Stratification and size segregation of ternary and polydisperse colloidal suspensions during drying.

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Abstract

By means of Brownian Dynamics simulations, we investigate the drying process of three component and polydisperse colloidal suspensions. We have previously reported [Phys. Rev. Lett. 116 p.118301 (2016)] on the drying of binary mixtures. For binary mixtures, we found that a gradient of colloidal osmotic pressure develops during drying, and that this leads to the final film being stratified with a layer of the smaller particles on top of a layer of the larger particles. Here, we find that stratification by size is very general, and also occurs in ternary and polydisperse mixtures. We name the segregation effect colloidal diffusiophoresis. In particular, we show that by changing the composition of a ternary mixture, you can achieve different stratification morphologies, and so tune the film properties. In polydisperse spheres, colloidal diffusiophoresis leads to an enrichment in the large particles at the bottom part of the film, while the top part is enriched in the smaller particles. This segregation means that in the final film, the particle size distribution depends on height. Thus properties of the film will then depend on height. We propose a model that predicts a power law dependence of the phoretic velocity on particle size. Results from the model and simulation show good agreement.
Introduction

Many coatings, from paints to cosmetics, form by the drying of a thin, initially liquid, film containing a dispersion of colloidal particles.\(^1\) Due to the importance of coatings made from drying colloidal suspensions, there is an extensive literature on this process.\(^2\text{--}15\) Particles used in coatings are rarely all of the same size, more commonly the film is made from a mixture of particles of different sizes and compositions, in order to provide the desired optical, mechanical and barrier properties of the films.\(^1\) Also, even a single species of particle will be synthesized not as particles all with identical diameters, but as particles with some distribution of sizes, i.e., there will be polydispersity in diameter. In recent work,\(^16\) we found that during drying of a film containing a mixture of smaller and larger particles, segregation leads to a layer of the smaller particles on top of a layer of the larger particles. Here we show that segregation and layering is very general and that three-component mixtures can segregate into three layers, with the smallest particles at top. We also show that during drying, polydisperse mixtures also tend to undergo size segregation, with the bottom of the film enriched in the larger particles, while the top is enriched in the smaller particles. Thus, we suspect that many films may have size distributions that depend on height, which may cause their properties to also depend on height.

The segregation we observe is a non-equilibrium effect, driven by the fact that during drying the water-air interface descends with a velocity \(v_{ev}\). See Fig. 1 for a schematic of a drying film of a colloidal suspension. For a film of initial thickness \(H\), the timescale for drying is \(H/v_{ev}\). On the other hand, colloidal particles with diffusion constant \(D\) will take a time \(H^2/D\) to diffuse across the height of the film. The ratio between these two time scales is called the film Péclet number and determines the extent to which drying drives the system away from equilibrium. It is defined as \(\text{Pe}_{\text{film}} = v_{ev}H/D\).\(^1,12\) When \(\text{Pe}_{\text{film}} \ll 1\) the drying is slow so the film is always near equilibrium, but here we are interested in the opposite limit, where \(\text{Pe}_{\text{film}} \gg 1\) and the drying film is far from equilibrium. The Péclet number has been widely used in studies of the drying of colloidal films.\(^1,3,5,6,8\text{--}12,17\text{--}19\)
The diffusion constant $D$ depends on particle size. In particular, in dilute suspensions the Stokes-Einstein expression tells us it varies as one over the diameter. Thus as Trueman et al.\textsuperscript{10} discussed, because larger particles diffuse slower (and hence have a higher Pe number) than smaller ones, there is a tendency in a mixture for the larger particles to accumulate near the top of the drying film. This tendency causes a partial segregation, with the larger particles at the top and smaller ones nearer the bottom. What happens is that the slower larger particles tend to be trapped just below the descending interface simply because their diffusion constant is small. This is clearly what happens in suspensions that are dilute enough that interactions between the colloidal particles can be neglected.

![Figure 1](image_url)

Figure 1: (a) Sketch of a drying film of water (cyan) with dispersed particles (yellow). The film is on a substrate (grey). Due to evaporation, the air/water interface moves vertically with a downward velocity $v_{ev}$. The particles are a polydisperse mixture of spherical particles with a range of diameters. (b) The particles accumulate beneath the descending top interface. Shown is the accumulation front between the the top region, which has a high density of particles, and the bottom region, with a low density of particles. (c) Reference frame used for the theoretical modeling, with the origin at rest on the air-water interface and therefore moving down at constant velocity $v_{ev}$. Because of particle accumulation a positive osmotic pressure gradient $\frac{\partial P}{\partial z}$ develops. In this reference frame a particle with diameter $d$ moves with velocity $v_{ev}$ towards the interface, plus a contribution proportional to both the cube of the particle diameter and the negative of the pressure gradient.
However, in drying suspensions the particles are not dilute because as the interface descends particles accumulate beneath it and the volume fraction of the particles becomes high, even for initially dilute suspensions. Then although larger particles may have an intrinsic tendency to diffuse slower because they feel larger drag forces from the fluid, they also feel larger forces from the concentration gradient of particles below the descending interface.

In earlier work on binary mixtures\textsuperscript{16} we have shown that these larger forces reverse the segregation, so that the smaller particles go to the top of the drying film, and the larger particles are pushed, by colloidal interactions, to the bottom. We found this both in Brownian dynamics simulations and in experiments. This stratification effect is strong at large concentration of small particles because this high concentration generates large osmotic pressure gradients during drying.

