A Critical and Quantitative Review of the Stratification of Particles during the Drying of Colloidal Films

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Abstract

For a wide range of applications, films are deposited from colloidal particles suspended in a volatile liquid. There is burgeoning interest in stratifying colloidal particles into separate layers within the final dry film to impart properties at the surface different to the interior. Here, we outline the mechanisms by which colloidal mixtures can stratify during the drying process. The problem is considered here as a three-way competition between evaporation of the continuous liquid, sedimentation of particles, and their Brownian diffusion. In particle mixtures, the sedimentation of larger or denser particles offers one means of stratification. When the rate of evaporation is fast relative to diffusion, binary mixtures of large and small particles can stratify with small particles on the top, according to physical models and computer simulations. We compare experimental results found in the scientific literature to the predictions of several recent models in a quantitative way. Although there is not perfect agreement between them, some general trends emerge in the experiments, simulations and models. The stratification of small particles on the top of a film is favoured when the colloidal suspension is dilute but when both the concentration of the small particles and the

solvent evaporation rate are sufficiently high. A higher ratio also favours stratification by size. This review points to ways that microstructures can be designed and controlled in colloidal materials to achieve desired properties.

Key words

Brownian diffusion; evaporation; drying; coatings; sedimentation; latex; diffusiophoresis

1. Introduction to Colloidal Films and Multi-Layers

Films deposited from colloidal particles in a volatile liquid are found in diverse applications. Often, the colloidal films use a mixture of two or more types of particles to define the properties of the composite. Stable dispersions of colloidal polymer particles in water, known as synthetic latex, are dried to create the binder in waterborne paints.^{1,2} Colloidal polymer particles (often in mixtures) are also the primary component in waterborne pressure-sensitive adhesives,³ sun screen,⁴ inks,⁵ binders for the active ingredients in agricultural treatments for crops,^{6–8} and coatings for drug encapsulation and controlled release.^{9,10}

Solid colloidal films are typically made by spreading a dispersion or suspension in liquid on a solid substrate and allowing the continuous liquid phase to evaporate. The key concepts relating to the physics of drying colloidal films have been presented in depth in a recent review article.¹¹ Soft colloidal particles, when packed in a layer, are deformed from their spherical shape under the action of capillary forces and the reduction of surface free energy. The particles coalesce to eliminate the void space between them to form a continuous phase.¹² In recent years, a deeper understanding of how to control the assembly of particles during film formation has been developed, and this topic has been recently reviewed.¹³

The vision behind this review is to consider ways in which colloids can be used to fabricate multi-layer coatings that assemble spontaneously in a “bottom-up” approach. An excellent example of a multi-layer coating is found in a typical automobile paint. There are several layers, each with a particular function. An analysis of the cross-section reveals a primer layer to provide adhesion to the metal substrate, a base coat containing organic pigment to provide colour, and a clear topcoat to provide gloss.¹⁴ The layers are applied in consecutive depositions, which add to the total time and cost required for the decoration. A coatings formulation in which a *single* deposition could be used to lay down three stratified layers is a long-term, challenging goal for the coatings industry.

Multi-layer films are used for a range of practical purposes, such as:

- to tailor the refractive index gradient of a coating,¹⁵ in order to reduce the optical reflectivity¹⁶ or to suppress reflection losses significantly in a broad bandwidth and under diffuse illumination;¹⁷
- to adjust the electrical properties to engineer the charge transport in photovoltaic devices;¹⁸
- to control the rate of drug release from medical implants and devices;^{19,20}
- to combine dissipative and elastic properties in a pressure-sensitive adhesive, leading to an increased work of adhesion on both high and low energy surfaces.²¹

In these particular examples, the films were not colloidal. Clearly there is huge potential to exploit colloidal stratification for these and other applications.

The remainder of this review is structured as follows. In the next sub-sections, we will review past work to tailor the properties of colloidal films through the stratification of a particular component in a surface layer or in the bulk region of a coating. Afterward, the two primary methods of depositing multilayer colloidal films will be reviewed. In Section 2,

before moving to the consideration of mixtures of colloids, we start by presenting models and experiments on the stratification of a *single* type of particle during the drying process. Then Section 3 reviews the self-stratification of two (or more) types of particles, whereby particles spontaneously form layered structures during the formation of a film. Three mechanisms for stratification are identified, and examples of their implementation are reviewed. The evidence for self-stratification of colloids, which is found in the literature, is identified in Section 4. These historical data are then used to compare to the predictions of recently-developed models of self-stratification. The review concludes in Section 5 with a summary and comments on issues that need to be resolved.

1.1 Properties of stratified colloidal films

Coatings are said to be stratified when they consist of two or more phases on top of each other, all lying parallel to the substrate. Typically, the lower region of a coating provides adhesion to the substrate. The interior region might provide a barrier to the transport of species, such as water or oxygen, thereby protecting the substrate. This region might also dissipate energy under mechanical impact, or it might absorb or scatter light to create colour and opacity. The surface region, in contrast, might perform other functions and define properties, such as wetting, hardness, blocking, tack, optical reflectivity, gloss, and electrical conductivity.

In recent years, there have been several demonstrations of tailored properties achieved via stratified colloidal films. Wetting properties were modified by Lopez *et al.*²² They created a super-hydrophobic coating (water contact angle $>150^\circ$) by stratifying fractal particles of a hard fluorinated polymer on a film surface. In other work, Nunes *et al.*²³ inadvertently used auto-stratification to tailor the mechanical properties in colloidal coatings by enriching the surface in hard particles, which led to greater hardness and a resistance to

fat. The electrical conductivity of the surface of a coating was increased through the enrichment of conductive gel particles of poly(3,4-ethylenedioxythiophene)/ poly(styrene sulfonate) there.²⁴ Gurney *et al.*²⁵ demonstrated that a layer of hard nanoparticles stratified in a pressure-sensitive adhesive reduces the tackiness. Similarly, stratification of hard particles at a film surface is an effective way to achieve higher block resistance.¹ Okubo *et al.*²⁶ showed that blending emulsions of acrylate terpolymer particles with ethyl-acrylate methacrylate (EAMA) copolymer particles could be used to adjust the porosity and tackiness of a colloidal film. The EAMA copolymer particles did not coalesce fully but created a network of voids at the substrate, whereas the terpolymer particles created a tacky surface. In organic photovoltaic devices, the stratification of electron acceptor nanoparticles (such as fullerene derivatives or n-type metal oxides) has a pronounced effect on charge extraction and the resulting power conversion efficiency.²⁷ In latex coating applications, a high specular gloss has been attributed to a stratified layer of small particles at the surface, which reduces the roughness.²⁸ These various reports exemplify why there is a continuing interest in stratified colloidal films.

There are a number of ways that colloids can be arranged in a film. Figure 1 illustrates four possible scenarios when particles labelled as “S” and “L” are mixed. There may be a random mixture without stratification (Figure 1a) or a linear concentration gradient (Figure 1b). One type of particle may be enriched at the surface, such as by filling void space around the other type of particle (Figure 1c). The main interest here is the case of stratification in which a complete layer of one type of particle develops along the interface with the substrate or air (Figure 1d). This review will focus specifically on methods in which stratification happens spontaneously, but in the next section we will consider the conventional methods of film deposition.

Figure 1. Definition of the types of stratification in colloidal films. For a blend of two types of particles (S and L), the concentrations (ϕ_S and ϕ_L) are shown as a function of the vertical position in a thick film. (a) Non-stratified film having a uniform distribution of the two particles, S and L. (b) Linear concentration gradients. (c) A surface enriched in S particles but with a uniform distribution of L particles. (d) A stratified layer enriched in S particles and depleted of L particles. (A stratified surface layer of L particles is also possible.)

1.2 Deposition of Multi-Layer Films from Colloids

There are several different possible methods to deposit colloidal films. One of the simplest is merely to spread a colloidal dispersion on a substrate and allow the continuous phase to evaporate. This is called the *horizontal deposition* method when the substrate is held perpendicularly to the direction of gravity. A bar with a spiral pattern, called a Mayer bar, can be used to spread the colloidal liquid evenly. In the *rapid convective deposition* method, a small drop of a colloidal liquid is held in place by capillary forces between a doctor blade and a substrate, which is translated horizontally using a linear motor.²⁹ Highly-ordered layers of particles can be deposited by these liquid-casting methods; a uniform film thickness requires a constant rate of spreading.

In the *dip-coating* method, the substrate is held vertically in the colloidal dispersion and withdrawn at a constant upward velocity. The number of particle layers that are deposited, and hence the thickness, is determined by the withdrawal velocity, the concentration of the colloidal liquid, evaporation rate, and the particle size.³⁰ Good control can be achieved, but the process tends to be quite slow. Colloidal films can also be deposited by *spin-coating*, in which the substrate spins about a central axis and the centrifugal forces cause outward flow of the deposited liquid and act to smooth it. This process is quite fast, but substrates must be planar, small enough to fit inside a spin-coater, and robust enough to withstand the stresses. Thick layers of colloids can also be spray-coated.^{9,22} Ink-jet printing, spraying of agricultural treatments on plants, and the spreading of cosmetics on skin are each examples of colloidal film formation.

To date, there have been two main conventional methods to manufacture multilayer colloidal films. One method is through the successive depositions of coatings; the second method exploits the reduction of surface energy to drive one of the components to a coating surface. These two methods are reviewed next.

1.2.1 Multiple deposition methods

To deposit multilayers of colloidal films, successive deposition methods are an obvious approach. Essentially any deposition method can be repeated to deposit a second layer onto a layer with a different composition. In one nice example, Lopez *et al.*³¹ used a two-step spray deposition method to deposit hard hydrophobic particles on a partially-dried colloidal film that served as an underlying binder. To obtain a mechanically robust surface using non-film-forming particles in the second layer, Lopez *et al.* applied the second layer before the first layer of film-forming particles had dried. They showed that some mixing between the layers embedded the hard particles in the first layer. In successive deposition methods there is still a necessity that the second layer deposition does not fully dissolve or re-disperse the colloids in the first layer.

