Stratification of mixtures in evaporating liquid films occurs only for a range of volume fractions of the smaller component

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I model the drying of a liquid film containing small and big colloid particles. Fortini et al. [A. Fortini et al., Phys. Rev. Lett. 116, 118301 (2016)] studied these films with both computer simulation and experiment. They found that at the end of drying the mixture had stratified with a layer of the smaller particles on top of the big particles. I develop a simple model for this process. The model has two ingredients: arrest of the diffusion of the particles at high density, and diffusiophoretic motion of the big particles due to gradients in the volume fraction of the small particles. The model predicts that stratification only occurs over a range of initial volume fractions of the smaller colloidal species. Above and below this range the downward diffusiophoretic motion of the big particles is too slow to remove the big particles from the top of the film, and so there is no stratification. In agreement with earlier work, the model also predicts that large Péclet numbers for drying are needed to see stratification.
INTRODUCTION

Fortini et al.\(^1\) studied the drying of a liquid film containing a mixture of large and small colloidal particles. They found spontaneous stratification in the final dry film, with a layer enriched in the small particles on top of a layer with the larger particles. This is a novel out-of-equilibrium self-organisation mechanism, and potentially has applications. For example, by using small and large particles with different properties, the properties of the top and bottom surfaces of the final film, could be independently controlled.

Not all mixtures stratify\(^2\). For example, both Martín-Fabiani et al.\(^3\), and Makepeace et al.\(^4\) studied systems with high initial volume fractions, and found no stratification. Motivated by this observation, I develop a simple model to predict which mixtures of small and large particles will stratify, and which will not. I combine earlier work by Sear and Warren\(^5\) on modelling dilute mixtures in drying films, with Okuzono et al.\(^6\)’s work on dynamical arrest in drying solutions of polymers. Okuzono et al.\(^6\) developed a simple model for a system where the dynamics arrests at high concentrations. My combined model makes simple analytical predictions for which films should stratify, and which should remain homogeneous.

I consider a thin liquid film of initial height \(H\) that contains a colloidal dispersion. This dispersion is a mixture of colloidal particles with a small radius, \(R_{\text{small}}\), and particles with the much larger radius, \(R_{\text{big}}\). The liquid is volatile, and as it evaporates the liquid/air interface descends at the velocity \(v_{\text{ev}}\). My model includes the effect of solvent flow, which Sear and Warren\(^5\) have shown to be important, but it has limitations. I can only consider the limit of a large size ratio, \(R_{\text{big}}/R_{\text{small}} \gg 1\), and dilute concentrations of large particles. See either Keddie and Routh’s book\(^7\) or Routh’s review\(^8\) for an introduction to drying films of colloidal particles, and their applications.

If evaporation is slow, then I assume that the colloidal mixture will slowly compress until it jams or crystallises, at a volume fraction of around 0.64\(^9\)\(^–\)12. However, fast evaporation velocities cause the particles to accumulate immediately beneath the descending interface\(^2,7\)\(^,\)8\(^,\)13,14. Here, for the small particles, ‘fast’ means a film evaporation Péclet number larger than one. The Péclet number for the smaller species is defined by

\[
\text{Pe}_{\text{film}} = \frac{v_{\text{ev}} H}{D_{\text{small}}} \tag{1}
\]

where \(D_{\text{small}}\) is the diffusion constant of the smaller species.
Drying suspensions of colloidal particles have been studied extensively at large Péclet numbers\textsuperscript{7,8}, and the accumulation of particles below the descending water/air interface is well understood. As large and small particles have different Péclet numbers, rapid drying always creates differential accumulation in mixtures of particles. A number of studies\textsuperscript{2,14–18} prior to that of Fortini et al.\textsuperscript{1} considered this differential accumulation and the resulting stratification.

The innovation of Fortini and co-workers\textsuperscript{1} was to show that stratification can be obtained by diffusiophoretic motion of the larger species. Diffusiophoretic motion is, by definition, motion of one species due to a gradient in concentration of another species\textsuperscript{19–27}. Here, diffusiophoretic motion is motion of the large colloidal particles in a concentration gradient of the small particles. This concentration gradient is produced by the descending water/air interface. Since the work of Fortini and co-workers, there have been a number of computer simulation, modelling and experimental studies of the drying of liquid films that contain mixtures of small and big particles. These studies have all observed stratification\textsuperscript{3–5,28–32}. The results of recent experimental work is mostly consistent with diffusiophoretic driven stratification\textsuperscript{3,4,32}, although the simple models used in theory and simulation clearly do not capture all the behaviour seen in experiment.