**Colloidal diffusiophoresis**

The segregation we study is driven by gradients in the concentrations of the colloidal particles. Whenever there are gradients in thermodynamic variables such as concentrations, temperature, etc these gradients drive movement. This movement is called phoresis.\textsuperscript{20–23} For example, thermophoresis is motion of particles due to a temperature gradient,\textsuperscript{22} electrophoresis is motion driven by a electric potential gradient (uniform electric field),\textsuperscript{20} and dielectrophoresis is motion driven by a gradient in the electric field.\textsuperscript{23} In our case, the motion of colloids is driven by a gradient in concentration, and so it is a type of diffusiophoresis. Diffusiophoresis usually refers to motion of a colloidal species due to a ionic or molecular solute’s concentration gradient,\textsuperscript{20,24,25} such as motion of a charged colloid in a salt gradient.\textsuperscript{24}

Here, the physical mechanism behind the segregation, is motion of one colloidal species in response to a gradient in another colloidal species. Therefore, we name our effect *colloidal diffusiophoresis*. Colloidal diffusiophoresis is the diffusion of one colloidal species in response to a gradient in the concentration of another colloidal species. As it is diffusion of one type of particle/molecule in response to a gradient in another type of particle/molecule, colloidal
diffusiophoresis is a type of cross-diffusion. Cross diffusion has been analysed in mixtures of evaporating solvents as well as experimentally measured in mixtures of colloids and polymers. Our colloidal diffusiophoresis is a special case of cross diffusion.

There exist other non-equilibrium segregation mechanisms for mixtures of particles. For example, applying opposite oscillatory external forces to two components of a mixture can cause them to segregate into lanes.

In this article, we expand on our previous work by analyzing with Brownian Dynamics computer simulations the effect of density gradients on ternary mixtures and on polydisperse colloidal suspensions during evaporation.

In this article, when we refer to ternary mixtures we mean a system with three species of colloidal particles suspended in a solvent.

Model and Simulation method

We model a system of $i = 1, N_{\text{tot}}$ spherical particles with diameters $d_i$ and mass $m_i$ in a simulation box with dimensions $L \times L \times H$. We use periodic boundary conditions for the $x$ and $y$ directions. In the $z$ direction the box is delimited at the bottom by a hard substrate. At the top a soft wall moves downward with velocity $v_{ev}$. This models the movement of the air-water interface during evaporation. A sketch of the model is shown in Fig. 1.

In the simulation, we do not explicitly simulate the solvent water molecules. We describe the motion of the colloidal particles using Langevin dynamics, which includes Brownian diffusion effects but neglects hydrodynamic flow.

The Langevin dynamics equation of motion for a particle $i$ with diameter $d_i$, mass $m_i$ at position $\mathbf{r}_i$ is

$$m_i \ddot{\mathbf{r}}_i = - \sum_j \nabla U_{ij}(\mathbf{r}_i, \mathbf{r}_j) - \xi_i \dot{\mathbf{r}}_i + \delta \mathbf{F}_i,$$  

where $\xi_i = 3\pi \nu d_i$ is the friction coefficient and $\nu$ is the viscosity of the solvent. The term $\delta \mathbf{F}_i$ is a random force with three components sampled from independent Gaussian distributions.
with width $\sqrt{k_BT\xi}$, where $k_B$ is the Boltzmann constant and $T$ the temperature.

The simulations of ternary mixtures were carried out using the LAMMPS simulation code$^{32}$ with a time step $dt = 0.0025\ t_0$, where $t_0 = \sqrt{m_0d_0^2/\epsilon_0}$, where $\epsilon_0$ is the interaction energy between the smallest particles, and $m_0$ and $d_0$ are the mass and diameter of the smallest particles of the ternary mixture, respectively. The mass of particles with diameters $d_i$ is defined as $m_i = (d_i/d_0)^3m_0$. The overdamped regime of the Langevin Dynamics is obtained with a friction coefficient for species $i \xi_i/\xi_0 = 100\ (d_i/d_0)$ and a temperature $k_BT/\epsilon_0 = 40$. Here $\xi_0 = m_0/t_0$. Thus, for the smallest component, in standard LAMMPS units and for the smallest species, the diameter and mass equal one, the temperature equals 40 and the friction equals 100. We define the Brownian time for particles of species $i$ as $\tau_B^i = d_i^2/D_i$, where $D_i = k_BT/\xi$ is the Stokes-Einstein diffusion coefficient. With our parameters, the Brownian time for particles of diameter $d_i$ is $\tau_B^i = 5/2(d_i/d_0)^3t_0$. The chosen friction coefficient and masses lead to an overdamped regime of the Langevin dynamics for the smallest particles. For larger particles, the overdamped regime approximation is not as good, but still in the friction dominated regime. The parameters were chosen as a compromise, to allow us simulate experimentally achievable values of the Péclet numbers in accessible simulation time frames. The Langevin dynamics was solved using the techniques of Gronbech-Jensen and Farago$^{33,34}$ that allows larger time steps than usual.

All simulations of ternary mixtures are started with particles in random positions. Simulations with constrained displacements were run until all overlaps between articles were removed. At this point the simulation was started with an equilibration period of a few $\tau_B^s$, the Brownian time of the species with the smallest diameter. At the end of the equilibration, the movement of the interface was started. In the supporting information, we investigated the effect of the length of the equilibration period before the evaporation is started.

During the simulation we measured the diagonal components $s_{xx}, s_{yy}, s_{zz}$ of the virial stress tensor for each particle.$^{35}$ The pressure at height $z$ can then computed as $p_z = -\frac{1}{3V_z} \sum_i (s_{xx}^i + s_{yy}^i + s_{zz}^i)$, where the sum runs over all particles with coordinate $z_i$ that
satisfies $|z - z_i| < a$. The parameter $a = 0.2d_0$ and the volume $V_z = aL_xL_y$.