Multilayer films have also been successfully deposited both by dip-coating and by spin-casting one layer on top of another. Bilayers of polymeric particles and gold nanoparticles were deposited in this way.³² Up to eight bilayers were dipped, and up to four bilayers were spin-coated. Latex films have been deposited with a Mayer bar, one on top of another, to fabricate multilayer coatings to tailor the permeability for biotechnology applications.³³

There has been a strong effort by colloids researchers to deposit colloidal crystals in the form of coatings. A colloidal crystal is analogous to an ionic crystal, such as NaCl, except that colloidal particles with defined size ratios take the place of ions in a lattice. A crystalline colloidal film can be considered to be stratified at the length-scale of particles. Rapid convective deposition has been applied to binary mixtures of silica microspheres and poly(styrene) nanoparticles. A monolayer of the microspheres was deposited, wherein the nanoparticles filled the void space between them.³⁴ Beautiful examples of dip-coated thick layers of binary colloidal crystals (composed of large and small particles) were presented by

Wang *et al.*³⁵ Elsewhere, Wang and Möhwald³⁶ showed that colloidal crystals could be manufactured via step-wise spin-coating.

1.2.2 Surface Energy Effects

A soft matter system will reduced its surface (and interfacial) free energy as a means to achieve a lower state of free energy, which is favourable at thermodynamic equilibrium. The surface free energy is the product of the surface energy of a particle surface or interface (expressed per unit area) and the area of that surface. In a coating system, there is therefore a driving force for the phase with the lower surface energy to wet the interface with air.³⁷ Likewise, it is favorable for the phase with the lowest interfacial energy with a substrate to wet that substrate. Stratified films have been cast from solutions of immiscible polymers in a common solvent, and the phases at the surface and substate interface were determined by the surface free energy.³⁸

In comparison to standard hydrocarbon polymers, compositions containing fluorine or silicon, in place of hydrogen or carbon, respectively, typically have a lower surface energy. There are numerous examples of the stratification of fluorinated or silanized polymers at the interface with air, driven by the reduction of surface free energy. This topic has been reviewed by Urban.³⁹

The extent of stratification in silicone-modified acrylics was found to be a function of molecular weight (which influences the chain mobility) and the end group composition, which influences surface energy. It is noteworthy that stratification was less pronounced in colloidal films in comparison to solution-cast films of the same composition.⁴⁰ Phase segregation in dry films requires molecular mobility for long-range diffusion and can be a slow process. Nevertheless, stratification was demonstrated by particles with fluorinated shells that break up and migrate to the surface during coalescence.⁴¹

In another strategy, Misra *et al.*⁴² synthesised lobed acorn-type particles, where one lobe was composed of a fluoropolymer and the other lobe was a poly(acrylate). The surface energy of the fluoropolymer was lower than the poly(acrylate)'s. The authors reported that in *single* layers the particles were oriented to minimize the surface free energy, depending on the type of substrate. On a substrate with a high surface energy, particles oriented with the low surface energy fluoropolymer lobe at the interface with the air, and with the poly(acrylate) adsorbed on the substrate. Note that this type of stratification was demonstrated in films with a thickness of one particle diameter. The acorn particles cannot make thick stratified films.

2. Stratification during Drying: Single Type of Particle

The process by which colloidal films form stratified layers spontaneously is called “auto-stratification,”⁴³ and also sometimes referred to as self-stratification. However, before we consider auto-stratification of particles in one layer on another, we must first consider which factors influence the distribution of individual particles during drying. To learn which parameters influence the particle distribution in the direction normal to the substrate, we will start by considering a single particle in a continuous liquid film.

Figure 2 shows the relevant processes of the problem. A particle is suspended in a liquid film of initial thickness, H . The particle undergoes Brownian diffusion and moves in random directions. The self-diffusion of an isolated particle is described by its Stokes-Einstein diffusion coefficient, D . In the early stages of drying, the evaporation rate of the continuous liquid will be constant. The evaporative flux is measured in units of mass per unit area per unit time. If this flux is divided by the density of the liquid, then the velocity, E , at which the water/air interface descends can be calculated.⁴⁴

Figure 2. Schematic diagram of factors that affect the distribution of particles in a colloidal film. A particle is suspended in a viscous liquid in a film of initial thickness, H . As a result of the evaporation of the continuous liquid phase, the top interface descends at a constant velocity, E . If the density of the particle is greater than the density of the liquid, then the particle will be subject to sedimentation. The particle will also undergo Brownian diffusion described by the Stokes-Einstein diffusion coefficient, D .

The time required for a particle to diffuse from the top of a film to the bottom is proportional to the square of the height of the film and inversely related to the diffusion coefficient: $\tau_{diff} \sim H^2/D$. The time for the liquid in the film to evaporate is proportional to the initial film thickness and inversely related to the evaporation rate: $\tau_{evap} \sim H/E$. Routh and Russel⁴⁵ used the ratio of these two times, which define the Péclet number, Pe , to determine which process (evaporation or diffusion) was dominant. Pe is defined as

$$Pe = \frac{\tau_{diff}}{\tau_{evap}} = \frac{H^2/D}{H/E} = \frac{HE}{D}. \quad (1)$$

When $Pe \gg 1$, evaporation is dominant. As the water/air interface descends, the particles will not be able to diffuse away at a sufficient rate to avoid being swept up. Hence, the particles

will accumulate at the top of the film during the drying process. When $Pe \ll 1$, on the other hand, diffusion is fast relative to evaporation, and the particles will be uniformly distributed throughout the depth of the film. Routh and Zimmerman⁴⁶ modelled stratification of single-size particles and predicted that when $Pe \gg 1$ a packed layer of particles accumulated at film/air interface. They derived an equation stating that the concentration gradient below the packed layer is proportional to Pe to a power of $1/2$.

Gromer *et al.*⁴⁷ developed a cell model to improve on the modelling of Routh and Zimmerman⁴⁶ by including repulsive interactions between particles. In follow-up work, they also considered the vertical distributions of surfactant using their cell model.⁴⁸ The distribution of colloidal particles in drying films has also been modelled using Monte Carlo simulations.⁴⁹ Large-scale molecular dynamics simulations⁵⁰, which included solvent explicitly, have confirmed that nanoparticles accumulate at the liquid/vapour interface when the evaporation rate is relatively fast. When the evaporation time is long relative to the diffusion time of the nanoparticles along this interface, then defect-free two-dimensional crystals are deposited. However, when the evaporation rate is too fast, there is insufficient time for the nanoparticles to rearrange, and defects develop in the crystal. Thus, there is an optimum evaporation rate for particle ordering at the top interface.

The effect of the electrostatic charge of colloids on the concentration profile during the consolidation in a drying front was investigated in experiments and modelling by Sarkar and Tirumkudulu.⁵¹ They argued that the fast diffusing counter-ions resist the effects of convection. The counter-ions set up an electric field that acts upon the charged colloids, which enhances their diffusivity and broadens the colloidal particle concentration profile moving away from the packed region.

Characterising the distribution of particles in a wet liquid presents myriad experimental difficulties. The temperature of the technique must be between the freezing and boiling points of the liquid phase, and the ambient pressure must be greater than the vapour pressure to avoid boiling. The characterisation technique must not perturb the liquid and must have sufficient resolution in time and distance. Alternatively, to determine whether a stratified coating has formed from a mixture of particles, the final dry state - rather than the wet state - can be characterized. The techniques that have been employed to characterize particle distributions in the wet and dry states are listed in Table 1. It is noteworthy that small angle X-ray scattering (SAXS) has been successfully employed to probe the drying process of colloidal films placed in a horizontal position, so that concentration gradients in the plane of the film could be examined.⁵² This experimental geometry does provide information about concentrations in the direction normal to the substrate.

When using cryogenic scanning electron microscopy, or cryoSEM, a drying wet film is frozen to enable images of the particle distributions in film cross-sections to be obtained.^{11,53–59} Such experiments on latex have shown that with moderately fast evaporation rates, colloidal particles accumulate near the air/water interface. A consolidated layer of particles grows from the top downwards.⁵³ Experiments on the drying of polystyrene colloids provided evidence for ordering at the liquid/air interface when the evaporation rate is fast relative to the particle diffusion⁶⁰. The most perfect ordering of particles occurred at intermediate evaporation rates, and disorder developed when the evaporation rate was too fast. This result is consistent with the molecular dynamics simulations on nanoparticles.

In experiments to explore the effects of Pe on particle distribution, Gorce *et al.*⁶¹ used NMR profiling to measure the water concentration when films were dried with a range of evaporation rates. In line with expectations from modelling,⁴⁵ they found that the water was

uniform with depth when E was low and $Pe < 1$. At fast evaporation rates, when $Pe > 1$, there was a water concentration gradient with more particles near the water/air interface.

Ekanayake *et al.*⁶² confirmed in NMR depth profiling experiments that the particle concentration gradient is steeper when Pe is increased, as was predicted by Routh and Zimmerman.⁴⁶ Kimber *et al.*⁶³ studied latex films dried at elevated temperatures for which the evaporation rate was very high. With the relatively low thickness of their films, on the order of $H = 20\ \mu\text{m}$, Pe was approximately 5. They used ultrafast techniques of infrared spectroscopy to identify that a layer of particles developed above a more dilute liquid layer, which is expected when evaporation dominates over diffusion.

When the densities of suspended particles and the continuous phase are matched, then the competition between evaporation and diffusion is adequate to describe the vertical distribution of particles. However, when the particles have a greater (or lower) density, then sedimentation (or creaming) must be considered. Cardinal, Jung *et al.*⁵⁴ defined a dimensionless sedimentation number, N_s , as the ratio of the sedimentation velocity, U_s , to the evaporation velocity: $N_s = U_s/E$. In turn, U_s is proportional to the square of the particle diameter and the difference in density between the particle and the continuous medium.