Within the model studied here, stratification occurs when the small particles accumulate, and then jam at high densities, under such conditions that this jammed layer of small particles excludes the big particles. This exclusion happens when the downward diffusiophoretic motion of the big particles is faster than the downward advance of the jammed layer of small particles. I have illustrated this in Fig. 1. As the diffusiophoretic velocity is proportional to the gradient in concentration of the small particles, this is equivalent to saying that stratification requires large enough concentration gradients below the jammed layer of small particles.

In the next section I describe my adaptation of Okuzono et al.’s model to describe the behaviour of the small colloidal particles. In the third and fourth sections, I derive expressions for the onset of jamming, and for diffusiophoresis, respectively. Results are in the fifth section, while the sixth section is a conclusion.
FIG. 1. Schematic illustrating what needs to happen for stratification to occur. As the water/air interface (black line) descends at speed $v_{ev}$, the small particles (red) accumulate beneath it until they are so dense that they jam. A growing jammed layer of small particles then descends at speed $v_{jam}$. In front of this jammed layer there is concentration gradient that drives diffusiophoretic motion of big particles (dark blue) at speed $U$. If $U > v_{jam}$ then big particles are excluded from the jammed layer of small particles, and there is stratification.

II. OKUZONO ET AL.’S MODEL APPLIED TO A ONE-COMPONENT COLLOIDAL DISPERSION IN A DRYING FILM

As a colloidal dispersion of hard spheres is compressed to higher and higher concentrations, the viscosity increases, and the diffusion of the particles slows\(^\text{10}\). Then one of two things happen: either the system crystallises\(^\text{11,12,33,34}\), at which point the dynamics arrest, or the volume fraction reaches values around 0.64\(^\text{9,10,35}\), at which point the system is a glass, because the particles have been pushed into contact and so their dynamics are again arrested. Here, for simplicity I follow Okuzono et al. and assume that the dynamics arrests and the system becomes a glass, at a threshold density. I set the threshold volume fraction to be $\phi_{jam} = 0.64$, and refer to it as jamming. When the particles are jammed I assume that the descending water interface cannot compress them further.

In Okuzono et al.’s\(^\text{6}\) model their polymer is an ideal solution up to a gelling concentration, at which point it becomes solid. They used this model to understand ‘skin’ formation in drying films of polymer solutions. This skin is a gelled layer that forms at the top of the film, where the concentration is highest. The film is assumed to be infinite and uniform in
the $xy$ plane, with the water/air interface moving down along the $z$ axis.

In my colloidal version of Okuzono et al.’s model, the small colloid is a diffusing ideal solution when its local volume fraction $\phi_{\text{small}}(z) < \phi_{\text{jam}}$, and is an incompressible solid at $\phi_{\text{small}}(z) = \phi_{\text{jam}}$. Therefore, the volume fraction profile of the small colloid $\phi_{\text{small}}(z,t)$ obeys the diffusion equation

$$\frac{\partial \phi_{\text{small}}}{\partial t} = \frac{\partial}{\partial z} \left( D(\phi_{\text{small}}) \frac{\partial \phi_{\text{small}}}{\partial z} \right)$$

(2)

with

$$D(\phi_{\text{small}}) = \begin{cases} D_{\text{small}} & \phi_{\text{small}} < \phi_{\text{jam}} \\ D_{\text{skin}} \to \infty & \phi_{\text{small}} > \phi_{\text{jam}} \end{cases}$$

(3)

The large $D_{\text{skin}}$ ensures that the ‘skin’ layer has a uniform volume fraction equal to $\phi_{\text{jam}}$, while the constant diffusion constant $D_{\text{small}}$ below $\phi_{\text{jam}}$ means that there Eq. (2) reduces to the diffusion equation for an ideal gas.

The boundary conditions are as follows. We have two walls, at the top and bottom. The bottom wall is fixed at $z = 0$, and models the substrate the film is on. The boundary condition at the bottom wall is zero flux.