The simulations of polydisperse spheres were carried out in the overdamped limit of the Langevin dynamics, Eq. (1). This is the $\xi_i \dot{r}_i / (m_i \ddot{r}_i) \gg 1$ for all $i$, limit. Equation (1) then simplifies to

$$\xi_i \dot{r}_i = - \sum_{i<j} \nabla U_{ij}(r_i, r_j) + \delta F_i . \tag{2}$$

A Brownian Dynamics$^{36}$ code for the solution of Eq. (2) was developed in-house, because LAMMPS doesn’t yet allow for particle level polydispersity. The polydispersity was modeled by distributing the particles diameters according to a Gaussian distribution with standard deviation $\gamma$ and centered around the diameter $d_{av}/d_0 = 1$. We fixed the time step $\delta t = 1 \times 10^{-5}t_0$ and the temperature $k_B T/\epsilon_0 = 1$. The friction coefficient is $\xi/\xi_0 = 1d_i/d_0$. The Brownian time for particles of diameter $d_i$, is $\tau_B = (d_i/d_0)^3t_0$.

All simulations are started with particles in random non-overlapping positions, followed by a brief equilibration period of a few $\tau_{av}^B$, the brownian time for particles of average diameter. The interface movement is then started to model evaporation. The runs are stopped when the accumulation front shown in Fig. 1(b) reaches the bottom substrate. This moment is identified by a value of the average volume fraction at the bottom substrate that is larger than the initial volume fraction. The stages of evaporation are labelled from 0% evaporation (beginning) to 100% evaporation (end).

The particle-particle and particle-surface interactions are the same for both simulation codes.

**Particle-particle interactions**

The interaction energy between particles is that of screened charged particles. The interparticle potential energy $u_{ij}$ between particles $i$ and $j$ of diameters $d_i$ and $d_j$ is a short range
truncated and shifted Yukawa interaction

\[
u_{ij}(r)/k_BT = \begin{cases} 
\frac{\epsilon}{k_BT} \left[ e^{-\kappa(r-\sigma)} - 1 \right] & r < r_c \\
0 & r \geq r_c
\end{cases}
\]  

(3)

where \( r \) is the center-to-center particle distance, \( \epsilon \) is the contact energy, and \( \kappa \) determines the steepness of the potential. The distance \( \sigma \) and cutoff \( r_c \) are equal, and given by \( \sigma = r_c = (d_i + d_j)/2 \). In this simulation, we choose \( \epsilon/k_BT = 0.625 \) and \( \kappa d = 20 \). Here \( d \) is the unit of distance, taken to be one of the \( d_i \) for our ternary mixtures, and the average diameter \( d_{av} \) for our polydisperse mixtures. As we have chosen \( \kappa d \gg 1 \), our potential is steeply (with respect to the particle diameter) repulsive and so the potential is not far from that of a hard sphere.

**Particle-surface interactions**

The interaction \( U_{iw}(h) \) between particle \( i \) and the substrate at the bottom is given by

\[
U_{iw}(h)/k_BT = \begin{cases} 
\frac{\epsilon_w}{k_BT} \left[ \left( \frac{d_i}{h} \right)^{12} - \frac{1}{2^{12}} \right] & h < 2d_i \\
0 & h \geq 2d_i
\end{cases}
\]  

(4)

where \( \epsilon_w/k_BT = 2.5 \) determines the strength of the repulsive interaction and \( h \) is the distance of a particle from the substrate.

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 \( z_{int}(t) = H - v_{ev}t \), where \( H \) is the initial height. Here, we assume that the solvent wets all particles, i.e., there is a contact angle of 0 between the solvent and the material of the particles. Then the interaction between a particle of species \( i \) and the interface, \( U_i(z) \), is purely repulsive, and we take it to have range equal to
the particle’s radius, $d_i/2$. For simplicity, we use just a simple harmonic repulsive potential:

$$
U_i(z) = \begin{cases} 
\frac{\alpha_i}{k_B T} (z - \left[z_{int}(t) - \frac{d_i}{2}\right])^2 & z > z_{int}(t) - \frac{d_i}{2} \\
0 & \text{otherwise} 
\end{cases}
$$

(5)

The strength of the interaction between a particle and the surface scales with the area of the particle, so we take $\alpha_i/k_B T = 25d_i^2/d_0^4$. This value gives us a repulsive interface with an energy scale that is much larger than $k_B T$. This is appropriate because even for small nanoparticles only a few nanometers across, the scale of the interaction free energy between a particle and the water/air interface is given by the surface tension of water times the area of a particle, and so it is many times $k_B T$.

The standard LAMMPS code was modified to implement the potential used for the top soft interface.

**Model of colloidal diffusiophoresis**

During drying, particles of all sizes move downwards. At the start, the particles are uniformly distributed over a height $H$ and so have an average height of $H/2$. At the end the particles have been compressed into a slab of height $H_{fin}$.

The distance a particle moves during drying will depend both on its initial position and on its size. Particles initially near the top of the film will, on average, move much larger distances down than those starting near the bottom, and we will find that larger particles move further than smaller ones. This segregation results from variations in the downward velocity with particle size.

