

Stratification in drying films: a diffusion-diffusiophoresis model

Supplementary Information

S1 Derivation and Methodology

This section provides supplementary information for Sections 1 and 2 of the main text.

S1.1 Coordinate transform

The boundary conditions at the bottom boundary, $\xi = 0$, are

$$(1 - \phi_1 - \phi_2) \left[\frac{[\phi_1 K_{11}(\phi_1, \phi_2) - \frac{9}{4}(\phi_1)^2 \phi_2 K_P(\phi_1, \phi_2)]}{\left(\phi_1 + \left(\frac{Pe_1}{Pe_2}\right)^3 \phi_2 \frac{\partial \mu_2 / \partial \xi}{\partial \mu_1 / \partial \xi}\right)} + \frac{\phi_1 \phi_2 K_{12}(\phi_1, \phi_2)}{\left(\left(\frac{Pe_2}{Pe_1}\right)^3 \phi_1 \frac{\partial \mu_1 / \partial \xi}{\partial \mu_2 / \partial \xi} + \phi_2\right)} \left(\frac{Pe_2}{Pe_1}\right)^3 \right] \\ \frac{\partial}{\partial \xi} \left[\left(\phi_1 + \left(\frac{Pe_1}{Pe_2}\right)^3 \phi_2 \right) Z(\phi_1, \phi_2) \right] = 0 \quad (S1.1)$$

and

$$(1 - \phi_1 - \phi_2) \left[\left(\frac{Pe_1}{Pe_2}\right)^3 \left[\frac{\phi_1 \phi_2 K_{21}(\phi_1, \phi_2) + \frac{9}{4} \left(\frac{Pe_2}{Pe_1}\right) \phi_1 \phi_2 (1 - \phi_2) K_P(\phi_1, \phi_2)}{\left(\phi_1 + \left(\frac{Pe_1}{Pe_2}\right)^3 \phi_2 \frac{\partial \mu_2 / \partial \xi}{\partial \mu_1 / \partial \xi}\right)} \right] + \frac{\phi_2 K_{22}(\phi_1, \phi_2)}{\left(\left(\frac{Pe_2}{Pe_1}\right)^3 \phi_1 \frac{\partial \mu_1 / \partial \xi}{\partial \mu_2 / \partial \xi} + \phi_2\right)} \right] \\ \frac{\partial}{\partial \xi} \left[\left(\left(\frac{Pe_2}{Pe_1}\right)^3 \phi_1 + \phi_2 \right) Z(\phi_1, \phi_2) \right] = 0. \quad (S1.2)$$

Since in the non-transformed system the top boundary is moving, the corresponding boundary condition at $\xi = 1$ is more complex. Matching the diffusive flux of the particles with the convection induced by the moving top boundary gives

$$(1 - \phi_1 - \phi_2) \left[\frac{[\phi_1 K_{11}(\phi_1, \phi_2) - \frac{9}{4}(\phi_1)^2 \phi_2 K_P(\phi_1, \phi_2)]}{\left(\phi_1 + \left(\frac{Pe_1}{Pe_2}\right)^3 \phi_2 \frac{\partial \mu_2 / \partial \xi}{\partial \mu_1 / \partial \xi}\right)} + \frac{\phi_1 \phi_2 K_{12}(\phi_1, \phi_2)}{\left(\left(\frac{Pe_2}{Pe_1}\right)^3 \phi_1 \frac{\partial \mu_1 / \partial \xi}{\partial \mu_2 / \partial \xi} + \phi_2\right)} \left(\frac{Pe_2}{Pe_1}\right)^3 \right] \\ \frac{\partial}{\partial \xi} \left[\left(\phi_1 + \left(\frac{Pe_1}{Pe_2}\right)^3 \phi_2 \right) Z(\phi_1, \phi_2) \right] = Pe_1 \phi_1 (1 - \tau) \quad (S1.3)$$

and

$$(1 - \phi_1 - \phi_2)$$

$$\left[\left(\frac{\text{Pe}_1}{\text{Pe}_2} \right)^3 \left[\frac{\phi_1 \phi_2 K_{21}(\phi_1, \phi_2) + \frac{9}{4} \left(\frac{\text{Pe}_2}{\text{Pe}_1} \right) \phi_1 \phi_2 (1 - \phi_2) K_P(\phi_1, \phi_2)}{\left(\phi_1 + \left(\frac{\text{Pe}_1}{\text{Pe}_2} \right)^3 \phi_2 \frac{\partial \mu_2 / \partial \xi}{\partial \mu_1 / \partial \xi} \right)} \right] + \frac{\phi_2 K_{22}(\phi_1, \phi_2)}{\left(\left(\frac{\text{Pe}_2}{\text{Pe}_1} \right)^3 \phi_1 \frac{\partial \mu_1 / \partial \xi}{\partial \mu_2 / \partial \xi} + \phi_2 \right)} \right] \frac{\partial}{\partial \xi} \left[\left(\left(\frac{\text{Pe}_2}{\text{Pe}_1} \right)^3 \phi_1 + \phi_2 \right) Z(\phi_1, \phi_2) \right] = \text{Pe}_2 \phi_2 (1 - \tau). \quad (\text{S1.4})$$