Cardinal, Jung *et al.*⁵⁴ solved the dimensionless conservation equation with a moving top boundary to obtain numerical results for the particle volume fraction profiles in the vertical direction. They used their model to construct drying regime maps to show the ranges of Pe and N_s for which the process of evaporation, diffusion, or sedimentation was dominant. When sedimentation dominates, particles increase in concentration near the substrate during the drying process. Interestingly, they identified a narrow region of parameter space in which both sedimentation and evaporation were dominant. Figure 3 validates the expectations of the

model by showing the cross-section of a drying film in which particles are accumulated at both the air (top) and the substrate (bottom) interfaces.

Figure 3. Cross-section cryoSEM image of a coating showing both sedimentation and evaporation. $Pe = 0.25$; $N_s = 2.1$. The inset shows the volume fraction of particles as a function of depth in the coating as estimated from the image. Reprinted with permission from reference ⁵⁴. Copyright © 2010 American Institute of Chemical Engineers (AIChE).

More recently, their model has been modified to include the changing viscosity of the continuous phase consisting of an evaporating polymer solution.⁶⁴ They comprehensively tested their model in coatings deposited from colloidal particles (silica and poly(styrene)) in a polymer solution in water.⁶⁵ In a system with a large polydispersity of particle size, the results of Cusola *et al.*⁶⁶ show that larger particles are subject to sedimentation to the bottom of the film, whereas smaller particles are enriched at the air interface.

Erkselius *et al.*⁶⁷ added salt to charge-stabilized latex to screen the charge repulsions. With added salt, they induced flocculation and sedimentation of the particles. The free surface of the water (no longer blocked by particles) allowed faster evaporation of the water phase. Their experiments nicely link together particle interactions, spatial distributions and the drying process.⁶⁷

3. Self-Stratification during Drying: Two Types of Particles

Now, we will turn our attention to mixture of two (or more) types of particles. There are at least four mechanisms through which the stratification of colloidal particles in a coating have been achieved. These mechanisms rely on (1) differences in particle density that cause sedimentation at different rates; (2) exploitation of interactions between particles and the particle chemistry; (3) the growth of new particles; and (4) differences in the particle diffusivity. Each of these four mechanisms will be reviewed next.

3.1. Sedimentation-Driven Stratification

An early example of stratification via a sedimentation mechanism in a colloidal mixture was reported by Grillet *et al.*⁶⁸ in mixtures of large polymer particles (360 nm diameter) and silica nanoparticles (18 nm). The silica aggregated to make larger clusters that sedimented during film formation as a result of being denser than the continuous water phase. The stable polymer particles created a binder for the sedimented silica layer. A cross-sectional image of their resulting stratified film is shown in Figure 4. The film formation of an adhesive layer also relied on the sedimentation of colloidally unstable phase.²⁶

Figure 4. Optical microscopy of a thin cross-sectional slice (prepared by means of microtome cutting) of a poly(butyl methacrylate) film containing 5% silica. The silica particles appear as the black dots, and the polymer phase appears as the grey regions. Scale bar = 100 μm . Reprinted with permission from reference ⁶⁸. © 2004 Society of Chemical Industry.

Lopez *et al.*³¹ demonstrated that sedimentation encourages stratification. As their intention was to stratify the denser particles at the top of the film, they inverted their samples during evaporation, such that the substrate lay above the wet film. Although effective, the method is not suitable for applications where the substrate cannot be inverted.

Cardinal, Jung *et al.*⁵⁴ mixed suspensions of silica particles of two sizes and dried them in such a way that the smaller particles were in the evaporation dominant regime and large particles were in the sedimentation dominant regime. Figure 5 shows that a stratified film resulted, with the non-sedimenting small particles mainly in a layer at the top, thus demonstrating the feasibility of the approach to bilayer film manufacture.

Figure 5. Cross-section image of a dried film prepared from a bimodal aqueous silica dispersion with $\alpha = 5$. Top right: higher magnification image of the top of the film. Bottom right: higher magnification of the bottom of the film. Scale bars are as shown. Evaporation is dominant for the small particles and sedimentation is dominant for the large particles. The film is stratified with a layer of small particles in a top layer, and a layer of mixed small and large particles in a bottom layer. Reprinted with permission from reference⁵⁴. Copyright © 2010 American Institute of Chemical Engineers (AIChE).

3.2 Particle interaction effects

Attractive and repulsive interactions between particles influence the colloidal stability in a suspension. Particle repulsions have been found in numerical simulations to push particles away from the descending air interface in a drying film. Atmuri *et al.*⁶⁹ modelled mixtures of particles with the same size but where one type was neutral and the other type had charge repulsion. They found a depletion of repulsive particles from the air interface. They also simulated four different combinations of repulsive and attractive interactions in mixtures of large and small particles by modifying the chemical potentials for particles of the same size. Particles having attractive interactions tended to accumulate near the film/air interface, whereas particles having repulsive interactions were pushed away.

In Brownian dynamics simulations of mixtures of particles with different surface potentials, Liao *et al.*⁷⁰ found that the particles with the lower surface potentials built clusters. These clusters were pushed downward by the descending top interface and were enriched in the middle section of films. Sand *et al.*⁷¹ considered colloidal particle interactions using the DLVO potential in a particle dynamics model. They modified the Stokesian dynamics approach with lubrication-type hydrodynamic interactions. In experimental work,⁷² the DLVO interactions were adjusted via the pH of a dispersion and increased the extent of particle aggregation, which then lowered the percolation threshold in mixtures.

Some experimental work has investigated the effects of surface charge and colloidal stability. In the experiments of Nikiforow *et al.*,⁷³ blends of particles with a similar size were considered. One type of particle was neutral (and sterically stabilized), and the other type was negatively charged. Using confocal microscopy, they observed that neutral particles were enriched at the film/air interface in results that are very similar to the modelling of Atmuri *et al.*⁶⁹ They concluded that the charged particles pushed other charged particles downward.

They also calculated how particle interactions increased the co-operative diffusivity at higher concentrations.

The effect of charge repulsion was studied experimentally in a binary colloidal system in which the charge on large particles decreased toward the isoelectric point when the pH was decreased to three. At a low pH, fewer of the large particles were excluded from the film surface, which was consistent with the results of modelling.⁶⁹ In the experiments of Sun *et al.*⁷² ceramic particles and polymer particles were mixed. The pH was varied to affect the colloidal stability, which influenced the surface structures.

3.3 Growth of New Particles at the Film Surface

In a recently-reported innovation, metal nanoparticles have been “grown” in the top region of a drying latex film. In experiments by Römermann *et al.*,⁷⁴ latex films with a continuous phase of either a gold or silver salt solution were exposed to a reducing plasma during drying. With a high enough salt concentration, a continuous metal layer formed at the drying film interface. At lower salt concentrations, a stratified layer of metal nanoparticles was formed near the film surface. The stratification mechanism relies on the fact that the plasma reaction occurs predominantly near the top interface.

3.4 Diffusive Causes of Stratification

As already reviewed here, it is well understood that slower-diffusing large particles will accumulate at a descending air/water interface when $Pe > 1$, and faster-diffusing small particles will be uniformly distributed when $Pe < 1$. In a mixture of large and small particles, the large particles will diffuse more slowly than the small particles. Trueman *et al.*⁴³ recognised the possibility of exploiting this phenomenon and aimed to achieve stratification of large particles at the top of colloidal films. Their numerical analysis⁴³ found that this type of stratification was possible if the evaporation rate was set such that Pe for the large

particles, Pe_L , and for the small particles, Pe_s , bracketed unity: $Pe_s < 1 < Pe_L$. Their work inspired several investigations that followed.

Fortini *et al.*⁷⁵ conducted Langevin dynamics simulations in parallel with confocal microscopy experiments on binary colloid with a particle size ratio, α , of 7. They found that a layer of *small* particles accumulated at the top of a film during drying when $Pe_L > Pe_s > 1$. A series of simulation snapshots showing the formation of a stratified layer is presented in Figure 6. Whereas when $Pe_s < 1$, Trueman *et al.* found a surface layer enriched in large particles, when $Pe_s > 1$, Fortini *et al.* found a surface layer enriched in small particles. Their results were subsequently corroborated through Langevin dynamics simulations by Tatsumi *et al.*⁷⁶, who additionally observed that the extent of stratification varied with the evaporation rate.

Fortini *et al.*⁷⁵ developed a physical model in which the concentration gradient of particles near the top of a drying colloidal film creates an osmotic pressure gradient. The downward force acting on larger particles is greater than on smaller particles. In a binary mixture, the difference in the velocity of the large and small particles was predicted to scale with α^2 and to be proportional to Pe . Fortini and Sear⁷⁷ later showed with Langevin dynamics simulations that stratification of particles by size occurs in ternary mixtures and in suspensions with a polydispersity of particle size. They referred to the mechanism of particle motion driven by a concentration gradient of particles as “colloidal diffusiophoresis” to distinguish it from standard diffusiophoresis in which diffusion is driven by a gradient in the concentration of a solute.

Figure 6. Snapshots of the side view of a simulation of the drying of a mixture of colloidal particles with $\alpha = 7$. Time is increasing from (a) to (e). A video showing a simulation is provided online in the Supplemental Material. Reprinted with permission from reference ⁷⁵. Copyright (2016) by the American Physical Society.

Howard *et al.*⁷⁸ used dynamical density functional theory to investigate stratification in binary colloidal films and found good agreement with the results of Fortini *et al.*⁷⁵ Their simulations found that a stratified layer of small particles grew faster and was thicker when α was higher. Stratification occurred even when $Pe \approx 1$ for the small particles.