To describe the relative downward velocities of the different species, Nikiforow et al.$^9$ started from a generalized Fick’s law. For two species $i$ and $j$, this is $J_i = -D_{ii} \nabla \rho_i - D_{ij} \nabla \rho_j$. McAfee and Annunziata$^{27}$ started from an expression in terms of gradients of the chemical potentials, not in the densities: $J_i = -L_{ii} \nabla \mu_i - L_{ij} \nabla \mu_j$, and Trueman et al.$^{10}$ used a more
complex model. Note that for McAfee and Annunziata’s expression, the Onsager reciprocal relation implies that \( L_{ij} = L_{ji} \).\(^{27}\) Here the \( D_{ij} \) are diffusion constants, while the \( L_{ij} \) are mobilities. By contrast, in our earlier work\(^{16}\) we started with an expression for the velocity of component \( i \), \( v_i \), and so did Zhou et al.\(^{37}\) We started with \( v_i = f_i / \zeta_i \), for \( f_i \) the average force on component \( i \), and Zhou et al.\(^{37}\) started with \( v_i = (-1/\zeta_i) \nabla \mu_i \). In both cases \( \zeta_i \) is a friction coefficient. Earlier modeling and experimental work on stratification has recently been reviewed by Routh.\(^{12}\)

For any of these five models, in order to calculate density profiles, further approximations need to be made for the size and volume fraction dependencies of the \( D_{ij} \), \( L_{ij} \), \( \mu_i \) and \( \zeta_i \) parameters. For example, in our earlier work\(^{16}\) we assumed that the force \( f_i \) came from a pressure gradient dominated by the smaller species, and used a Stokes-Einstein expression for \( \zeta_i \). We further develop this model here, and apply it to polydisperse mixtures.

All these five models use uncontrolled approximations, and so require validation, for the parameter range of interest. To do this we compare the predictions of our model, which we develop below, with the results of simulations. Once hydrodynamic interactions are neglected, computer simulations make no further approximations. Thus, computer simulations allow us to test the approximations made in theories. For example, in earlier work we showed that the pressure gradient was dominated by the smaller species (Figure 4 of Fortini et al.\(^{16}\)), while Zhou et al.\(^{37}\) found that within their approximation it was the cross-term that dominated the interaction part of their expression for the velocity of the larger species. Thus our simulations supports that part of Zhou et al.\(^{37}\)'s theory.

### Physical model of colloidal diffusiophoresis

In a drying film containing a colloidal dispersion, particles accumulate in front of the moving air/water interface creating a concentration gradient, which leads to a pressure gradient. If the pressure \( P \) is uniform then there is no net average force on a particle. However, where there is a pressure gradient there is a net force on particles, acting down this gradient. In
colloidal diffusiophoresis, this force is due to a gradient in the concentration of colloidal particles.

So, if at some height \( z \) there is a pressure gradient \( \partial P/\partial z \) which is approximately constant over a particle diameter \( d \), then the forces due to this pressure on the top and bottom of the particle will not balance, and there will be a net force, \( f(d) \), due to this pressure gradient. This net force will be approximately

\[
f(d) \approx \frac{\pi d^2}{4} \times -d \frac{\partial P}{\partial z} \approx -d^3 \frac{\partial P}{\partial z}.
\]

The force is simply the cross-sectional area of the sphere, \( \pi d^2/4 \), times the pressure difference across the sphere, \(-d(\partial P/\partial z)\).

Colloidal particles have overdamped dynamics, therefore the force in Eq.(6), on average, gives a particle of diameter \( d \) a diffusiophoretic velocity\(^{38}\) \( v_{\partial P} = f(d)/\xi(\eta, d) \), where \( \xi(\eta, d) \) is the friction coefficient at volume fraction \( \eta \). This coefficient can be written as \( \xi(\eta, d) = K(\eta, d)\xi_0 \),\(^{38,39}\) with \( \xi_0 = 3\pi d\nu \) the Stokes friction coefficient and \( \nu \) the viscosity of water. \( K(\eta, d) \) is the sedimentation coefficient, defined as one over the ratio of the sedimentation velocity at volume fraction \( \eta \) to that in its dilute limit.\(^{39}\)

During evaporation, the air/water interface moves downward with velocity of magnitude \(|v_{ev}|\), in the reference frame of the simulation box. We now switch to a reference frame at rest with respect to the water-air interface, and so moving at a velocity \(-v_{ev}\) with respect to the simulation box frame. Then in the absence of a pressure gradient, a particle has a positive velocity \( v_{ev} \) but particles in a pressure gradient, move with a velocity that is the sum of \( v_{ev} \) and a contribution \( v_{\partial P} \) from the pressure gradient force. The total velocity of a particle of diameter \( d \) is

\[
v_{\text{tot}}(d) = v_{ev} + v_{\partial P} = v_{ev} - \frac{d^3}{K(\eta, d)\xi_0} \frac{\partial P}{\partial z} = v_{ev} - \frac{d^{2-\alpha} \partial P}{3\pi \nu A} \frac{\partial P}{\partial z}.
\]
In Eq. (7) we have assumed that the sedimentation coefficient can be written as $K(\eta, d) = A(\eta)d^\alpha$, i.e., as a product of a function of volume function times a power law function of diameter. Simulation data that confirms that this expression is a good approximations is shown in Figure S1 in the Supporting Information. In the low-volume-fraction limit $\alpha = 0$ and $A = 1$, leading to the standard Stokes-Einstein expression. At high volume fractions $\alpha = 1$, due to the contribution of other colloidal particles to the friction coefficient.  

**Physical model of segregation by size due to colloidal diffusiophoresis**

We would like to develop a simple approximate model for segregation driven by colloidal diffusiophoresis. Segregation is driven by particles moving faster or slower than the average particles, i.e., it is driven by velocity differences. The velocity at which particles segregate is the difference $\Delta v = v_d - v(d_{av})$ between the velocity of particles of diameter $d$, and the velocity of particles with average diameter $d_{av}$. This can be derived from Eq. (7) as

\[
\Delta v(d, z, t) = -\left(\frac{\partial P(z, t)}{\partial z} \frac{1}{3\pi \nu A}\right) (d^{2-\alpha} - d_{av}^{2-\alpha})
\]

\[
\Delta v(d, z, t) = v_{av}(z, t) \left[(\frac{d}{d_{av}})^{2-\alpha} - 1\right]
\]

where in the second equation we have written the difference in velocity to that of particles of the average diameter, as the velocity of particles of average diameter, $v_{av} = -[(\partial P/\partial z)/(3\pi \nu A)]d_{av}^{2-\alpha}$, times a power law function only of $d$. Note that in our simple model, the velocity of particles of diameter $d$ is a product of the pressure gradient times a function, which only depends on $d$. For $\alpha < 2$, particles with diameter greater than the average diameter have a larger phoretic velocity with respect to particles with average diameter, and so will tend to be pushed to the bottom of the film. On the other hand, particles smaller than the average move slower downwards and will accumulate more at the top interface.