S1.2 Diffusiophoretic slip velocity

Marbach *et al.* (2017) derive the diffusiophoretic slip velocity for infinite R_2 and for arbitrary concentration of particles of type one. In the geometry of infinite R_2 , diffusiophoresis is the same effect as diffusio-osmosis, as referred to by Marbach *et al.* We consider a flat wall (component two) in contact with a solution of component one. The general result of Marbach *et al.* is

$$\mathbf{U}_P = -\frac{1}{\eta} \int_0^\infty y' \left[\frac{c(x, y')}{c(x, y' = \infty)} - 1 \right] dy' \frac{\partial \Pi_1[c(x, y = \infty)]}{\partial x}, \quad (\text{S1.5})$$

where x and y denote directions tangential and perpendicular, respectively, to the wall surface. The concentration of particles of type one is denoted by c , and the osmotic pressure by Π_1 . The subscript 1 is used to distinguish the osmotic pressure in this scenario from the two-component mixture considered in equation (2.16) in the main text. Relating this osmotic pressure to the local force acting on the fluid due to the wall is the basis for the derivation of Marbach *et al.*

This osmotic pressure is related to the chemical potential of component one via

$$\frac{\partial \Pi_1[c(x, y)]}{\partial x} = c \frac{\partial \mu_1}{\partial x}, \quad (\text{S1.6})$$

from the one-component version of the Gibbs-Duhem equation.

The concentration profile of component one used in the Asakura-Oosawa model is

$$c = 0, \quad y < R_{DP}, \quad (\text{S1.7a})$$

$$c = c(x, y = \infty), \quad y > R_{DP}. \quad (\text{S1.7b})$$

Substituting equations (S1.6)–(S1.7) into (S1.5) obtains

$$\mathbf{U}_P = \frac{c}{\eta} \frac{\partial \mu_1}{\partial x} \frac{1}{2} R_{DP}^2. \quad (\text{S1.8})$$

Applying this result to diffusiophoresis in a two-component mixture, where $c = n_1$ and $\phi_1 = n_1 \frac{4}{3} \pi R_1^3$, obtains

$$\mathbf{U}_P = -\frac{3\phi_1}{8\pi\eta} \frac{R_{DP}^2}{R_1^3} \nabla \mu_1, \quad (\text{S1.9})$$

as is given in equation (2.25) of the main text.

S1.3 Numerical resolution

For reproducibility, Table S1 gives the time step, $\Delta\tau$, and grid size, $\Delta\xi$, used to generate each figure in the main text.

Table S1: Resolutions used to obtain the data for the figures in the main text.

Phenomena included	Figure	Pe_1	Pe_2	$\Delta\tau$	$\Delta\xi$
Diffusion only	3a	0.175	0.35	0.01	10^{-8}
	3b	0.70	1.40	0.005	10^{-8}
	3c	2.8	5.6	0.005	10^{-9}
	8	10	20	0.005	10^{-9}
Add non-enhanced diffusiophoresis	4a	0.175	0.35	0.01	10^{-7}
	4b	0.70	1.40	0.005	5×10^{-9}
	4c	2.8	5.6	0.005	2.5×10^{-9}
Add enhanced diffusiophoresis	5a	0.175	0.35	0.01	10^{-8}
	5b	0.70	1.40	0.003	10^{-8}
	5c	2.8	5.6	0.0025	5×10^{-9}
	9	10	20	0.005	10^{-9}

S2 Asymptotic solution for large Pe

This section provides supplementary information for Section 5 of the main text.

