1 - \exp[-u_{ij}(r)/k_BT]) dr ,
\]

which gives the distance where the repulsive interaction is of the order of 1 \(k_BT\). For our parameters, the effective diameters are \(d_{eff}^i = 7.19\) and \(d_{eff}^s = 1.19\), for large and small particles, respectively. The effective size ratio therefore is \(d_{eff}^i / d_{eff}^s = 6.04\). The model neglects deformability and coalescence of the particles, which can occur when film forming particles are used in experiments.

The interaction \(U_{iw}(z)\) between particle \(i\) with diameter \(d_i\) and the hard substrate at the bottom is modeled by

\[
U_{iw}(h)/k_BT = \begin{cases} \frac{\epsilon_w}{k_BT} \left(\frac{d_i}{h}\right)^{12} & h < d_i/2 \ 
0 & h \geq z_c \end{cases}
\]

where \(\epsilon_w/k_BT = 100\) determines the strength of the repulsive interaction and \(h\) is the distance of a particle from the substrate.
Figure 1. Evolution with time of the density profiles of the small particles, for a mixture with size ratio $d_l/d_s = 7$ and number ratio $N_r = 151$. (a)-(e) are snapshots at times $t = 7.5 \times 10^2 \tau_B$, $6.6 \times 10^3 \tau_B$, $1.25 \times 10^4 \tau_B$, $1.83 \times 10^4 \tau_B$ and $2.4 \times 10^4 \tau_B$, respectively. The corresponding density profiles are plotted in (f); $\rho_s$ is the number density of small particles. The top surface is at $z/d_s = 0$ and is at the right.

Figure 2. Snapshots of the top regions of the final configurations. (a) Size ratio $d_l/d_s=2$, and $N_r=17$. (b) Size ratio $d_l/d_s=14$, and $N_r=9000$.

Figure 3. Snapshots of the top regions of the final configurations for mixtures with size ratio 7:1 and number ratio $N_r=150$ for different initial volume fractions. (a) $\eta_0=0.1$ (b) $\eta_0=0.2$ (c) $\eta_0=0.4$.

We model the solvent evaporation process by a moving soft wall, which pushes the particles toward the bottom substrate at constant velocity $v_{ev}$. The position of the soft-wall (interface) as a function of time is defined by $z_{int}(t) = H - v_{ev}t$. The interaction between the soft wall and a particle $i$ with diameter $d_i$ is described by a harmonic potential, which models the Pickering effect.
due to the change in interfacial free energy when particles are trapped at a interface [3]

\[
U_i(z)/k_B T = \frac{\alpha i}{k_B T}(z - r_0 - z_{int}(t)),
\]

(5)

where \(z\) is the particle coordinate, and \(r_0\) determines the contact angle \(\theta = \arccos(2r_0/d_i)\). We have chosen \(r_0 = d_i/4, d_s/2\), for large and small particles, respectively. The strength of the air-water interface attraction was chosen to be proportional to the area of the particle, i.e., \(\alpha_i/k_B T = 1000\ (d_i/d_s)^2\). Effects like the capillarity attraction between the particles trapped at the interface or effective dipolar interactions are neglected in this model.

**DETAILS OF THE EXPERIMENT**

We investigated the room temperature drying of latex particle mixtures experimentally. The initial colloidal dispersions were prepared by blending two acrylic copolymer lattices with different mean particle sizes. Both types of particles were mutually repulsive and were colloidally-stable in water initially and when mixed together.

The large particles were made of a copolymer of methyl methacrylate and \(n\)-butyl acrylate in a weight ratio of 40/60. The initial solids content is 20 wt%. They were synthesized by radical emulsion polymerization using Synerponic NP30 and sodium dodecylsulfate surfactants (99/1 wt% ratio) at a total concentration of 3 g L\(^{-1}\). Sodium persulfate (0.5 wt% relative to monomers) was used as the initiator.

The \(z\)-average diameter was determined by dynamic light scattering (DLS) (NanoZS from Malvern Instruments) to \(D_z = 385\) nm. These particles were labelled with fluorescent Rhodamine B (0.2 wt% based on monomers). Analysis of the supernatant after centrifugation found that there was no Rhodamine B in the aqueous phase. A zeta potential was normalized by dividing by the film thickness.

The small particles are composed of amphiphilic block copolymers obtained by polymerization-induced self-assembly (PISA) [4]. Controlled radical polymerization (namely, reversible addition-fragmentation chain transfer (RAFT) polymerization) of methacrylic acid (MAA) was performed to obtain firstly a PMAA macroRAFT agent (about 4000 g mol\(^{-1}\)) [5], which was then chain-extended with a mixture of \(n\)-butyl acrylate (BA) and styrene (S) (55/45 wt%) to form self-stabilized particles [6]. A \(z\)-average diameter \(D_z = 55\) nm with a dispersity of 0.064 were measured by DLS. Electrostatic stabilization was provided by anionic sulfate groups contained in the initiator. The pH of the colloidal mixture was measured to be 3.5. At this pH, which is below the value of PMAA’s pKa of 5.5, the PMAA chains at the particle surface are only weakly ionized and are collapsed [7]. Hence, the PMAA is expected to offer neither significant steric stabilization nor charge stabilization.

After blending the calculated amounts of these two dispersions to achieve the desired number ratio, we added deionized water in order to match the initial solids content used in the simulations. The final solids content was always in the range of 9-13 wt.% for all dispersions. Films of these blends were cast on glass substrates (18 × 18 mm\(^2\)), previously cleaned with acetone and a UV ozone treatment (Bioforce Nanosciences, model UV.TC.EU.003).

Height and phase images of the top surface of the films were acquired by atomic force microscopy (AFM), using an NT-MDT Ntegra Prima microscope with intermittent contact. Images were analyzed using NOVA software.

A Zeiss LSM510 confocal microscope (on an Axiovirt 200M microscope) was used to obtain stacks of plane images at different depths within the sample. A drop of large (750 nm diameter, purchased from Fluoresbrite) green fluorescent particles was cast on top of the dried films. They provided a marker for the top surface position. The green and red fluorochromes were excited using an argon laser (488 nm) and a HeNe laser (543 nm), respectively.

Two-dimensional images (132 × 132 \(\mu\)m\(^2\)) were acquired every 0.5 \(\mu\)m when moving from the substrate at the bottom toward the top of the dry film. Results were analysed using the image processing package Fiji (a version of Image J). The position of the fluorescent green marker particles in the images was used to define the top surface. A second-order polynomial equation was fit to the intensity of the red channel as a function of depth from the surface and then used to define a baseline, to correct for the depth-dependence of the detected intensity. The corrected intensity was normalized by dividing by the maximum intensity in the profile, and the vertical position was normalized by dividing by the film thickness.

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