\[\text{1}\text{This is equivalent to the friction of small particles in a solvent.}^{40,41}\]
During drying, the pressure gradient $\partial P/\partial z$ depends on both $z$ and $t$, and this dependence will be rather complex due to the presence of a moving front in the drying film. The pressure gradient as a function of time felt by a particle will depend on $d$: larger particles will move down faster and so experience a different part of the pressure gradient profile from smaller particles that start at the same initial height. It will also depend on height.

In order to obtain a simple model, we simply assume that the dominant contribution to the diameter dependence of the segregation at the end of drying, is from the power law function in Eq. (9). This segregation is measured by the function

$$\delta_d = \langle \Delta z(d) \rangle - \langle \Delta z(d_{av}) \rangle$$

with $\langle \Delta z(d) \rangle$ the average of the change in height from the start to the end of the drying process, taken over all particles of diameter $d$, and $\Delta z(d_{av}) = \Delta H$ is the average change in height of all particles. Then we have for the final phoretic spread $\delta_d$

$$\delta_d = \Delta \left[ 1 - \left( \frac{d}{d_{av}} \right)^{2-\alpha} \right] ,$$

for $\Delta$ a constant. Equation (11) is a simple approximation because particles experience different pressure gradients over time that also depend on the initial particles’ position in the simulation box. However, we will see that the predictions of Eq. (11) are at least qualitatively consistent with our simulation results.

**Simulation Results for Ternary Mixtures**

We have studied two sets of ternary mixtures. The first set consists of mixtures with size ratios relatively close to one. We call these mixtures A and B. Even here we see significant segregation. The second set has larger size ratios, and we observe the formation of three distinct layers. These are mixtures C1, C2 and C3.
Table 1: Ternary mixtures analyzed with simulations, with components $i = 1, 2, 3$. We list size ratios, the size of the simulation box $L$ and $H$, and the number of particles of the three species. The last three columns report the fraction of solid content of the three species $\eta_i/\eta_{\text{tot}} \times 100$.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$d_2/d_1$</th>
<th>$d_3/d_1$</th>
<th>$L/d_1$</th>
<th>$H/d_1$</th>
<th>$H_{\text{fin}}/d_1$</th>
<th>$N_1$</th>
<th>$N_2$</th>
<th>$N_3$</th>
<th>$\eta_1/\eta_{\text{tot}}$</th>
<th>$\eta_2/\eta_{\text{tot}}$</th>
<th>$\eta_3/\eta_{\text{tot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.8</td>
<td>1.2</td>
<td>10.9835</td>
<td>1500</td>
<td>154.1</td>
<td>16191</td>
<td>1827</td>
<td>1982</td>
<td>79%</td>
<td>4.5%</td>
<td>16.5%</td>
</tr>
<tr>
<td>B</td>
<td>0.7</td>
<td>2.0</td>
<td>13.9988</td>
<td>1500</td>
<td>154.4</td>
<td>16160</td>
<td>1794</td>
<td>2046</td>
<td>49%</td>
<td>2%</td>
<td>49%</td>
</tr>
<tr>
<td>C1</td>
<td>4.0</td>
<td>8.0</td>
<td>111.691</td>
<td>1500</td>
<td>94.4</td>
<td>20258</td>
<td>13631</td>
<td>1011</td>
<td>1%</td>
<td>62%</td>
<td>37%</td>
</tr>
<tr>
<td>C2</td>
<td>4.0</td>
<td>8.0</td>
<td>55.0843</td>
<td>1500</td>
<td>86.9</td>
<td>31462</td>
<td>2251</td>
<td>242</td>
<td>11%</td>
<td>48%</td>
<td>41%</td>
</tr>
<tr>
<td>C3</td>
<td>4.0</td>
<td>8.0</td>
<td>73.2233</td>
<td>1500</td>
<td>56.9</td>
<td>176793</td>
<td>2751</td>
<td>456</td>
<td>30%</td>
<td>30%</td>
<td>40%</td>
</tr>
</tbody>
</table>

Figure 2: Three snapshots of ternary mixture B showing the development of the accumulation layer and size segregation. In each case we show just the region below the descending water-air interface, which is at the top of all three snapshots. The majority-species particles are blue (dark grey), the smaller particles, $d_2/d_1 = 0.7$, are yellow (light-grey); and the larger particles, $d_3/d_1 = 2.0$, are green (light-grey). (a) Initial configuration. The particles are uniformly distributed at a total volume fraction $\eta_{\text{tot}} = 0.06$. (b) At 17% of evaporation ($t = 1950t_0$), the particles have accumulated beneath the descending interface, and the resulting pressure gradient has already pushed away the larger particles from a layer below the interface. (c) At 36% of evaporation ($t = 4050t_0$), the layer from which the larger particles are excluded has grown.
Figure 3: Density, pressure and pressure gradient profiles in the drying film at 90% of evaporation time, for ternary mixtures A, (a)-(c), and B, (d)-(f). The top surface is at $z/d_m = 0$. The blue (dark grey) curves represent the majority species, the green (thick light grey) curves represent the larger species and the yellow (dashed light grey) curves represent the smaller species. (a),(d) Densities of particles as a function of the distance from the interface, plotted as $\rho_i(z)/\rho_i^0$, where $\rho_i(z)$ is the number density of species $i$ at $z$ at that time, and $\rho_i^0$ is the initial (uniform) number density. (b),(e) Osmotic pressure as a function of the distance from the top interface. Here $\beta = 1/k_B T$. (c),(f) Vertical gradients of the osmotic pressure as a function of the distance from the top interface. The black thick line is the total osmotic pressure gradient. The vertical dotted lines indicate the position of the top interface.