Martín-Fabiani *et al.*⁷⁹ demonstrated a way to control stratification. They showed using confocal microscopy that a dilute aqueous dispersion with an initial volume fraction of 0.1 and $\alpha = 7.7$ stratifies with the small particles on top. When the small particles were swelled so that α decreased to 4.1 and the volume fraction increased to 0.45, there was no stratification, in agreement with Langevin dynamics simulations (Figure 7). Their result shows the effects of particle crowding in reducing mobility and also reducing the time available for stratification.

Figure 7. (a) Confocal image of a binary colloidal film with $\alpha = 7.1$ and initial volume fraction of 0.1. The small particles contain a green fluorescent dye and are seen in a layer at the top of the film. A snapshot of the final structure obtained from Langevin dynamics simulations for this system is shown at the right. (b) Image of the same materials system when $\alpha = 4.1$ and the initial volume fraction is 0.45. The red and green particles are distributed uniformly with depth. A snapshot of the corresponding Langevin dynamics simulations is shown to the right. Adapted with permission from reference ⁸⁰. Copyright (2016) American Chemical Society.

In the same way as Trueman *et al.*,⁴³ Fortini *et al.*,^{75,77} and Howard *et al.*,⁷⁸ the effects of concentration gradients in particles were considered by Zhou *et al.*.⁸¹ They reached the same result as in these earlier works by arguing that the effect of cross-interaction between large and small particles in a binary mixture is not symmetric: it is stronger on the large particles. For brevity, we refer to their model hereafter as the ZJD model.

The second-order virial coefficient in ZJD's free energy density equation for hard spheres depends on the square of the sum of the radii of the two interacting spheres. In turn, the chemical potential is found from a partial differential of the free energy density. Gradients in the chemical potential set the velocity of the colloidal particles. (The calculations of

Trueman *et al.*⁴³ did not consider this cross-term in their free energy expression.) For a binary mixture, Zhou *et al.*⁸¹ derived that the velocity of the large particles is affected by α more strongly than are the small particles, and thus the downward velocity of large particles is expected to be greater when α is larger. Also, this velocity is greater when there is a stronger concentration gradient of *small* particles. These findings are the same as in previous modelling and simulations.^{66,67,68} Zhou *et al.* derived the condition required for stratification of small particles on top of large particles to be

$$\alpha^2(1 + \text{Pe}_s)\phi_s > C, \quad (2)$$

where Pe_s is the Péclet number for the small particles, and C is a constant taken to be on the order of one. Surprisingly, in the ZJD model, the stratification depends on the volume fraction of small particles, ϕ_s , but is independent of the volume fraction of large particles, ϕ_L .

Zhou *et al.*⁸¹ derived and presented state diagrams to show the parameter space in which stratification is expected. In the ZJD diagrams, $\alpha^2(1 + \text{Pe}_s)$ is plotted against ϕ_s . Stratification of small particles at the top is expected in the region in the upper right corner, which lies above the boundary given by Equation 2. An example of a diagram with $\alpha = 7$ is shown in Figure 8. Here, Zhou *et al.* identified a parameter space where the large particles will remain enriched at the top when close-packed, because their downward velocity is slower than the small particle velocity.

Figure 8. State diagram obtained from the ZJD model using $\alpha = 7$. The labels identify the regions where stratification with small particles on top is expected (upper right), where large particles are expected, and where randomly packed particles are expected (bottom left). The red line is obtained from Equation 2. Reprinted figure with permission from Jiajia Zhou, Ying Jiang and Masao Doi, APS *Physical Review Letters* 118, 108002 (2017) (reference ⁸¹).

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The state diagram developed from the ZJD model provides a useful way to represent the effects of experimental parameters on the stratification of binary colloidal films. The original ZJD model makes a few approximations:

- 1) the solvent is implicit and static, such that flow past the particles during evaporation is neglected;
- 2) only a second virial coefficient approximation is used for the particle interactions;
- 3) a simple Stokes-Einstein diffusion coefficient is used, which neglects crowding effects and applies only in the dilute limit.

Because of these approximations, the model might not accurately explain all experimental results. Nevertheless, it is expected to capture the general trends. In the next section, we will explore the effectiveness of the model in agreeing with experimental observations.

4. Experimental Tests of the ZJD Model and New Explicit Solvent Models

There are several early examples of anecdotal remarks in the literature which are consistent with models of stratification by size but for which the underlying mechanism was not appreciated at the time. For instance, Eckersley and Helmer¹ found a greater extent of stratification of small hard particles at a binary latex film surface, when the size ratios were high. Figure 9 shows their evidence for size stratification, which is one of the earliest reports of this effect.

Figure 9. Scanning electron micrographs of the cross-sections of latex films made from 60% soft large particles and 40% hard small particles. The small hard particles appear as bright circles. The soft large particles coalesce to make a continuous phase, which appears as dark grey. Image (a) was obtained from near the top of the film. The air interface runs vertically on the left side. Small particles are accumulated there. Image (b) shows the interior of the film near the substrate. The small particles are distributed throughout the continuous phase, and their concentration is lower than at the surface. Reprinted with permission from reference 1. Copyright © Springer Science+Business Media 1997

In another example, in a study of bimodal latex films, Tzitzinou *et al.*⁸² commented that at low concentrations of small particles, the top surface of the film was covered entirely with large particles. As ϕ_s was increased, the surface was mainly covered with small particles.

However, these authors did not analyse the surface coverage to determine if it was greater than expected from random mixing, and hence it is not possible to conclude stratification by size according to the ZJD model.

Nunes *et al.*²³ expected to see a higher concentration of large particles at the top of their binary films because of slower diffusion (as per the Trueman model), but instead they found an accumulation of small hard particles, which, in turn, led to greater film hardness. From our best estimates, some of their experimental parameters were in the ZJD regime where diffusive cross-interaction leads to stratification by size. Several other qualitative observations of stratification by size have been reported in binary colloidal films^{53,59,83,84}. However, in these cases where the parameters were not measured with high precision, any meaningful comment on the ZJD model's validity becomes difficult.

In AFM and SEM images of colloidal film surfaces, occasionally it is reported that the apparent particle size is smaller than what is measured for single particles using dynamic light scattering.⁸⁵ One explanation is that light scattering measures the hydrodynamic diameter, which is larger than the physical size. However, another feasible explanation could be polydispersity in the particle size distribution, leading to the stratification of smaller particles on the top, as was found in Fortini and Sear's simulations.⁷⁷ Thus, the effects of stratification might have been observed in the older literature, without the underlying mechanism being appreciated. Indeed, a systematic experimental study of polydisperse lignin particles (ranging from 50 nm to *ca.* 2 μ m) has confirmed that with a high Pe, the fraction of small particles at the top of a film is enriched.⁶⁶

Makepeace *et al.*⁵⁵ provided the first experimental test of the ZJD model using binary colloidal mixtures with $\alpha = 2$ and $\alpha = 7$. In dilute systems, the model and experiments were in general agreement. However, when the total initial volume fraction was set to 0.4,

stratification was not observed with $\alpha = 2$ but only with $\alpha = 7$ at high ϕ_s values. It is not surprising that stratification is restricted at higher concentrations of particles because of crowding effects and hydrodynamic interactions, which the model does not consider. Liu *et al.*⁸⁶ have also tested the ZJD model through the analysis of the surface structures of blends of silica and polymer particles, and they likewise found adequate agreement.

Figure 10 presents ZJD state diagrams with results obtained throughout the literature from studies of binary colloidal films. To construct these diagrams, we used the values of the parameters that were provided in the publications to calculate α , Pe_s and ϕ_s . In some cases, evaporation rates were not reported. If the evaporation took place near room temperature and with intermediate relative humidities, we used $E = 1.1 \times 10^{-7} \text{ ms}^{-1}$, which was reported by Utgenannt *et al.*⁸⁷ For experiments at elevated temperatures, values were also taken from reference⁸⁷. For particles with a radius of R , our calculations used the Stokes-Einstein equation⁴⁵:

$$D = \frac{k_B T}{6\pi\mu R}, \quad (3)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and μ is the viscosity of continuous phase, which was taken to be $1 \times 10^{-3} \text{ Pa}\cdot\text{s}$ for water at room temperature. Table 2 lists the parameter values obtained from the literature.

Using comments made by the original authors, and by examining the published micrographs, we deduced whether the films were stratified, non-stratified, or had some surface enrichment of small particles. Films were considered stratified when there was full coverage of the surface with small particles *or* when at least 50% of the surface was covered with small particles and sufficient information on the bulk composition was provided to enable conclusions to be drawn. Films were considered to be surface-enriched when the concentration of small particles was greater than expected from a random mixture. The

analyses are presented in Figure 10a for dilute systems (in which the initial total volume fraction was less than 0.2) and in Figure 10b for more concentrated systems. Symbols are used to specify the type of stratification for each experiment. Stratification is expected from the ZJD model in the parameter space above the boundary defined by Equation 2, shown as the solid line.

Figure 10. Experimental data from binary colloidal films presented in relation to the state diagram derived from the ZJD model (using Equation 2). (a) Dilute systems in which $\phi_{\text{tot}} < 0.2$. (b) Concentrated systems in which $\phi_{\text{tot}} > 0.2$. Open red symbols (squares and circles) represent films that show stratification of small particles. Filled blue symbols (squares and circles) represent films that show no stratification. Symbols shaded half blue/half red represent films that show some surface enrichment of small particles. All data were taken from publications in the literature, as are listed in Table 2.

Some general trends emerge in this analysis. In both dilute and concentrated systems, experiments exhibited stratification only in the region where the ZJD model predicts stratification. Experiments with parameters that fell below the Equation 2 boundary did not show stratification or only presented some surface enrichment.