The top wall is the water/air interface. This interface starts at $z_{\text{int}}(t = 0) = H$ and then descends at the fixed evaporation speed $v_{\text{ev}}$. The position of the interface at time $t$ is given by

$$z_{\text{int}}(t) = H - v_{\text{ev}}t = H(1 - t^*)H$$

(4)

where we have defined the reduced time

$$t^* = \frac{v_{\text{ev}}t}{H} \quad (\leq 1)$$

(5)

The boundary condition at the descending top interface is again zero flux. The final boundary condition is an initial condition, i.e., it is the initial state of the state. At $t = 0$, the small colloid is uniformly distributed with a constant volume fraction $\phi_0$.

A. Example results for accumulation and jamming during drying

In Fig. 2, I have plotted concentration profiles at a number of different times during drying. This is for a film with $P_{\text{film}} = 10 \gg 1$. As the water/air interface descends, the small particles accumulate immediately below this interface. During drying, the concentration will reach $\phi_{\text{jam}}$, and this occurs first where the concentration is largest, which is at the descending...
FIG. 2. Plots of the volume fraction as a function of height, for a single-component dispersion of the small colloid. The profiles are at times $t^* = 0$ (red), 0.044 (green), 0.22 (blue), 0.40 (yellow), 0.58 (brown) and 0.76 (black). $P_{e\text{film}} = 10$, the initial concentration $\phi_0 = 0.15$, and $\phi_{\text{jam}} = 0.64$. Profiles are obtained by numerically solving the diffusion PDE, with $D_{\text{skin}}/D_{\text{small}} = 1000$.

interface. So a jammed layer starts at the top interface and grows in thickness during drying. As it does so it is pushed down until it reaches the bottom, at which time the dynamics in our simple model stops.

We can compare the profiles of our simple model, which is an ideal solution up the jamming concentration, with the results of computer simulations$^{1,29,30}$ and density-functional theory$^{29,30}$, which include excluded-volume interactions at all concentrations. We note that our model underestimates the width of the accumulation zone, compare our Fig. 2, with Fig. 2 of Fortini et al.$^1$, and with Fig. 4 of Howard et al.$^{29}$. As we will see in the next section, within our model the accumulation zone has a width of $D_{\text{small}}/v_{\text{ev}}$. Whereas when interactions are taken into account the profiles are a few times wider than this.

III. APPROXIMATE THEORY FOR JAMMING AND FOR THE VOLUME-FRACTION GRADIENTS

Here I develop an approximate theory for the onset of jamming in the $P_{e\text{film}} \gg 1$ regime. As in the previous section I assume that the volume fraction of the big particles is so small that it does not affect the small particles, which can be treated as a one-component system.
**A. Fedorchenko and Chernov solution for a diffusing ideal gas below a descending interface**

As in the earlier work of Sear and Warren\(^5\), I will use the exact solution of Fedorchenko and Chernov\(^5,36,37\), for a diffusing ideal gas in a film of infinite thickness \((H \to \infty)\). As discussed by Sear and Warren\(^5\), this solution can be used for finite \(H\), so long as the Péclet number satisfies \(\text{Pe}_{\text{film}} \gg 1\). After a short time \(t^* = 1/\text{Pe}_{\text{film}}\), an accumulation zone is established below the interface. In that regime \((t^*\text{Pe}_{\text{film}} \gg 1)\), the solution of Fedorchenko and Chernov\(^36\) (given in Appendix C of Sear and Warren\(^5\)) simplifies to

\[
\phi_{\text{small}}(z, t) \approx \phi_0 \left( 1 + \text{Pe}_{\text{film}}t^* \exp \left[ \frac{|z - z_{\text{int}}|}{D_{\text{small}}/v_{\text{ev}}} \right] \right)
\]

(6)

At the surface \(z = z_{\text{int}}\), and we have

\[
\phi_{\text{small}}(z_{\text{int}}, t^*) = \phi_0 (1 + \text{Pe}_{\text{film}}t^*)
\]

(7)

These equations only hold so long as \(\phi_{\text{small}} < \phi_{\text{jam}}\), beyond that jamming occurs. Note that, see Eq. (6), the accumulation zone has a constant width \(D_{\text{small}}/v_{\text{ev}}\), and the maximum concentration is at the interface and increases linearly with time.