**Segregation in ternary mixtures**

We simulate a ternary mixture of particles characterized by one majority component with diameter $d_1$, representing the unit of distance, and two minority components with sizes $d_2/d_1$ and $d_3/d_1$ in a simulation box of height $H/d_1 = 1500$ and a total number of particles $N_{\text{tot}} = 2 \times 10^4$. The evaporation velocity is $v_{ev}t_0/d_1 = 0.1$. Mixtures A and B have the same initial total volume fraction, $\eta_{\text{tot}} \simeq 0.059$, and number ratios of $N_1/N_2 \simeq 8$ and $N_1/N_3 \simeq 9$, respectively.
with small variations due to the random nature of the box initialization. The mixture A has size ratios $d_2/d_1=0.8$ and $d_3/d_1=1.2$, while the film Péclet numbers are $\text{Pe}_{\text{film}}=375$, 240, and 540, for species 1, 2 and 3, respectively. Mixture B has size ratios $d_2/d_1=0.7$ and $d_3/d_1=2.0$, with $\text{Pe}_{\text{film}}=375$, 183.75, and 1500, for species 1, 2 and 3, respectively. Other specific parameters are collected in Table 1.

The progressive nature of the size segregation is shown in the simulation snapshots (Fig. 2) of mixture B taken at different times. Over time, the segregation of the larger particles toward the bottom becomes noticeable.

According to Eq. (7), we expect particles with the smaller diameter, $d_2$, to segregate to the interface, while the particles with the larger diameter, $d_3$, are pushed to the bottom. This is exactly what we observe in the density profiles of mixture A in Fig. 3(a) and of mixture B in Fig. 3(d). The density profiles for the larger particles are shown as the solid green curves in Fig. 3(a) and (d). The depletion of large particles from the top of the drying film (towards the right) is clear in both, and particularly strong for the larger size ratio (Fig. 3(d)). The yellow dashed curves show an increase of density of the smaller particles at the top.

We find measurable size segregation even for small size asymmetries. In agreement with the model, we also note that the segregation effect is stronger for particles with size ratio $d_3/d_1 = 2$ (Fig. 3(d)), then for particles with size ratio $d_3/d_1 = 1.2$ (Fig. 3(a)). The corresponding osmotic pressure gradients are shown in Figs. 3(c) and (f), for systems A, and B, respectively. There are substantial pressure gradients below the descending interface that push the particles downwards, and do so with larger forces on larger particles.

Thus, in summary, our simulation results provide evidence that the physical model of colloidal diffusiophoresis introduced in the previous section is qualitatively correct. Recently, Zhou et al.\textsuperscript{37} have developed a simple model for colloidal diffusiophoresis. This models the interactions between the small and the larger particles using a second-virial coefficient approximation, rather than, as we do, estimating the force on the larger particles due to a density gradient of the small particles. However, qualitatively our results are the same,
and we both predict that stratification is driven by the cross-interaction between the small particles and the larger particles.

**Formation of multiple layers**

Here, we look at the mixtures C1, C2 and C3, which have larger size ratios, of 8:4:1, than A and B (see Table 1). We kept the fraction of the volume occupied by the largest species (species 3) approximately constant in all three mixtures. Then C3 had the largest amount of the smallest species (species 1), while C1 had the smallest. The solid fraction percentages are 1:62:37, 11:48:41 and 30:30:40, for C1, C2 and C3, respectively. So C3 has approximately the same volume fractions of all three species, while C1 has only small amounts of the smallest species, and C2 is intermediate between C1 and C3.

We set the evaporation velocity \( v_{ev} \tau/d_1 = 0.1 \), and the total initial volume fraction \( \eta_{tot} \approx 0.036 \). The height of the simulation box is \( H/d_1 = 1500 \) and total number of particles is in the range \( N_{tot} = 3.5 \times 10^4 - 2 \times 10^5 \). The Péclet numbers are \( Pe_{film} = 375, 6000, \) and \( 24000 \), for species 1, 2, and 3, respectively.

Figure 4 shows the result of the computer simulations of these systems. When we have small numbers of the small particles, they clearly accumulate at the top but without forming a layer. They fill the spaces between the intermediate-size particles in a similar fashion to the case we reported in Ref.\(^{42}\) for binary mixtures. We also find a clear segregation of larger particles towards the bottom of the film.

Fig. 4(c),(d) show the profiles and snapshot of mixture C2. A clear layer of small particles is located at the top of the film, completely depleted of particles of the other two species. Both the snapshot and the density profiles, show that the larger particles are segregated towards the bottom, but without a sharp transition between layers of the intermediate and largest species. On the other hand, in mixture C3 (Fig. 4(e),(f)) we find three layers with well defined boundaries. The first layer has only small particles. The second layer has small and intermediate-size particles. Layer three contains all three types of particles.
Figure 4: Density profiles and snapshots at 100% evaporation time (15000 $t_0$) for ternary mixtures C1 ((a) and (b)), C2 ((c) and (d)) and C3 ((e) and (f)). We use yellow dashed lines for the small particles of diameter $d_1$, full blue lines for particles of intermediate size $d_2$, and dotted green lines for large particles of diameter $d_3$.

Although the stratification has some features in common with equilibrium phase separation, it appears to be unrelated. We observed stratification in binary mixtures of small and large particles in earlier work\textsuperscript{16} but such mixtures are miscible at all compositions in the fluid phase.\textsuperscript{43} When the size ratio is large, then at high volume fractions, there is a broad fluid-crystal coexistence region but we do not see crystallization in our simulations.

