UNIVERSITY OF CAMBRIDGE

***Email:***
*crr34@cam.ac.uk*

# Formulating stratified films: exploiting diffusion and diffusiophoresis

**Clare R. Rees-Zimmerman & Alex F. Routh**

BP INSTITUTE FOR MULTIPHASE FLOW

## 1. Introduction

- A variety of particle arrangements in dried films has been seen experimentally, including a thin layer of small particles at the top surface. However, it is not understood why this would occur.
- The motivation for understanding this is the desire to engineer the drying process such that expensive components are only located where they are required.
- This poster explores the relative importance of diffusion and diffusiophoresis in affecting particle arrangement.

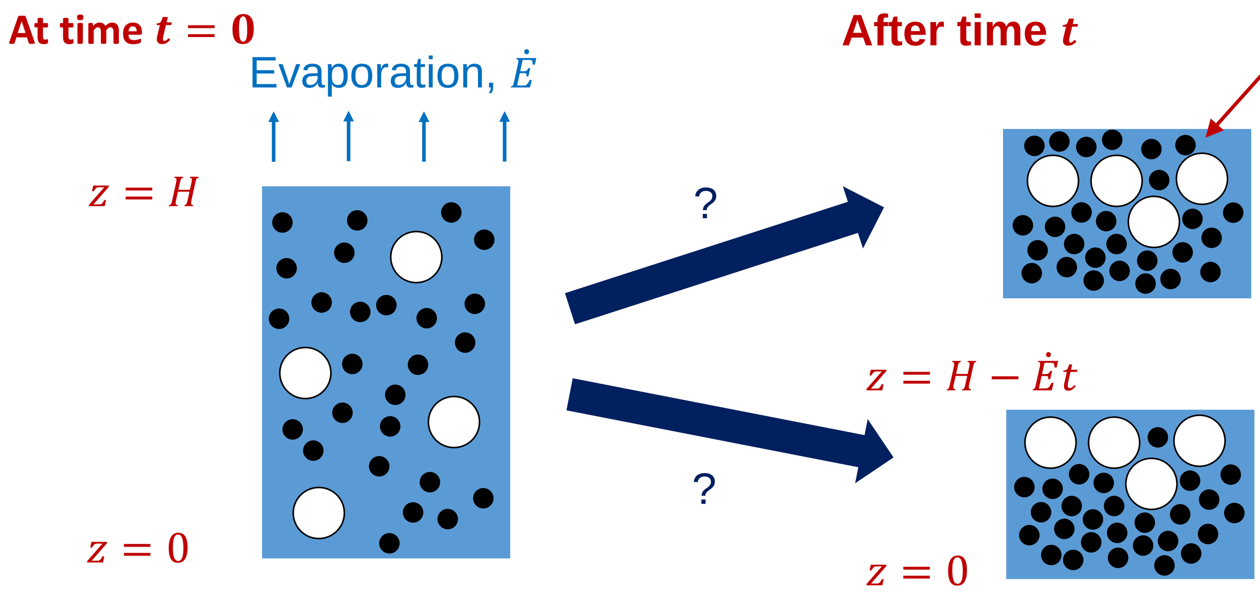


***Figure 1:*** *Schematic of the drying of a film containing two types of particles.*

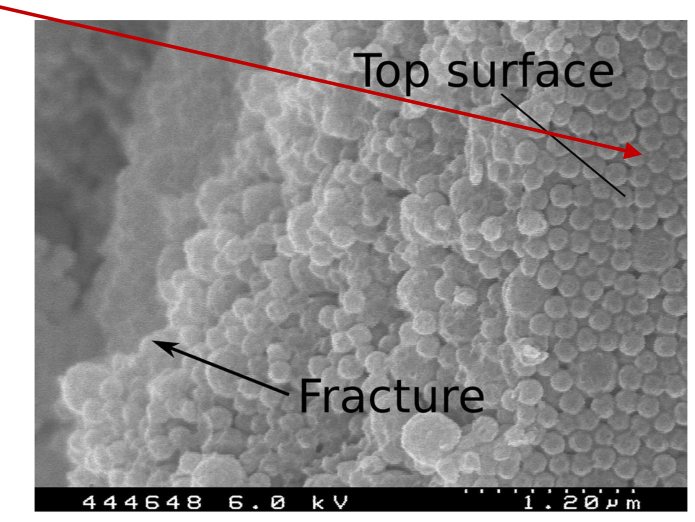


***Figure 2:*** *Cryo-SEM image showing an accumulation of small particles at the top surface (Atmuri et al., 2012).*

## 2. Why include diffusiophoresis?

- Diffusiophoresis has been suggested as an explanation of the accumulation of small particles on the top surface.