**B. Jamming**

Jamming starts first at the surface as that is where \(\phi_{\text{small}}\) is highest. It starts when the volume fraction there reaches the jamming volume fraction:

\[
\phi_{\text{small}}(z_{\text{int}}, t^*_{\text{jam}}) = \phi_{\text{jam}}
\]

(8)

which defines the reduced evaporation time at which jamming starts, \(t^*_{\text{jam}}\). If we use the simple approximation of Eq. (7), which is valid for \(t^*\text{Pe}_{\text{film}} \gg 1\), we obtain an estimate for the time at which jamming starts

\[
t^*_{\text{jam}} \approx \frac{\phi_{\text{jam}}/\phi_0 - 1}{\text{Pe}_{\text{film}}}
\]

(9)

Drying films always jam. Evaporation increases the volume fraction until it hits \(\phi_{\text{jam}}\). However, to observe stratification, jamming is not sufficient, we need the jammed layer to be preceded by an accumulation zone where there is a steep concentration gradient.
This concentration gradient needs both a time of order $\frac{1}{Pe_{\text{film}}}$ to become established and space to be established, a reduced height $z/H$ of $\frac{1}{Pe_{\text{film}}}$ is enough. Thus, we only have a jammed layer preceded by a steady-state concentration profile unaffected by the bottom of the film, when

$$t_{\text{jam}}^* < 1 - \frac{1}{Pe_{\text{film}}}$$

Using, Eq. (9), this becomes

$$\phi_0 > \frac{\phi_{\text{jam}}}{Pe_{\text{film}}}$$

which must be satisfied for the jammed layer to appear early enough.

Once a jammed layer has appeared, we can use simple mass conservation to obtain the steady-state downward velocity of the jamming front, $v_{\text{jam}}$. The flux of small colloidal particles into the jammed region is just $\phi_0 v_{\text{jam}}$, while the rate of growth of the total volume fraction of small particles in the jammed region is $\phi_{\text{jam}} (v_{\text{jam}} - v_{\text{ev}})$, where $v_{\text{jam}} - v_{\text{ev}}$ is the velocity at which the height of the jammed region is increasing. If we just equate the flux to the growth rate, and rearrange, we get

$$v_{\text{jam}} \simeq \frac{v_{\text{ev}}}{1 - \phi_0/\phi_{\text{jam}}}$$

The position of the jamming front is then

$$\frac{z_{\text{jam}}(t^*)}{H} \simeq 1 - t^* - (t^* - t_{\text{jam}}^*) \left( \frac{v_{\text{jam}}}{v_{\text{ev}}} - 1 \right) \quad t^* > t_{\text{jam}}^*$$

From mass conservation, the jamming front reaches the bottom at time

$$t_{\text{end}}^* \simeq 1 - \frac{\phi_0}{\phi_{\text{jam}}}$$

defined by $z_{\text{jam}}(t_{\text{end}}^*) = 0$, and we neglected a term of order $1/Pe_{\text{film}}$. The accumulation zone will hit the bottom approximately $1/Pe_{\text{film}}$ earlier.

Once a jammed layer has formed the maximum gradient is at the front, at $z = z_{\text{jam}}$. At steady state, this maximum gradient is, see Appendix A,

$$\max \left( \frac{\partial \phi_{\text{small}}(z, t)}{\partial z} \right) = \frac{v_{\text{jam}} (\phi_{\text{jam}} - \phi_0)}{D_{\text{small}}}$$

1. Comparison of predicted gradients with experiment

Using Eq. (12) the maximum gradient can also be written as

$$\max \left( \frac{\partial \phi_{\text{small}}(z, t)}{\partial z} \right) = Pe_{\text{film}} H \frac{\phi_{\text{jam}} - \phi_0}{1 - \phi_0/\phi_{\text{jam}}}$$
At constant initial film height and initial volume fraction, my simple model predicts that the gradients in front of the jammed region scale linearly with Pe_{film}. This is close to the Pe_{film}^{0.8} dependence found in experiments by Ekanyake et al.\textsuperscript{38}. Ekanyake et al.\textsuperscript{38} varied Pe_{film} at constant $H$ by increasing $v_{ev}$, and they report that the gradient is measured below a ‘packed layer’, so the experiments are in comparable conditions to those assumed by the model. The difference between linear scaling, and scaling as the power 0.8 is small, so we have semiquantitative agreement here. Ekanyake et al.\textsuperscript{38} compare with the model of Routh and Zimmerman\textsuperscript{13}, which predicts a Pe_{film}^{1/2} scaling. As the experimental scaling lies in between the two predictions, it is possible that combining ideas from the two models could give a model in quantitative agreement with experiment, but we leave this to future work.