We note that both in our earlier work and here, we are working at Péclet numbers, $\text{Pe}_{\text{film}} \gg 1$, typically a few hundred. The Péclet number is a measure of how far away we are from equilibrium. Equilibrium is for $v_{ev} = 0$ where $\text{Pe}_{\text{film}}=0$, and close to equilibrium is when $\text{Pe}_{\text{film}} \ll 1$. Thus all our systems are very far from equilibrium. So for example the
pressure is not uniform as it is at equilibrium, instead we have very large gradients, as can be seen in Fig. 3 where the pressure varies by factors of more than ten from top to bottom of the system. So, as we far from equilibrium and as our mixtures show no equilibrium phase separation, we conclude that our observed stratification is unrelated to any equilibrium phase separation.

**Simulation Results for Polydisperse Mixtures**

We investigate colloidal diffusiophoresis in a system of $N_{\text{tot}} = 11000$ polydisperse particles. We use Gaussian distributed diameters with an average diameter $d_{\text{av}}$, which we will use as our unit of length. The amount of polydispersity is characterized by the standard deviation of the distribution $\gamma/d_{\text{av}}=0.05$, 0.1, 0.15, and 0.24. The initial volume fractions $\eta_i \approx 0.05$.

The simulation box has lateral size $L/d_{\text{av}} = 12$ and height $H/d_{\text{av}} = 800$. The evaporation velocity is $v_{ev} \tau_B/d_{av} = 1$, corresponding to $\text{Pe}_{\text{film}}=800$, for particles of diameter $d_{av}$. The simulation stops when the accumulation front reaches the bottom substrate. The final height of the box at $H_{\text{fin}}$ is reported in Table 2.

In order to quantify the segregation during drying in our polydisperse mixtures, we plot the mean diameter at a given height $z$, $\langle d(z) \rangle$, as a function of this height, in Fig. 5(a). In the center of the film, the mean diameter is close to the mean of the whole sample, $d_{av}$. But for all four values of the size polydispersity, $\gamma$, the mean diameter is $\approx 0.5\gamma$ larger at the bottom, and $\approx -\gamma$ smaller at the top. Any property of the final film that depends on particle size, will therefore vary across the film thickness.

So, the mean diameter varies by about $1.5\gamma$ from the bottom to the top of the film. In Figs. 5(b)-(d) we plot size distribution functions for particles at the bottom, middle and top, for the system with polydispersity $\gamma/d_{av} = 0.24$. To do this, the simulation box was divided vertically in sections of width $\Delta h = 10d_{av}$. In the middle the size distribution

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2Mixtures with different polydispersities have different volume fractions, but the difference is negligible at low densities
Figure 5: (a) The difference between the average diameter at height \( z \), \( \langle d(z) \rangle \) and the average diameter, \( d_{av} \), as a function of height. We show results for systems with polydispersities \( \gamma/d_{av} = 0.05, 0.1, 0.15, \) and 0.24, and in each case the difference is scaled by the polydispersity width \( \gamma \). (b)-(d) The probability density functions, \( P_d(d) \) at the end of the run, for a system with polydispersity \( \gamma/d_{av} = 0.24 \). (b) The bottom section of width 10\( d_{av} \). (c) The middle part, the region of height 10\( d_{av} \) a centered at \( H_{fin}/2 \). (d) The top part. In (b)-(d), 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.

is almost identical to the parent Gaussian distribution (see Figure S5 of the Supporting information). However, at the bottom, the distribution of particle sizes is not only shifted to larger diameters, the small \( d \) tail is depleted and the large \( d \) tail is greatly enriched. At the top we see the reverse, the large diameter tail is essentially removed, and the small diameter tail is greatly enriched. The parameters of Gaussian fits to these distributions are in Table 2.
Table 2: Final system heights $H_{\text{fin}}$ and Gaussian fit parameters for our four polydisperse colloidal suspensions. The height at the start is $H = 800d_{\text{av}}$. The polydispersity for each mixture is reported in the first column. The third and fourth columns are the best fit mean, $\langle d \rangle_{\text{fit}}$, and standard deviation $\gamma_{\text{fit}}$, of a Gaussian fit to the size distribution at the top of the system at the end of the run. The fifth and sixth, and seventh and eighth columns, are means and standard deviations of the fits at the middle and top of the system.

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$H_{\text{fin}}/d_{\text{av}}$</th>
<th>Top $\langle d \rangle_{\text{fit}}$ $\gamma_{\text{fit}}$</th>
<th>Middle $\langle d \rangle_{\text{fit}}$ $\gamma_{\text{fit}}$</th>
<th>Bottom $\langle d \rangle_{\text{fit}}$ $\gamma_{\text{fit}}$</th>
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</thead>
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<tr>
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<td>0.90</td>
<td>0.13</td>
<td>0.99</td>
</tr>
<tr>
<td>0.24</td>
<td>83.25</td>
<td>0.87</td>
<td>0.20</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Segregation of the largest and smallest particles

Figure 6 shows the distribution of heights of both the largest and the smallest particles in the polydisperse mixture. It shows the distribution for particles with diameter $1.5 < d/d_{\text{av}} < 4$ (full red line) and those with diameter $0 < d/d_{\text{av}} < 0.5$ (dashed blue line). In order to quantify the amount of separation for particles of these sizes we calculated the overlap index (OVI), i.e., the fraction of overlap area between the two distributions. For the distributions in Fig. 6, the OVI is 21%.