However, in both cases (dilute and concentrated systems), some experiments were found to have no stratification, even though the model predicted it. This phenomenon is more prominent in concentrated systems and could be due to particles jamming at earlier times, thus prohibiting stratification.

Luo *et al.*⁵⁶ provide an early example of a systematic study of the parameters affecting stratification in a binary colloidal mixture. They added inorganic nanoparticles to a latex and varied the evaporation rate during film formation. In nearly all experiments, there was an enrichment of nanoparticles at the top of the film, but there was not complete coverage. They attributed the transport of small particles through a consolidated layer of larger particles at the top of the drying film to convective flow driven by evaporation from the particle menisci. In light of recent theory and simulations, the mechanism is better described as the motion of the liquid phase in relation to the packed bed of large particles at the top of the film that moves downwards during evaporation. Luo *et al.* commented on the necessity of a fast evaporation rate to achieve “top-down” drying. They also recognised the need for a high particle size ratio (>6.7) to allow transport of small particles through a packed layer of large particles.

We have plotted the parameters reported (or implied) by Luo *et al.*⁵⁶ for a series of experiments on a ZJD diagram in Figure 11. They increased the film formation temperature, which increased the evaporation rates and hence Pe_s . For the highest Pe_s , the surface is nearly covered with small particles, whereas for the lowest Pe_s , small particles are found only in the valleys between protruding large particles. This trend toward greater stratification when Pe_s increases is seen in Figure 11 to be in good agreement with the ZJD model. The initial concentration of small particles is very low in their experiments (< 0.015). With relatively so few small particles, the distance of travel becomes greater to form a stratified layer, and there could be some kinetic hindrance, which prevents full stratification.

Figure 11. Experimental parameters of Luo *et al.*⁵⁶ plotted according to the ZJD model. The extent of stratification is indicated by the symbols: red open squares = stratified; blue filled squares = non-stratified; and red/blue-shaded squares = surface enriched. Inset are AFM topographic images for the three samples corresponding to the data points. The film formation temperature decreases from 60 °C to 40 °C to 22 °C moving from the top to the bottom, and Pe_s likewise decreases. Adapted with permission from reference ⁵⁶. Copyright © 2008, American Chemical Society.

Trueman *et al.*⁵⁷ varied the size ratio of particles, α , while ensuring that $Pe_s < 1$. Figure 12 presents their results on a ZJD diagram. Experiments in which α is increased fall on a vertical line on the diagram. With higher values of α (4.97 and 4.19), the surfaces are almost entirely covered with stratified small particles, as is expected by the model. When $\alpha = 1.73$, however, there is no evidence for stratification, as is also expected. NMR profiling showed that there was a steeper concentration gradient of particles when α was increased. Thus, the ZJD model seems to explain why stratification with large particles on the top were not found in experiments.

Figure 12. Experimental parameters from the experiments of Trueman *et al.*⁵⁷ represented on a ZJD diagram. AFM images for four different values of size ratio (α) are shown in the inset. Open red symbols represent films that show stratification of small particles. Filled blue symbols represent films that show no stratification. Symbols shaded half blue and half red represent films that show some surface enrichment of small particles. Adapted with permission from reference⁵⁷. Copyright (2012) American Chemical Society.

In other experiments by Trueman *et al.*,⁵⁷ equal volume fractions of large and small particles were used, but the fraction of large particles at the dry film surface was unexpectedly found to be < 0.5 , despite being in the regime where $Pe_s < 1 < Pe_L$. It is possible that the ZJD diffusive effects (and gradients in the osmotic pressure) reduced the fraction of large particles at the film surface.

Howard *et al.*⁸⁸ performed Langevin dynamics simulations for mixtures of colloids and polymers in solution and well as solutions of polymer mixtures. They showed that stratification of polymer coils at the top of a film occurs in the same way as in mixtures of colloids of different size when the radius of gyration, R_g , is smaller than the radius, R , of the colloid. However, there was no such stratification when $R_g > R$. Their model using dynamical density functional theory agreed quantitatively with their simulations. The stratification of polymer coils had not been considered in previous modelling and experiments^{56,65} on the drying of polymer solutions containing colloidal particles.

Sear and Warren⁸⁹ likewise modelled mixtures of colloids and polymers in solution. They extended previous modelling and simulations that treated the solvent implicitly, *e.g.* as a continuous phase with a constant viscosity and pressure. Considering the solvent explicitly in colloidal diffusiophoresis, they pointed out that there is a gradient in the solvent pressure that balances the osmotic pressure gradient of colloidal particles. The downward drift velocity of colloidal particles arises from the gradient in solvent pressure in the exclusion region of that particle. Considering the solvent backflow when particles are pushed

downward, Sear and Warren found that stratification occurs when Pe_s and ϕ_s are high; large particles are depleted from the surface layer at later drying times, which is consistent with predictions of the ZJD model. However, neglecting the solvent backflow, as in previous models, over-estimates the downward drift velocity. Sear and Warren neglected interactions between the colloidal particles, but they captured the essential physics. Their model applies to dilute colloids with $\alpha \gg 1$, although in previous work, α is often smaller (Table 2). In Figure 13a, we plot the experimental data in the literature to the Pe_s - ϕ_s state diagram proposed in the Sear-Warren model. Here, the boundary between the stratified (small on top) and homogeneous regions is given as

$$Pe_s = \frac{1}{t^* \phi_s} \quad (4)$$

where t^* is the reduced time when the stratified structure develops and can be taken to be 0.5.

Figure 13. a) Experimental data from binary colloidal films presented in relation to the state diagram derived from the Sear and Warren⁸⁹ model (black solid line, using equation 4 with $t^* = 0.5$) and the Sear⁹⁰ model including jamming (grey dashed line, using equation 5 with $\phi_{jam}=0.64$). Both models predict that large particles are excluded from the top layer for parameters above the boundary line. The size ratio in all of the presented data is $\alpha \geq 7$ to satisfy the $\alpha \gg 1$ condition of the two models. Open red symbols represent films that show stratification of small particles. Filled blue symbols represent films that show no stratification. Symbols shaded half-blue/half-red represent films that show some surface enrichment of small particles. All data were taken from publications in the literature, as are listed in Table 2. b) An illustration of the side view of a jammed layer of small particles (red circles above the dashed line) descending downward with the air/liquid interface with a velocity of v_{jam} . A large particle (blue) is excluded from the jammed layer when its velocity, U , is greater than v_{jam} . Reprinted from reference ⁹⁰, with the permission of AIP Publishing.

In work that followed, Sear⁹⁰ considered the effects of jamming of the small particles in a solid-like layer at the top of a drying binary film. Sear argued that at fast enough evaporation rates ($Pe_s > 1$), a layer of small particles accumulates at the descending air/liquid interface. Above a certain volume fraction, ϕ_{jam} , the small particles are so close together, they jam into a solid-like structure. This jammed layer descends downward with a velocity of v_{jam} .

In order for the large particles to be excluded from the jammed layer of small particles, the downward velocity of the large particles, U , must be greater than v_{jam} . This mechanism is illustrated in Figure 13b.

Sear pointed out that when the initial volume fraction of small particles, ϕ_s , is too great, the downward diffusiophoretic velocity is too slow to push the large particles ahead of the jammed layer. Assuming that jamming occurs when spherical particles are randomly packed, and hence taking the jamming particle fraction to be $\phi_{\text{jam}} = 0.64$, he derived the upper boundary for small-on-top stratification to be $\phi_s = 0.2$. At higher concentrations, stratification is not possible.

Sear⁹⁰ also proposed a modified $\text{Pe}-\phi_s$ diagram with a new boundary below which the jammed layer forms too late in the drying process to exclude the large particles. This boundary is given by

$$\text{Pe}_s = \frac{\phi_{\text{jam}}}{\phi_s}. \quad (5)$$

The model assumes that the size ratio is very large, and it neglects large particle interactions. The boundary is shown on the diagram in Figure 13a. The experimental data from the literature (Table 2) that is plotted in Figure 13a shows a broad trend. Apparent stratification of small particles on top of large particles tends to be found in experiments having a higher Pe_s and/or a higher ϕ_s . Both the Sear-Warren and the Sear models likewise expect stratification with a higher Pe_s and ϕ_s , however the boundary for both models falls at values of Pe higher than the values of the experimental data where stratification is observed (see Figure 13a). In fact, most experiments did not use the very high evaporation rates needed to achieve the large Pe_s required to compare to the models. Hence, the models cannot be adequately tested against data in the literature. It should be noted that when classifying the

experimental systems as being stratified or non-stratified, we made inferences from microscopy of the top surface of films. There is uncertainty.

Sear⁹⁰ raised the possibility of colloidal crystallization in a stratified layer of small particles as a direction for future work. Already Wang and Brady⁹¹ have used Brownian dynamics simulations to investigate crystallization in drying films of mono-sized colloids over a range of evaporation rates. When $Pe \gg 1$, the particles accumulate at the descending liquid/air interface, and epitaxial crystallisation is observed. With slower evaporation rates, the stratified layer is amorphous.

The earliest computer simulations of *binary* colloidal film drying used an implicit solvent, *i.e.* described the continuous phase with a viscosity and ignored the hydrodynamic flow. The first simulations of colloid stratification to use an explicit solvent was performed by Cheng and Grest.⁹² They carried out simulations of nanoparticles in a continuous phase of polymers dissolved in an evaporating solvent. Their simulations considered the effects of the wettability of the nanoparticle by the polymer. When the polymer completely wets the nanoparticles, they were found to create well defined layers at the drying interface in a polymer-rich skin layer. However, if the polymer is only partially wetting, the nanoparticles are depleted from the polymer-rich skin layer.