S2.1 Diffusion

S2.1.1 Change of variables

To leading order in Pe_2 , equations (3.3) and (3.4) with $K_p(\phi_1, \phi_2) = 0$ become

$$\begin{aligned} \frac{d\phi_1}{dX} \left[\frac{P(\tau)}{1-\tau} - \frac{dP(\tau)}{d\tau} \right] &= \left(\frac{Pe_2}{Pe_1} \right) \frac{1}{(1-\tau)^2} \frac{d}{dX} \left[\left[\frac{\phi_1 K_{11}(\phi_1, \phi_2)}{\left(\phi_1 + \left(\frac{Pe_1}{Pe_2} \right)^3 \phi_2 \frac{d\mu_2/dX}{d\mu_1/dX} \right)} + \frac{\phi_1 \phi_2 K_{12}(\phi_1, \phi_2)}{\left(\phi_1 \frac{d\mu_1/dX}{d\mu_2/dX} + \left(\frac{Pe_1}{Pe_2} \right)^3 \phi_2 \right)} \right] \right. \\ &\quad \left. (1 - \phi_1 - \phi_2) \frac{d}{dX} \left[\left(\phi_1 + \left(\frac{Pe_1}{Pe_2} \right)^3 \phi_2 \right) Z(\phi_1, \phi_2) \right] \right] \end{aligned} \quad (S2.1)$$

and

$$\begin{aligned} \frac{d\phi_2}{dX} \left[\frac{P(\tau)}{1-\tau} - \frac{dP(\tau)}{d\tau} \right] &= \frac{1}{(1-\tau)^2} \frac{d}{dX} \left[\left[\frac{\phi_2 K_{22}(\phi_1, \phi_2)}{\left(\phi_2 + \left(\frac{Pe_2}{Pe_1} \right)^3 \phi_1 \frac{d\mu_1/dX}{d\mu_2/dX} \right)} + \frac{\phi_1 \phi_2 K_{21}(\phi_1, \phi_2)}{\left(\phi_2 \frac{d\mu_2/dX}{d\mu_1/dX} + \left(\frac{Pe_2}{Pe_1} \right)^3 \phi_1 \right)} \right] \right. \\ &\quad \left. (1 - \phi_1 - \phi_2) \frac{d}{dX} \left[\left(\phi_2 + \left(\frac{Pe_2}{Pe_1} \right)^3 \phi_1 \right) Z(\phi_1, \phi_2) \right] \right]. \end{aligned} \quad (S2.2)$$

The boundary conditions become:

As $X \rightarrow -\infty$,

$$\phi_1 \rightarrow \phi_1(\tau = 0), \phi_2 \rightarrow \phi_2(\tau = 0), \quad (S2.3)$$

$$\begin{aligned} &\left[\frac{\phi_1 K_{11}(\phi_1, \phi_2)}{\left(\phi_1 + \left(\frac{Pe_1}{Pe_2} \right)^3 \phi_2 \frac{d\mu_2/dX}{d\mu_1/dX} \right)} + \frac{\phi_1 \phi_2 K_{12}(\phi_1, \phi_2)}{\left(\phi_1 \frac{d\mu_1/dX}{d\mu_2/dX} + \left(\frac{Pe_1}{Pe_2} \right)^3 \phi_2 \right)} \right] \\ &\quad (1 - \phi_1 - \phi_2) \frac{d}{dX} \left[\left(\phi_1 + \left(\frac{Pe_1}{Pe_2} \right)^3 \phi_2 \right) Z(\phi_1, \phi_2) \right] \rightarrow 0 \end{aligned} \quad (S2.4)$$

and

$$\left[\frac{\phi_2 K_{22}(\phi_1, \phi_2)}{\left(\phi_2 + \left(\frac{Pe_2}{Pe_1} \right)^3 \phi_1 \frac{d\mu_1/dX}{d\mu_2/dX} \right)} + \frac{\phi_1 \phi_2 K_{21}(\phi_1, \phi_2)}{\left(\phi_2 \frac{d\mu_2/dX}{d\mu_1/dX} + \left(\frac{Pe_2}{Pe_1} \right)^3 \phi_1 \right)} \right]$$

$$(1 - \phi_1 - \phi_2) \frac{d}{dX} \left[\left(\phi_2 + \left(\frac{Pe_2}{Pe_1} \right)^3 \phi_1 \right) Z(\phi_1, \phi_2) \right] \rightarrow 0. \quad (S2.5)$$

As $X \rightarrow \infty$,

$$\phi_1 + \phi_2 \rightarrow \phi_m, \quad (S2.6)$$

$$\begin{aligned} & \left[\frac{\phi_1 K_{11}(\phi_1, \phi_2)}{\left(\phi_1 + \left(\frac{Pe_1}{Pe_2} \right)^3 \phi_2 \frac{d\mu_2/dX}{d\mu_1/dX} \right)} + \frac{\phi_1 \phi_2 K_{12}(\phi_1, \phi_2)}{\left(\phi_1 \frac{d\mu_1/dX}{d\mu_2/dX} + \left(\frac{Pe_1}{Pe_2} \right)^3 \phi_2 \right)} \right] \\ & (1 - \phi_1 - \phi_2) \frac{d}{dX} \left[\left(\phi_1 + \left(\frac{Pe_1}{Pe_2} \right)^3 \phi_2 \right) Z(\phi_1, \phi_2) \right] \\ & \rightarrow \left(\frac{Pe_1}{Pe_2} \right) \phi_{1,X \rightarrow \infty} (1 - \tau) \end{aligned} \quad (S2.7)$$