IV. DIFFUSIOPHORESIS IN A DRYING FILM

Having calculated the gradients in the volume fraction of the small particles, I now determine the diffusiophoretic velocities of the larger colloidal species. The required expression for the diffusiophoretic velocity $U$ in a suspension of much smaller particles that are excluded from a layer of radius $R_{small}$ from the larger particle’s surface is

$$U(z,t) = -\frac{R_{small}^2 k T}{2\eta} \nabla \rho_{small}$$

(17)

where $\rho_{small}$ is number density of the smaller colloid, and $\eta$ is the viscosity. This expression is well known\textsuperscript{19,22}, and was used by Sear and Warren\textsuperscript{5} for the Asakura-Oosawa ideal polymer model\textsuperscript{39}, although they were not the first to derive it\textsuperscript{19,22}. Here we use this expression not for an ideal polymer but for hard particles. The two models differ only in the interactions between the small spheres. Thus, Eq. (17) will be a good approximation except at high volume fractions of the small colloidal particles.

Using $\phi_{small} = (4\pi/3) R_{small}^3 \rho_{small}$ and $D_{small} = k_B T/(6\pi \eta R_{small})$, we can rewrite Eq. (17) as

$$U(z,t) = -\frac{9}{4} D_{small} \nabla \phi_{small}$$

(18)

This is a general expression, we just need the gradient in the drying film.

Before jamming, the gradient is the derivative of Eq. (6), which gives

$$U(z < z_{int}, t^* < t_{jam}^*) = \frac{9\phi_0 Pe_{film} t^* v_{ev}}{4} \exp \left[ -\frac{|z - z_{int}|}{D_{small}/v_{ev}} \right]$$

(19)
In the presence of a jammed layer, the gradient in the part of the film below the jamming front is given by Eq. (A2). So, the diffusiophoretic speed in the dilute phase is

\[ U(z < z_{jam}, t^* > t_{jam}^*) = \frac{9(\phi_{jam} - \phi_0)v_{jam}}{4} \exp\left[-\frac{|z - z_{jam}|}{D_{small}/v_{jam}}\right] \]

which can also be written as

\[ U(z < z_{jam}, t^* > t_{jam}^*) = \frac{9\phi_{jam}v_{ev}}{4} \exp\left[-\frac{|z - z_{jam}|}{D_{small}/v_{jam}}\right] \]

if we use Eq. (12) for \( v_{jam} \). The maximum diffusiophoretic velocity in front of a jammed layer is always simply \( (9/4)\phi_{jam}v_{ev} \), in our simple model. This is because as \( \phi_0 \) increases, the increasing \( v_{jam} \) tends to increase the steepness of the gradient, but this is exactly canceled by the decreasing total concentration difference across the accumulation region: \( \phi_{jam} - \phi_0 \).

Following Sear and Warren, I assume that the diffusion of the large particles is negligible. Then the dynamics of the large particles is just downward motion at speed \( v_{big}(z, t) \), which is just diffusiophoretic motion in the presence of a gradient of the small particles, or motion at \( v_{ev} \) for particles at the interface or trapped in the jammed state. Thus, when there is a jammed layer, the speed of a large colloid is

\[ v_{big}(z, t^* > t_{jam}^*) = \begin{cases} -v_{ev} & (z > z_{jam}) \\ -U & (z < z_{jam}) \end{cases} \]

V. RESULTS

Now that I have expressions for both when jamming occurs, and for the diffusiophoretic velocity, I can make predictions for the behaviour of the large colloidal particles. I neglect diffusion of the large colloidal particles. Then the position of a large particle \( z_{big} \) is simply obtained by integrating \( dz_{big}/dt = v_{big} \), with the initial condition being the initial position of the particle in the film.