Statt *et al.*⁹³ performed non-equilibrium molecular dynamics simulations to compare stratification predicted by an implicit solvent model to stratification by an explicit solvent model. In their explicit solvent model of particles in a drying polymer solution, they used a similar approach to Cheng and Grest⁹² where polymers represented as linear chains with monomers of diameter, σ and mass, m are immersed in solvent beads of equal mass and size. Statt *et al.*⁹³ found that implicit solvent models tend to over-predict stratification meaning that stratification is more likely to occur in these simulations. Further investigations into the

possible source of the differences between models showed that the missing hydrodynamic interactions in the implicit solvent model are responsible for the effect. Other differences between the models, such as in the chemical potentials and equilibrium diffusion coefficients, and temperature gradients induced by evaporative cooling, were considered but ruled out after careful analysis. Their work underscores the necessity of considering the solvent in future modelling and simulations. The simulations have not yet been compared to experimental results.

Unfortunately, computer simulations with explicit solvents are very demanding of computer time, which necessitates simulations of thinner films (smaller system sizes) and faster evaporation rates than are typically used in applications and in experiments. Hence, Tang *et al.*⁹⁴ used very fast evaporation rates in their large-scale molecular dynamics simulations of binary colloidal film drying. They simulated evaporation by allowing the solvent to escape into the vapor phase. An ultrafast evaporation resulted in significant decreases in temperature near the film surface, because of evaporative cooling. The resulting temperature gradient led, in turn, to a density gradient with a lower density near the top interface. They discovered that particles moved down the density gradient by phoresis, and the effect was stronger for large particles. Hence, with ultrafast evaporation, large-on-top stratification was enhanced and countered the diffusive effects that result in small-on-top stratification. Figure 14 compares the output of their large-scale explicit solvent simulations at two different evaporation rates. As the evaporation rate is decreased, the “usual” small-on-top stratification is enhanced. The results of Tang *et al.*⁹⁴ underscore that the stratification phenomenon is observed when the solvent is considered explicitly, and observations can differ from implicit solvent simulations.

Figure 14. Snapshots of simulations explicitly including solvent using two different evaporation rates: (a) ultrafast and (b) slower than ultrafast by a factor of size. The time of simulation is printed below each snapshot in units of Lennard-Jones time, t . The large particles are presented in orange, the small particles are green, and the solvent molecules are blue. (Only 5% of the solvent molecules are shown for the purposes of clarity.) Reprinted with permission from reference ⁹⁴. Copyright 2018 American Chemical Society.

5. Concluding Summary and Future Directions

This review has presented several important concepts, which are summarised here.

- Stratified colloidal films consist of one or more layers of one type of particle on another.
- Single colloidal particles in a liquid film are subject to the effects of evaporation, Brownian diffusion, and sedimentation (if not density matched with the liquid).

- Stratified colloidal films can be made from mixtures by exploiting the effects of diffusion, sedimentation, colloidal interactions (*e.g.* charge repulsion), and surface free energy reduction.
- When the evaporation rate is greater than the rate of diffusion (Péclet number, $Pe > 1$), concentration gradients develop in drying films in the direction normal to the substrate. The resulting pressure gradient can induce downward motion in other species.
- In binary blends, the model of Zhou, Jia and Doi⁸¹ identifies three important parameters determining whether stratification by size will occur during drying: Pe , the concentration of small particles, and the size ratio. Surprisingly, the concentration of large particles does not influence stratification in the model.
- Our survey of the literature has found numerous examples, some described anecdotally, of the stratification of binary colloidal films with small particles on top, which are in broad agreement with the expectations of the ZJD model. There are insufficient data to test properly the implicit solvent model of Sear and Warren.^{89,90}
- Hydrodynamic interactions and the backflow of liquid have an effect on colloidal stratification,⁸⁹ and should not be ignored in models. Computer simulations that use an implicit solvent have been found to predict a greater amount of stratification than found in explicit solvent simulations,⁹³ and more stratification than found in experiments.⁵⁵
- All of the previous modelling, simulations and experimentation agree that small particles will create a stratified surface layer in a drying binary colloidal film when the Pe is sufficiently high and when the concentration of small particles is sufficiently large. However, if the concentration of small particles is too high, the downward velocity of large particles ahead of the jammed layer is too slow, and stratification by

size is suppressed.⁹⁰ Furthermore, stratification appears to be stronger when the particle size ratio is higher in experiments,⁵⁵ simulations,⁷⁸ and the ZJD implicit solvent model.⁸¹

Despite the recent progress that has been made in fabricating multilayer colloidal films and controlling their structures and properties, more research in this field is still needed. Some of the unresolved issues and opportunities are highlighted hereafter.

- Existing and emerging models of stratification need thorough testing with experiments and simulations, and future work could consider non-spherical colloids, such as two-dimensional platelets (e.g. clays and graphene) and nanofibers, and a variety of inorganic and natural nanoparticles.⁶⁶
- New non-invasive and fast analytical techniques are required to track the positions of particles over time when in the wet state. Grazing-incidence small-angle X-ray scattering is a powerful, non-invasive probe of surface structure of wet colloidal systems.⁹⁵ It is a good candidate technique to characterize structure formation during the stratification process. Laser speckle imaging⁹⁶ has been demonstrated to provide information on heterogeneous particle dynamics in drying colloid films and paints with a spatial resolution of micrometres and a time resolution of milliseconds. In the future, it could be employed as a powerful complementary technique in the study of stratifying systems. Optical coherence tomography⁹⁷ has been recently demonstrated to acquire cross-sectional images of flow patterns within drying lyotropic liquid crystal droplets in a non-invasive way. (Polystyrene particles were used as tracers.) This technique could likewise be applied to the visualisation of colloidal stratification in the future.

- The influence of stratified structures on the resultant functional properties needs to be explored and evaluated, which will pave the way to new applications of stratified films.
- Three-layer stratified colloidal coatings, using a combination of sedimentation and diffusive phenomena, could be designed and demonstrated.
- The thickness of stratified layers in colloidal films should be measured and correlated with the relevant processing and materials parameters.
- The model of Sear and Warren⁸⁹ could be extended to lower values of size ratio, α , and to a higher volume fraction of large particles when their interactions cannot be neglected.
- Future modelling could extend the arguments of Sarkar and Tirumkudulu⁵¹ and specifically consider the effects of electric field that arise from differences in the diffusivity between charge colloids and their counter-ions in drying systems. Along these same lines, it is worth noting that concentration gradients in electrolytes (anions and cations) can arise in fast-evaporating systems, which in turn can drive the diffusion of charged colloids in that gradient, via the mechanism of diffusiophoresis.⁹⁸ This possibility should also be considered in stratifying colloidal systems.
- Although computational modelling that explicitly considers the solvent at the molecular level is time-intensive, it produces a more realistic result and should continue to be used in future work.
- Mixtures of colloids with polymers (or other molecules) in solution should be further investigated in experiments, in order to compare to recent models and simulations,^{88,89,92} which suggest that the polymer coils will stratify when both Pe and the concentration of the polymer solution are high, but can also display other behaviour depending on interactions with colloids.

- The effects of simultaneous crystallisation and stratification of colloids remain largely unexplored in theory, simulations and experiments, but this topic promises a rich variety of phenomena.
- There is a growing realisation that self-stratification mechanisms can be used to tailor the microstructure of heterogeneous materials.⁹⁹ There is a tremendous opportunity for applying designed materials in specific applications, ranging from membranes and batteries to photonics.

Conflicts of Interest

There are no conflicts to declare.

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References

- 1 S. T. Eckersley and B. J. Helmer, *J. Coatings Technol.*, 1997, **69**, 97–107.
- 2 H. M. van der Kooij and J. Sprakel, *Soft Matter*, 2015, **11**, 6353–6359.
- 3 R. Jovanović and M. A. Dubé, *J. Macromol. Sci. Part C Polym. Rev.*, 2004, **44**, 1–51.
- 4 S. A. Wissing and R. H. Müller, *Int. J. Cosmet. Sci.*, 2001, **23**, 233–243.
- 5 E. Tekin, P. J. Smith and U. S. Schubert, *Soft Matter*, 2008, **4**, 703–713.
- 6 M. A. Faers and R. Pontzen, *Pest Manag. Sci.*, 2008, **64**, 820–833.
- 7 M. A. Hampton, T. A. H. Nguyen, A. V. Nguyen, Z. P. Xu, L. Huang and V. Rudolph, *J. Colloid Interface Sci.*, 2012, **377**, 456–462.
- 8 P. Taylor, *Curr. Opin. Colloid Interface Sci.*, 2011, **16**, 326–334.
- 9 S. Obara and J. W. McGinity, *Int. J. Pharm.*, 1995, **126**, 1–10.
- 10 F. Lecomte, J. Siepmann, M. Walther, R. J. MacRae and R. Bodmeier, *Pharm. Res.*, 2004, **21**, 882–890.
- 11 A. F. Routh, *Reports Prog. Phys.*, 2013, **76**, 046603 (30pp).
- 12 H. M. van der Kooij, M. de Kool, J. van der Gucht and J. Sprakel, *Langmuir*, 2015, **31**, 4419–4428.
- 13 S. Jiang, A. Van Dyk, A. Maurice, J. Bohling, D. Fasano and S. Brownell, *Chem. Soc. Rev.*, 2017, **46**, 3792–3807.
- 14 M. Maric, W. van Bronswijk, S. W. Lewis, K. Pitts and D. E. Martin, *Forensic Sci. Int.*, 2013, **228**, 165–169.
- 15 I. Lee, J. Y. Park, S. Gim, K. Kim, S. H. Cho, C. S. Choi, S. Y. Song and J. L. Lee, *ACS Appl. Mater. Interfaces*, 2016, **8**, 3326–3332.
- 16 S. Chhajed, M. F. Schubert, J. K. Kim and E. F. Schubert, *Appl. Phys. Lett.*, 2008, **93**, 251108.
- 17 E. T. Yu and J. van de Lagemaat, *MRS Bull.*, 2011, **36**, 424–428.
- 18 Q. Xu, Y. Lv, C. Dong, T. S. Sreeprasad, A. Tian, H. Zhang, Y. Tang, Z. Yu and N.