- This is relevant in a mixture of small ($R_1$) and large particles ($R_2$), when the small particles are excluded from a layer of solvent of thickness $R_{\mathrm{DP}}$ around each of the large particles.

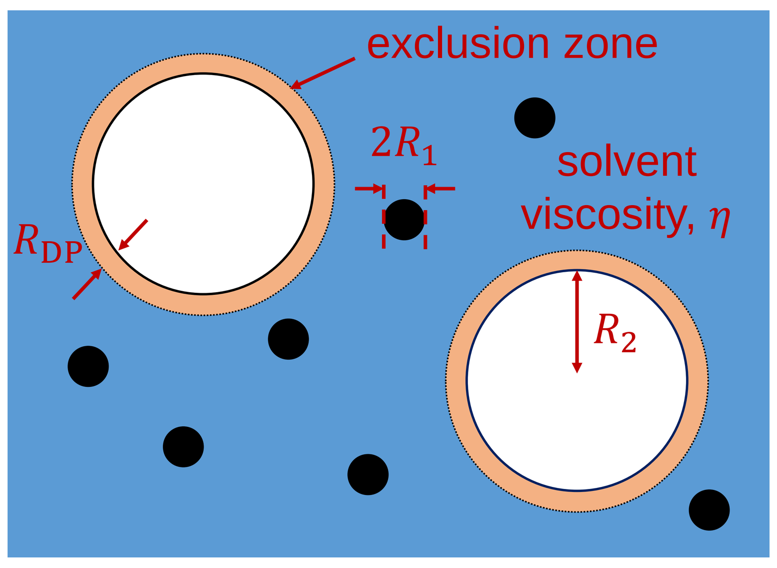


***Figure 3:*** *Schematic of the exclusion zones around the larger particles, which give rise to diffusiophoresis.*

## 3. Governing equations

### Conservation equation

- For components 1 and 2, the conservation equation for the volume fraction $\phi_i$ of component $i$ is

$$\frac{\partial \phi_i}{\partial t} + \nabla \cdot \boldsymbol{N_i} = 0.$$

- There are contributions to the flux $\boldsymbol{N_i}$ due to diffusion and diffusiophoresis (**DP**):

$$\boldsymbol{N}_2^{\mathrm{DP}} = -\frac{3\phi_1\phi_2(1-\phi_2)K(\phi_1,\phi_2)}{8\pi\eta}\frac{R_{\mathrm{DP}}^2}{R_1^3}\,kT\,\nabla \ln \phi_1.$$

- $K(\phi_1, \phi_2)$ accounts for hydrodynamic effects.