In Fig. 3, I have plotted the trajectories during drying of a set of particles with equispaced initial positions in the film. This is done for three values of the initial volume fraction of the smaller colloid. In Fig. 3(a) the film has a small initial volume fraction of the small
FIG. 3. Trajectories $z_{\text{big}}(t)$ (red curves) of tracer large colloidal particles as a function of reduced time $t^*$. (a), (b) and (c) are for initial volume fractions $\phi_0 = 0.05, 0.15$ and 0.30, respectively. In each panel two of the trajectories have arrows to indicate the direction of the movement. The position of the top interface, $z_{\text{int}}$, is shown in black. The jammed region is shaded in cyan, and the yellow line is the jamming front at $z_{\text{jam}}$. Calculations are for $Pe_{\text{film}} = 10$ and

particles. Then the volume fraction of small particles at the interface only becomes large when drying is almost over, and the water/air interface is close to the bottom surface. So no large gradients develop and there is no stratification with a layer of small on top of a
Note the convergence of the trajectories of the big particles at the top interface, the slow moving big particles accumulate at the top. By neglecting diffusion of the big particles we have effectively set their Péclet number to be infinite. Trueman et al.\textsuperscript{14,16} have developed models and present experimental data, for the accumulation of big particles at the top of the drying film, due to the large Péclet number of this species. At very low concentrations of the small particles, interactions between the small and big colloidal particles may be insignificant, and so the dominant difference between the small and big particles is the much larger Péclet number of the big particles.

In Fig. 3(b) the film has an intermediate volume fraction of the small particles. A jammed layer appears at $t^* = 0.33$, and so at an initial height $z/H = 0.67$. So when the jammed layer appears there is space underneath it for a large concentration gradient to form. This large gradient drives fast diffusiophoretic motion of the big particles, and so the final film is stratified. Note that just below the descending jamming front (yellow line) there is strong curvature of the trajectories (red) away from the front.

It is worth noting that in this model the large particles concentrate in a narrow region in front of the descending jammed region — the red curves in Fig. 3(b) converge on each other and on the yellow line marking the descending front. Similar localisation of particles due to diffusiophoresis is seen in systems where diffusiophoresis is due to salt gradients\textsuperscript{24,26,40,41}. There this convergence is called focusing.

Finally, in Fig. 3(c), the film has a large initial volume fraction of the small particles. A jammed layer appears at $t^* = 0.11$, and so at an initial height $z/H = 0.89$. So as at the intermediate volume fraction, Fig. 3(b), a jamming layer forms with concentration gradients underneath it. However, the diffusiophoretic velocity $U$ is too slow for the big particles to outrun the descending jamming front, and big particles are incorporated into the jammed layer. Note the red trajectories that start in the unjammed region (white) but are incorporated in the growing jammed region (cross the yellow line into the cyan region).
FIG. 4. A contour plot of the ratio \( \max(U)/v_{\text{jam}} \) in the \( \phi_0-P_{\text{film}} \) plane. Superimposed on this is a black dotted curve, which is Eq. (11), and separates the regions of the plane where jamming occurs before the accumulation zone is limited by the bottom of the film (to right and above the curve), from the region where jamming only occurs when the interface is already close to the bottom of the film.

A. Region of the \( \phi_0-P_{\text{film}} \) plane where a jammed layer forms and excludes the big particles

In my simple model, stratification forms when a jammed layer of the small particles forms and excludes the big particles. Thus, there are two conditions that need to be met for stratification: 1) a jammed layer must form early enough in drying so that there is space (\( \sim D_{\text{small}}/v_{\text{jam}} \)) below the jammed layer for concentration gradients, and 2) the diffusiophoretic velocity due to these concentration gradients must be fast enough to push the big particles ahead of the jammed layer, \( U > v_{\text{jam}} \).