- Li, *Nanoscale*, 2015, **7**, 10883–10895.
- 19 A. N. Zelikin, *ACS Nano*, 2010, **4**, 2494–2509.
- 20 K. C. Wood, H. F. Chuang, R. D. Batten, D. M. Lynn and P. T. Hammond, *Proc. Natl. Acad. Sci.*, 2006, **103**, 10207–10212.
- 21 C. Carelli, F. Dé, L. Boissonnet and C. Creton, *J. Adhes.*, 2007, **83**, 491–505.
- 22 A. B. López, J. C. de la Cal and J. M. Asua, *Polymer (Guildf.)*, 2017, **124**, 12–19.
- 23 J. S. Nunes, S. J. Bohórquez, M. Meeuwisse, D. Mestach and J. M. Asua, *Prog. Org. Coatings*, 2014, **77**, 1523–1530.
- 24 J. Sun, W. W. Gerberich and L. F. Francis, *J. Polym. Sci. Part B Polym. Phys.*, 2003, **41**, 1744–1761.
- 25 R. S. Gurney, D. Dupin, J. S. Nunes, K. Ouzineb, E. Siband, J. M. Asua, S. P. Armes and J. L. Keddie, *ACS Appl. Mater. Interfaces*, 2012, **4**, 5442–5452.
- 26 M. Okubo, A. Terada and Y. Kagawa, *J. Appl. Polym. Sci.*, 2003, **90**, 2027–2033.
- 27 Y. Yan, X. Liu and T. Wang, *Adv. Mater.*, 2017, **29**, 1601674.
- 28 US 8,921,477 B2, 2014.
- 29 B. G. Prevo and O. D. Velev, *Langmuir*, 2004, **20**, 2099–2107.
- 30 A. S. Dimitrov and K. Nagayama, *Langmuir*, 1996, **12**, 1303–1311.
- 31 A. B. López, J. C. de la Cal and J. M. Asua, *Langmuir*, 2016, **32**, 7459–7466.
- 32 M. Kiel, S. Mitzscherling, W. Leitenberger, S. Santer, B. Tiersch, T. K. Sievers, H. Möhwald and M. Bargheer, *Langmuir*, 2010, **26**, 18499–18502.
- 33 O. K. Lyngberg, C. P. Ng, V. Thiagarajan, L. E. Scriven and M. C. Flickinger, *Biotechnol. Prog.*, 2001, **17**, 1169–1179.
- 34 P. Kumnorkaew and J. F. Gilchrist, *Langmuir*, 2009, **25**, 6070–6075.
- 35 J. Wang, S. Ahl, Q. Li, M. Kreiter, T. Neumann, K. Burkert, W. Knoll and U. Jonas, *J. Mater. Chem.*, 2008, **18**, 981.
- 36 D. Wang and H. Möhwald, *Adv. Mater.*, 2004, **16**, 244–247.

- 37 U. Steiner, J. Klein, E. Eiser, A. Budkowski and L. J. Fetters, *Science* (80-.), 1992, **258**, 1126–1129.
- 38 M. Geoghegan, R. A. L. Jones, R. S. Payne, P. Sakellariou, A. S. Clough and J. Penfold, *Polymer (Guildf)*., 1994, **35**, 2019–2027.
- 39 M. W. Urban, *Curr. Opin. Colloid Interface Sci.*, 2014, **19**, 66–75.
- 40 K. Satoh and M. W. Urban, *Prog. Org. Coatings*, 1996, **29**, 195–199.
- 41 Z. Liu, Y. Zhao, J. Zhou and X. Yuan, *Colloid Polym. Sci.*, 2012, **290**, 203–211.
- 42 A. Misra and M. W. Urban, *Macromol. Rapid Commun.*, 2010, **31**, 119–127.
- 43 R. E. Trueman, E. Lago Domingues, S. N. Emmett, M. W. Murray and A. F. Routh, *J. Colloid Interface Sci.*, 2012, **377**, 207–212.
- 44 E. Gonzalez, M. Paulis, M. J. Barandiaran and J. L. Keddie, *Langmuir*, 2013, **29**, 2044–2053.
- 45 A. F. Routh and W. B. Russel, *Ind. Eng. Chem. Res.*, 2001, **40**, 4302–4308.
- 46 A. F. Routh and W. B. Zimmerman, *Chem. Eng. Sci.*, 2004, **59**, 2961–2968.
- 47 A. Gromer, M. Nassar, F. Thalmann, P. Hébraud and Y. Holl, *Langmuir*, 2015, **31**, 10983–10994.
- 48 A. Gromer, F. Thalmann, P. Hébraud and Y. Holl, *Langmuir*, 2017, **33**, 561–572.
- 49 Y. Kameya, *J. Nanoparticle Res.*, 2017, **19**, 214 (10pp).
- 50 S. Cheng and G. S. Grest, *J. Chem. Phys.*, 2013, **138**, 64701.
- 51 A. Sarkar and M. S. Tirumkudulu, *Langmuir*, 2009, **25**, 4945–4953.
- 52 S. Kim, K. Hyun, Y. S. Kim, B. Struth, C. Clasen and K. H. Ahn, *Langmuir*, 2013, **29**, 10059–10065.
- 53 Y. Ma, H. T. Davis and L. E. Scriven, *Prog. Org. Coatings*, 2005, **52**, 46–62.
- 54 C. M. Cardinal, Y. D. Jung, K. H. Ahn and L. F. Francis, *AIChE J.*, 2010, **56**, 2769–2780.
- 55 D. K. Makepeace, A. Fortini, A. Markov, P. Locatelli, C. Lindsay, S. Moorhouse, R. Lind, R. P. Sear, J. L. Keddie, *Soft Matter*, 2017, **13**, 6969–6980.

- 56 H. Luo, C. M. Cardinal, L. E. Scriven and L. F. Francis, *Langmuir*, 2008, **24**, 5552–5561.
- 57 R. E. Trueman, E. Lago Domingues, S. N. Emmett, M. W. Murray, J. L. Keddie and A. F. Routh, *Langmuir*, 2012, **28**, 3420–3428.
- 58 H. Luo, L. E. Scriven and L. F. Francis, *J. Colloid Interface Sci.*, 2007, **316**, 500–509.
- 59 F. Buss, C. C. Roberts, K. S. Crawford, K. Peters and L. F. Francis, *J. Colloid Interface Sci.*, 2011, **359**, 112–120.
- 60 S. H. Im and O. O. Park, *Langmuir*, 2002, **18**, 9642–9646.
- 61 J.-P. Gorce, D. Bovey, P. J. McDonald, P. Palasz, D. Taylor and J. L. Keddie, *Eur. Phys. J. E. Soft Matter*, 2002, **8**, 421–429.
- 62 P. Ekanayake, P. J. McDonald and J. L. Keddie, *Eur. Phys. J. Spec. Top.*, 2009, **166**, 21–27.
- 63 J. A. Kimber, M. Gerst and S. G. Kazarian, *Langmuir*, 2014, **30**, 13588–13595.
- 64 S. Baesch, P. Scharfer, W. Schabel and L. Francis, *J. Compos. Mater.*, 2017, **51**, 3391–3403.
- 65 S. Baesch, K. Price, P. Scharfer, L. Francis and W. Schabel, *Chem. Eng. Process. Process Intensif.*, 2018, **123**, 138–147.
- 66 O. Cusola, S. Kivistö, S. Vierros, P. Batys, M. Ago, B. L. Tardy, L. G. Greca, M. B. Roncero, M. Sammalkorpi and O. J. Rojas, *Langmuir*, 2018, [acs.langmuir.8b00650](https://doi.org/10.1021/acs.langmuir.8b00650).
- 67 S. Erkselius, L. Wadsö and O. J. Karlsson, *J. Colloid Interface Sci.*, 2008, **317**, 83–95.
- 68 A.-C. Grillet, S. Brunel, Y. Chevalier, S. Usoni, V. Ansanay-Alex and J. Allemand, *Polym. Int.*, 2004, **53**, 569–575.
- 69 A. K. Atmuri, S. R. Bhatia and A. F. Routh, *Langmuir*, 2012, **28**, 2652–2658.
- 70 Q. Liao, L. Chen, X. Qu and X. Jin, *J. Colloid Interface Sci.*, 2000, **227**, 84–94.
- 71 A. Sand, M. Toivakka and T. Hjelt, *J. Colloid Interface Sci.*, 2009, **332**, 394–401.
- 72 J. Sun, B. V. Velamakanni, W. W. Gerberich and L. F. Francis, *J. Colloid Interface Sci.*, 2004, **280**, 387–399.