The polydisperse suspensions allow us to test our simple model (Eq. (11)) that predicts that the segregation of particles of different diameters during drying is a power-law function of diameter. We calculate the average displacement during drying over all particles, $\langle \Delta z_{d_{\text{av}}} \rangle$, and the average displacement $\langle \Delta z_d \rangle$ of particles of diameter $d$. The diameter parameter space was binned in windows of size $0.02/d_{\text{av}}$.

The distance travelled by particles of diameter $d$, is plotted in Fig. 7. This is for a polydispersity $\gamma/d_{\text{av}}=0.24$. The tail of the curve shows plateaus in correspondence of half of the final box height. We fit data outside the tails to Eq. (11). The fit parameters are $\Delta/d_{\text{av}} = 14.8$ and $\alpha = 0.13$. In order to better judge the fit quality we plot $|\delta_d|$ on a semilogarithmic scale in Fig. 7(b). The function predicted by our model (black line) fits the simulation data reasonably well.
Figure 6: Probability distribution functions for the height $z/H_{fin}$, of the largest, and of the smallest, particles. The red solid curve is the distribution for particles with diameters in the range $1.5 < d/d_{av} < 4$, while the dashed blue line is the distribution for particles with diameters in the range $0 < d/d_{av} < 0.5$. Each distribution is normalized to one.

**Conclusions**

We investigated the non-equilibrium segregation of mixtures by size in drying films. The segregation was driven by colloidal diffusiophoresis, and we studied it in ternary and polydisperse mixtures, by means of Brownian Dynamics simulations. We also presented a physical model for colloidal diffusiophoresis. The model predicts that particles with diameter greater than the average diameter have a larger phoretic velocity, i.e., move downwards faster, than particles with average diameter. On the other hand, particles smaller than the average move down slower. It is this difference in diffusiophoretic velocities that drives segregation by size.

Here, we derived a simple model to explain the effect of the osmotic pressure gradient on particles of different sizes. A more complete theory based on collective diffusion and taking into account the flux and mobilities of the particles represent a challenge for the future.

We investigated colloidal ternary mixtures and found segregation, as predicted by the model, even for diameter variations as small as 20 or 30%. We also investigated the effect of
Figure 7: (a) Distance travelled $\delta_d = \langle \Delta z_d \rangle - \langle \Delta z_{d_{av}} \rangle$ by particles of different diameters $d/d_{av}$ for the system with polydispersity $\gamma/d_{av}=0.24$. Error bars are one standard deviation of $\langle \Delta z_d \rangle$. (b) Absolute value of the travelled distance $|\delta_d|$ in semilogarithmic scale. The horizontal dashed line is a guide to the eye, corresponding to half the final height of simulation box. The full lines are fit to the data.

colloidal diffusiophoresis during drying on polydisperse particles. In all the cases we studied, we found that in the final film, the composition varies with height, with the top of the film containing more small particles and the bottom containing more large particles. The distribution of particle sizes is a function of height within the final system. At the bottom, we find an average diameter larger than the total average and a distribution skewed towards larger sizes. In the middle of the box we do not find a change in average diameters, but the tails of the distribution are depleted. At the top, we find that the distribution is skewed toward smaller sizes.

All our results were obtained by Brownian Dynamics, or by Langevin Dynamics set up to mimic Brownian Dynamics. That is, we are modeling particles diffusing in a solvent with viscosity, but have neglected hydrodynamic interactions. Also, the solvent is uniform by construction, we do not allow either its temperature or other properties to vary during drying. Thus our model is highly approximate and neglects a number of features present in
real drying films of colloidal particles. In particular the model only allows gradients in the concentration of the colloidal particles. In earlier work on binary mixtures we found at least qualitative agreement between our simulations, and experiments. This gives us confidence that the model is reasonable. Recently, Cheng and Grest\textsuperscript{45} found segregation in agreement with our findings in simulations of binary mixtures with explicit solvent. Drying liquid films containing colloidal particles are complex non-equilibrium systems. During drying there are complex variations in variables such as the concentration of the particles in both space and time. Thus further work will be needed to understand these complex, widespread and important systems.

Osmotic pressure gradients are also important in the problem of sedimentation colloidal particles\textsuperscript{46} and it would be interesting to investigate the effects of the osmotic gradients on particles of different sizes also in this context.

The layering we have observed here and in our earlier work,\textsuperscript{16} is potentially useful. For example, Nunes et al.\textsuperscript{15} studied film formation in mixtures of hard nanospheres with larger softer particles. They observed that the small hard nanospheres improved the surface hardness of the coating, which is desirable, and suggested that this may be due to high concentrations of the smaller particles near the top of the film. Our findings provide a potential explanation for this finding, and suggest that it could be both generic and controllable. Nunes et al.\textsuperscript{15} were not able to directly observe segregation in their films. In a different system, that of small droplets of dispersions that were allowed to dry, Antonietti et al.\textsuperscript{2} did observe size segregation in the final dry particle aggregates. However, Boulogne et al.\textsuperscript{47} didn’t detect size segregation, likely due to their material becoming viscoelastic early in the evaporation process.

It is clear that both multicomponent and polydisperse mixtures, show interesting and potentially useful variations in composition with height. Further experiments will be needed to show how to use this variation to make coatings with superior properties.
Acknowledgement

It is a pleasure to acknowledge helpful discussions with Ignacio Martin-Fabiani and Joe Keddie. We acknowledge funding from the European Union Seventh Framework Programme BARRIER-PLUS project (FP7-SME-2012-2, no. 304758).

Supporting Information Available

The following files are available free of charge.

The supporting information contain calculations of the diffusion coefficients of large tracer particles suspended in a colloidal suspension and a discussion of finite size effects. Fig4f.avi shows the evolution of the system of Fig.4, from the initial homogeneous distribution to the final stratified structure.

References


Graphical TOC Entry

Homogeneous ternary mixture of particles with different sizes

Size segregated ternary mixture

Evaporation