Condition 1) is just Eq. (11). For condition 2) we need the maximum diffusiophoretic velocity. Before jamming, as determined by Eq. (11), the maximum is at the interface, see Eq. (19). When there is jamming, the maximum of \( U \) is at \( z_{\text{jam}} \), from Eq. (20). So,

\[
\max(U) = \begin{cases} 
(9/4)\phi_0P_{\text{film}}t^*v_{\text{ev}} & t^* < t_{\text{jam}}^* \\
(9/4)(\phi_{\text{jam}} - \phi_0)v_{\text{jam}} & t^* > t_{\text{jam}}^*
\end{cases}
\]  

(23)

Thus we can determine the value of the ratio \( \max(U)/v_{\text{jam}} \) at all values of \( \phi_0 \) and \( P_{\text{film}} \). Figure 4 is a contour plot of the ratio \( \max(U)/v_{\text{jam}} \) (note that both \( U \) and \( v_{\text{jam}} \) depend on
FIG. 5. Plot of the $\phi_0$-Pe$_{\text{film}}$ plane, with the region where there is stratification shown in blue. This is the region which satisfies Eq. (11), and where $\max(U) > \phi_{\text{jam}}$.

$\phi_0$). The orange contour at 1.0 separates the region where $U$ is fast enough for stratification, from the region where it is too slow. At its right-hand side the contour at 1.0 is vertical, i.e., is independent of Pe$_{\text{film}}$, because both the competing velocities ($U$ and $v_{\text{ev}}$) are linear in Pe$_{\text{film}}$.

We can determine this right-hand boundary of the stratified region by finding where the ratio $\max(U)/v_{\text{jam}} = 1$. Using Eq. (23) in the jammed region, we then have that $(9/4)(\phi_{\text{jam}} - \phi_0) = 1$, or $\phi_0 = \phi_{\text{jam}} - 4/9 = 0.20$, with $\phi_{\text{jam}} = 0.64$. When the initial volume fraction of the small particles is greater than 0.20, the diffusiophoretic velocity is too slow to push the big particles ahead of the advancing jammed layer, and stratification is impossible.

However, if the initial volume fraction of the small particles is below $\phi_{\text{jam}}/\text{Pe}_{\text{film}}$ then the jammed layer forms too late in drying to drive stratification. The jammed layer only forms when the accumulation zone of width $D_{\text{small}}/v_{\text{ev}}$ has already reached the bottom. So stratification only occurs for $\phi_0$ between $\phi_{\text{jam}}/\text{Pe}_{\text{film}}$ and 0.20.

In Fig. 5, I show the $\phi_0$-Pe$_{\text{film}}$-plane, and have shaded in blue the region where stratification occurs. This figure follows a similar plot made by Zhou et al.$^{31}$ for their model. Sear and Warren$^5$ show this type of plot, for a model without jamming, and Makepeace et al.$^4$ and Liu et al.$^{32}$ both plot experimental data in this way. See the review of Schulz and Keddie$^2$ for earlier experimental work including the conditions where stratified and non-stratified films have been observed.
VI. CONCLUSION

As we can see in Fig. 5, drying films stratify over a range of initial volume fractions of the small colloid. The lower limit to stratification decreases as the Péclet number increases. This lower limit is set by the fact that below it, there are so few small particles that jamming only occurs when the water/air interface is already close to the bottom of the film ($z_{\text{int}}/H < 1 - 1/\text{Pe}_{\text{film}}$). The upper limit is set by the fact that as the concentration of the small particles increases, the speed of advance of the jamming front increases but the diffusiophoretic velocity does not. So at volume fractions $\phi_0 > 0.20$, the big particles no longer move fast enough to outrun the advancing jamming layer.

The prediction that large initial concentrations of small particles do not result in stratification is consistent with the results of both Martín-Fabiani et al.\textsuperscript{3} and Makepeace et al.\textsuperscript{4}, and with the results surveyed in Fig. 10 of the review of Schulz and Keddie\textsuperscript{2}. Schulz and Keddie plot the results of many experiments on drying films of colloidal films, and find only few stratify at volume fractions of the smaller species above 0.2, and none above a volume fraction of approximately 0.3, although it should be noted that there is a little data in that region. Schulz and Keddie also find that most systems where the initial volume fraction of the smaller particles is much less than 0.1, also do not stratify.