### Extension to concentrated solution

- The Gibbs-Duhem equation relates the chemical potentials in the system ($\mu_i$ = chemical potential, $n_i$ = number density of component $i$, $s$ = solvent):

$$n_1\nabla\mu_1 + n_2\nabla\mu_2 + n_s\nabla\mu_s = 0.$$

- An expression, valid up to close-packing, relates $\mu_s$ to the osmotic pressure, $\Pi$ ($kT$ = thermal energy, $Z(\phi_1, \phi_2)$ = compressibility):

$$\Pi = \left(\frac{\phi_1}{\frac{4}{3}\pi R_1^3} + \frac{\phi_2}{\frac{4}{3}\pi R_2^3}\right) kT Z(\phi_1, \phi_2).$$

## 4. Model results

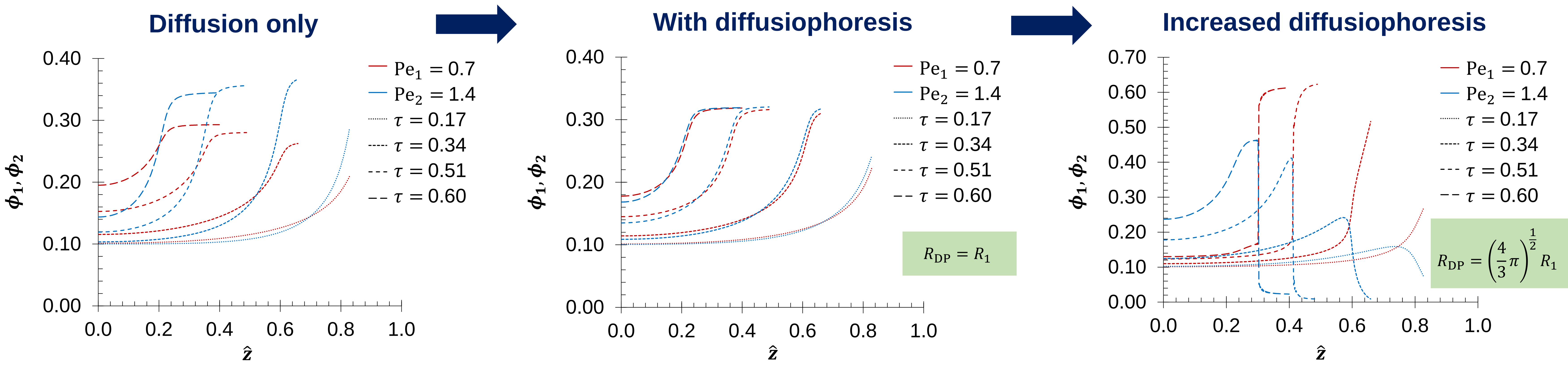


***Figure 4:*** *Model results without (left) and with (centre and right) diffusiophoresis at different values of* $R_{\mathrm{DP}}$. *The model uses* $K(\phi_1, \phi_2) = (1 - \phi_1 - \phi_2)^{6.55}$ *and* $Z(\phi_1, \phi_2) = (\phi_{\mathrm{m}} - \phi_1 - \phi_2)^{-1}$.

## 5. Conclusions and future work

### Conclusions

- **Scaling:** Both diffusion and diffusiophoresis are important.
- **Without diffusiophoresis:** Larger diffusive flux of the smaller particles leads to accumulation of the larger particles at the top surface.
- **With diffusiophoresis:** Increasing the strength of diffusiophoresis results in more small particles at the top surface.

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### Unanswered questions

In order to run the model up to close-packing, suitable expressions need to be found for:

- $K(\phi_1, \phi_2)$
- $Z(\phi_1, \phi_2)$

?

### Future work: interactions

Experiments suggest that interactions affect particle arrangements, so these will be added to the chemical potential expressions.

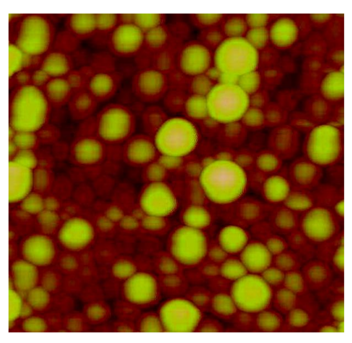

***Figure 5:*** *AFM image of a dried polystyrene latex film at pH 5. At higher pH, there were fewer large particles the top surface (Atmuri et al., 2012).*

**Preliminary result:** Small-on-top stratification is promoted by attractive small particle interactions and repulsive large particle interactions.