- 73 I. Nikiforow, J. Adams, A. M. König, A. Langhoff, K. Pohl, A. Turshatov and D. Johannsmann, *Langmuir*, 2010, **26**, 13162–13167.
- 74 H. Römermann, A. Müller, K. Bomhardt, O. Höfft, M. Bellmann, W. Viöl and D. Johannsmann, *J. Phys. D Appl. Phys. Press* [https](https://doi.org/10.1088/1361-6463/aa9b0a), 2018, **51**, 215205.
- 75 A. Fortini, I. Martín-Fabiani, J. L. De La Haye, P.-Y. Dugas, M. Lansalot, F. D’Agosto, E. Bourgeat-Lami, J. L. Keddie and R. P. Sear, *Phys. Rev. Lett.*, 2016, **116**, 118301.
- 76 R. Tatsumi, T. Iwao, O. Koike, Y. Yamaguchi and Y. Tsuji, *Appl. Phys. Lett.*, 2018, **112**, 53702.
- 77 A. Fortini and R. P. Sear, *Langmuir*, 2017, **33**, 4796–4805.
- 78 M. P. Howard, A. Nikoubashman and A. Z. Panagiotopoulos, *Langmuir*, 2017, **33**, 3685–3693.
- 79 I. Martín-Fabiani, A. Fortini, J. Lesage de la Haye, M. L. Koh, S. E. Taylor, E. Bourgeat-Lami, M. Lansalot, F. D’Agosto, R. P. Sear and J. L. Keddie, *ACS Appl. Mater. Interfaces*, 2016, **8**, 34755–34761.
- 80 I. Martín-Fabiani, A. Fortini, J. Lesage de la Haye, M. L. Koh, S. E. Taylor, E. Bourgeat-Lami, M. Lansalot, F. D’Agosto, R. P. Sear and J. L. Keddie, *ACS Appl. Mater. Interfaces*, 2016, **8**, 34755–34761.
- 81 J. Zhou, Y. Jiang and M. Doi, *Phys. Rev. Lett.*, 2017, **118**, 108002.
- 82 A. Tzitzinou, J. L. Keddie, J. M. Geurts, A. C. I. A. Peters and R. Satguru, *Macromolecules*, 2000, **33**, 2695–2708.
- 83 T. Tashima and M. Yamamura, *J. Coatings Technol. Res.*, 2017, **14**, 965–970.
- 84 S. Lim, K. H. Ahn and M. Yamamura, *Langmuir*, 2013, **29**, 8233–8244.
- 85 E. Pérez and J. Lang, *Langmuir*, 1996, **12**, 3180–3187.
- 86 X. Liu, W. Liu, A. J. Carr, D. Santiago Vazquez, D. Nykypanchuk, P. W. Majewski, A. F. Routh and S. R. Bhatia, *J. Colloid Interface Sci.*, 2018, **515**, 70–77.
- 87 A. Utgenannt, R. Maspero, A. Fortini, R. Turner, M. Florescu, C. Jeynes, A. G. Kanaras, O. L. Muskens, R. P. Sear and J. L. Keddie, *ACS Nano*, 2016, **10**, 2232–

- 2242.
- 88 M. P. Howard, A. Nikoubashman and A. Z. Panagiotopoulos, *Langmuir*, 2017, **33**, 11390–11398.
- 89 R. P. Sear and P. B. Warren, *Phys. Rev. E*, 2017, **96**, 62602.
- 90 R. P. Sear, *J. Chem. Phys.*, 2018, **148**, 134909.
- 91 M. Wang and J. F. Brady, *Soft Matter*, 2017, **13**, 8156–8170.
- 92 S. Cheng and G. S. Grest, *ACS Macro Lett.*, 2016, **5**, 694–698.
- 93 A. Statt, M. P. Howard and A. Z. Panagiotopoulos, *arXiv Prepr. arXiv1804.00066*.
- 94 Y. Tang, G. S. Grest and S. Cheng, *Langmuir*, 2018, **34**, 7161–7170.
- 95 S. V Roth, G. Herzog, V. Körstgens, A. Buffet, M. Schwartzkopf, J. Perlich, M. M. Abul Kashem, R. Döhrmann, R. Gehrke, A. Rothkirch, K. Stassig, W. Wurth, G. Benecke, C. Li, P. Fratzl, M. Rawolle and P. Müller-Buschbaum, *J. Phys. Condens. Matter*, 2011, **23**, 254208.
- 96 H. M. van der Kooij, R. Fokkink, J. van der Gucht and J. Sprakel, *Sci. Rep.*, 2016, **6**, 34383.
- 97 Z. S. Davidson, Y. Huang, A. Gross, A. Martinez, T. Still, C. Zhou, P. J. Collings, R. D. Kamien and A. G. Yodh, *Nat. Commun.*, 2017, **8**, 15642.
- 98 D. Velegol, A. Garg, R. Guha, A. Kar and M. Kumar, *Soft Matter*, 2016, **12**, 4686–4703.
- 99 J. Lee, S. Sung, Y. Kim, J. D. Park and K. H. Ahn, *Curr. Opin. Chem. Eng.*, 2017, **16**, 16–22.
- 100 S. Di Risio and N. Yan, *Colloids Surfaces A Physicochem. Eng. Asp.*, 2006, **289**, 65–74.
- 101 O. Cusola, S. Kivistö, S. Vierros, P. Batys, M. Ago, B. L. Tardy, L. G. Greca, M. B. Roncero, M. Sammalkorpi and O. J. Rojas, *Langmuir*, 2018, acs.langmuir.8b00650.
- 102 S. Baesch, K. Price, P. Scharfer, L. F. Francis and W. Schabel, *Chem. Eng. Process. Process Intensif.*, 2018, **123**, 138–147.

- 103 I. Ludwig, W. Schabel, M. Kind, J.-C. Castaing and P. Ferlin, *AIChE J.*, 2007, **53**, 549–560.
- 104 H. Hagiwara, W. J. Suszynski and L. F. Francis, *J. Coatings Technol. Res.*, 2014, **11**, 11–17.
- 105 E. Ciampi and P. J. McDonald, *Macromolecules*, 2003, **36**, 8398–8405.
- 106 J. Perlich, M. Schwartzkopf, V. Körstgens, D. Erb, J. F. H. Risch, P. Müller-Buschbaum, R. Röhlberger, S. V. Roth and R. Gehrke, *Phys. status solidi - Rapid Res. Lett.*, 2012, **6**, 253–255.
- 107 X. Chen, S. Fischer and Y. Men, *Langmuir*, 2011, **27**, 12807–12814.
- 108 S. Kim, K. Hyun, B. Struth, K. H. Ahn and C. Clasen, *Macromolecules*, 2016, **49**, 9068–9079.
- 109 J. Li, B. Cabane, M. Sztucki, J. Gummel and L. Goehring, *Langmuir*, 2012, **28**, 200–208.

Symbols

D	Stokes-Einstein self-diffusion coefficient for a colloidal particle in a liquid; derived for a dilute suspension in which the particle does not interact with its neighbours
E	evaporation rate of the continuous phase, expressed as the velocity at which the top surface descends
H	initial thickness of a wet film
N_S	sedimentation number
Pe	Péclet number, which depends on the ratio of the evaporation rate to the self- diffusion of the particles. (Subscript S and L used to designate small and large particles, respectively, in a mixture.)
t^*	reduced drying time found by dividing by the total drying time (H/E).
T	absolute temperature
U	diffusiophoretic velocity of particles
U_S	sedimentation velocity
v_{jam}	downward velocity of the layer of jammed small particles at the top of a film
α	size ratio of large to small particles in a colloidal mixture
ϕ_s	volume fraction of small particles in the original colloidal suspension prior to drying
ϕ_{jam}	volume fraction of particles at which jamming occurs
μ	viscosity of the continuous phase in a colloidal suspension

TABLES

Table 1. Experimental techniques used to characterise stratification

Method	Demonstrated for wet systems?	Demonstrated for systems with one type of particle?	Demonstrated for systems with two types of particles?	Reference(s)
Atomic force microscopy	N	Y	Y	55,57,79,86,100
Scanning electron microscopy (SEM)	N	Y	Y	55,57 ¹⁰¹
Cryogenic SEM	Y (ice)	Y	Y	11,53–59 ¹⁰²
Fluorescent and confocal microscopy	N	Y	Y	73,75,79,84
Optical microscopy	N	Y	Y	68
Photoluminescence	N	Y	Y	83
Infrared spectroscopy	N	Y	Y	40,63
Raman spectroscopy	Y	Y	Y	65,74,103,104
NMR profiling/imaging	Y	Y	Y	57,61,62,105
X-ray scattering	Y	Y	Y	52,106–109

Table 2. Parameters used in stratification experiments and simulations on binary colloid films

Binary System	α	Pe_s	ϕ_s	Reference
Polymer particles	1 – 4	181.5	0.15 - 0.25	1
Polymer particles	1.4 - 4.2	1.0 - 2.1	0.032 - 0.119	23
Polymer particles	4.3, 5.1	2.4 - 2.6	0.07 - 0.165	25
Polymer particles	5.5	10.8 - 21.6	0.035 - 0.164	28
Polymer particles	5.3 - 10.6	3.4 - 6.8	0.029 - 0.069	⁵³
Silica particles	5	14.9	0.1	⁵⁴
Polymer particles	2, 7	2.2, 7.4	0.004 - 0.16	⁵⁵
Silica and polymer particles	3.7 - 78.6	10.2 – 219	0.0026 - 0.0125	⁵⁶
Alumina and polymer particles	10	80	0.003	
Antimony-doped tin oxide and polymer particles	18	44.5	0.003	
Polymer particles	1.2 - 5.0	0.12 - 4.5	0.0625 - 0.225	⁵⁷
Silica particles	3.3	11	0.02	⁵⁹
Silica particles in water-soluble polymer solution	3.3	Not known	0.02	
Polymer particles	1	0.16 - 3.5	0.165	⁷³
Polymer particles	7	9.9	0.0028 - 0.595	⁷⁵
Spherical particles (simulation)	2, 4	0.075-50	0.05	⁷⁶

Spherical particles (simulation)	2-8	0.15-15	0.03	⁷⁸
Polymer particles	4.1 - 7.1	8.4 - 14.7	0.07 - 0.37	⁷⁹
Polymer particles	6	1.6	0.05 - 0.22	⁸²
Polymer particles in water-soluble polymer solution	2, 80	Not known	0.004	⁸³
Polymer particles in water-soluble polymer solution	81	4050-6940	0.004	⁸⁴
Gold nanoparticles and polymer particles	14 - 32	0.14 - 77.5	0.000141	⁸⁷
Polymer and silica particles	2.1-11.3	0.33-0.6	0.0091-0.011	⁸⁶
Lignin	Polydisperse: Up to <i>ca.</i> 40	1 - 250	0.04	¹⁰¹