With the exception of the work of Cheng and coworkers\textsuperscript{42,43}, computer simulation studies\textsuperscript{1,3,4,28–30} have studied systems with implicit not explicit solvent. As discussed in detail by Sear and Warren\textsuperscript{5}, computer simulations of models without explicit solvent, neglect solvent flow effects and so overpredict stratification. So, it is only because our model includes solvent-flow effects, that it is able to make the prediction that stratification only occurs over a limited range of volume fractions of the smaller species. Simulations with explicit solvent\textsuperscript{42,43} are very challenging computations, and so are forced to study systems at larger evaporation rates and thinner films, than studied in experiment. This makes it difficult to directly compare the interesting results of simulations with explicit solvent, with experiment.

I would like to end by making a few remarks on future work. We now have a number of experimental studies with data on the final dry films\textsuperscript{2}. We also have models for the dynamics during drying that make clear predictions. However, there is still a lot of work to do before we can confidently say we understand and can rationally engineer drying films containing...
Our current models are all incomplete and make approximations. Here I assumed that the volume fraction of the big particles was so small that I could neglect interactions between big particles, and also that the size ratio $R_{\text{big}}/R_{\text{small}} \gg 1$. In addition, not all possible behaviour has been considered. For example, the coupling of stratification and crystallisation has not been considered. Mixtures can often only crystallise with difficulty\textsuperscript{44-47}, however, stratification demixes mixtures and creates a layer of almost pure small particles, which may then go to crystallise. Thus stratification may allow mixtures that would otherwise remain amorphous to crystallise. Future modelling work could consider this. It could also consider the effect of varying the size ratio, $R_{\text{big}}/R_{\text{small}}$, by using available expressions for $U$ as a function of size ratio\textsuperscript{48}.

Further experiments are also needed. Most experimental studies report only on the final dry film, although the work of Ekanayake \textit{et al.}\textsuperscript{38}, and that of Cardinal \textit{et al.}\textsuperscript{49} are exceptions. So, we have little data on the dynamics of colloidal mixtures during drying. To fully understand the processes during drying that lead to stratification, future experimental work will need to study particle dynamics during the drying process.

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**Appendix A: Concentration gradient in the small particles below a jammed layer**

For an ideal gas in front of an advancing jammed front at position $z_{\text{jam}}$, the decay to the uniform value is exponential, with a characteristic width $D_{\text{small}}/v_{\text{jam}}$, as shown by Okuzono \textit{et al.}\textsuperscript{6} (see their Eq. (18)). The profile is then given by

$$
\phi_{\text{small}}(z,t) \approx \begin{cases} 
\phi_{\text{jam}} & z_{\text{jam}} < z < z_{\text{int}} \\
\phi_0 + (\phi_{\text{jam}} - \phi_0) \exp \left[ -\frac{|z-z_{\text{jam}}|}{D_{\text{small}}/v_{\text{jam}}} \right] & z < z_{\text{jam}}
\end{cases}
$$

Note that below the descending interface there is an accumulation zone, where the volume fraction $\phi_{\text{small}} > \phi_0$. This zone is of constant width $D_{\text{small}}/v_{\text{jam}}$. The gradient in volume
The fraction of small particles is then

\[
\frac{\partial \phi_{\text{small}}(z,t)}{\partial z} \approx \begin{cases} 
0 & z_{\text{jam}} < z < z_{\text{int}} \\
\frac{(\phi_{\text{jam}} - \phi_0)v_{\text{jam}}}{D_{\text{small}}} \exp \left[ -\frac{|z - z_{\text{jam}}|}{D_{\text{small}}/v_{\text{jamp}}} \right] & z < z_{\text{jam}}
\end{cases}
\]  

(A2)

The maximum in the gradient is at the advancing jamming front, i.e., at \(z_{\text{jam}}\). Putting \(z = z_{\text{jam}}\) in Eq. (A2) yields Eq. (15). Equation (15) applies so long as the accumulation zone, of width \(D_{\text{small}}/v_{\text{ev}}\), that precedes the jamming front, does not hit the bottom of the film, i.e., so long as \(z_{\text{jam}} > D_{\text{small}}/v_{\text{jam}}\). The solution for this system in the \(H \to \infty\) limit is given by Landau\(^{50}\).

REFERENCES


\( \phi_0 = 0.05 \)
$t^* = 0.15$

$\phi_0 = 0.15$
jammed layer of small on top of layer of big