and

$$\begin{aligned} & \left[\frac{\phi_2 K_{22}(\phi_1, \phi_2)}{\left(\phi_2 + \left(\frac{Pe_2}{Pe_1} \right)^3 \phi_1 \frac{d\mu_1/dX}{d\mu_2/dX} \right)} + \frac{\phi_1 \phi_2 K_{21}(\phi_1, \phi_2)}{\left(\phi_2 \frac{d\mu_2/dX}{d\mu_1/dX} + \left(\frac{Pe_2}{Pe_1} \right)^3 \phi_1 \right)} \right] \\ & (1 - \phi_1 - \phi_2) \frac{d}{dX} \left[\left(\phi_2 + \left(\frac{Pe_2}{Pe_1} \right)^3 \phi_1 \right) Z(\phi_1, \phi_2) \right] \\ & \rightarrow \phi_{2,X \rightarrow \infty} (1 - \tau). \end{aligned} \quad (S2.8)$$

S2.1.2 Solve for $P(\tau)$

Integrating (S2.1) and (S2.2) across the discontinuity from $X = -\infty$ to $X = \infty$, with use of the boundary conditions, gives

$$\left[\frac{P(\tau)}{1-\tau} - \frac{dP(\tau)}{d\tau} \right] [\phi_{1,X \rightarrow \infty} - \phi_{1,\tau=0}] = \frac{\phi_{1,X \rightarrow \infty}}{(1-\tau)} \quad (S2.9)$$

and

$$\left[\frac{P(\tau)}{1-\tau} - \frac{dP(\tau)}{d\tau} \right] [\phi_{2,X \rightarrow \infty} - \phi_{2,\tau=0}] = \frac{\phi_{2,X \rightarrow \infty}}{(1-\tau)}. \quad (S2.10)$$

Summing equations (S2.9) and (S2.10) and integrating, using that when $\tau = 0$, $P = 1$:

$$\left[\frac{P(\tau)}{1-\tau} - \frac{dP(\tau)}{d\tau} \right] [\phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0})] = \frac{\phi_m}{(1-\tau)}. \quad (S2.11)$$

This can be integrated, giving

$$P(\tau) = \frac{1 - \frac{\phi_m}{\phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0})} \tau}{1 - \tau}, \quad (\text{S2.12})$$

as is stated in equation (5.1) in the main text.

S2.1.3 Form differential equations for $X(\phi_1, \phi_2)$

Equation (S2.11) is substituted into equations (S2.1) and (S2.2):

$$\begin{aligned} \frac{d\phi_1}{dX} \frac{\phi_m}{[\phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0})]} &= \left(\frac{\text{Pe}_2}{\text{Pe}_1} \right) \frac{1}{(1-\tau)} \frac{d}{dX} \left[\left[\frac{\phi_1 K_{11}(\phi_1, \phi_2)}{\left(\phi_1 + \left(\frac{\text{Pe}_1}{\text{Pe}_2} \right)^3 \phi_2 \frac{d\mu_2/dX}{d\mu_1/dX} \right)} + \frac{\phi_1 \phi_2 K_{12}(\phi_1, \phi_2)}{\left(\phi_1 \frac{d\mu_1/dX}{d\mu_2/dX} + \left(\frac{\text{Pe}_1}{\text{Pe}_2} \right)^3 \phi_2 \right)} \right] \right. \\ &\quad \left. (1 - \phi_1 - \phi_2) \frac{d}{dX} \left[\left(\phi_1 + \left(\frac{\text{Pe}_1}{\text{Pe}_2} \right)^3 \phi_2 \right) Z(\phi_1, \phi_2) \right] \right] \end{aligned} \quad (\text{S2.13})$$

and

$$\begin{aligned} \frac{d\phi_2}{dX} \frac{\phi_m}{[\phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0})]} &= \frac{1}{(1-\tau)} \frac{d}{dX} \left[\left[\frac{\phi_2 K_{22}(\phi_1, \phi_2)}{\left(\phi_2 + \left(\frac{\text{Pe}_2}{\text{Pe}_1} \right)^3 \phi_1 \frac{d\mu_1/dX}{d\mu_2/dX} \right)} + \frac{\phi_1 \phi_2 K_{21}(\phi_1, \phi_2)}{\left(\phi_2 \frac{d\mu_2/dX}{d\mu_1/dX} + \left(\frac{\text{Pe}_2}{\text{Pe}_1} \right)^3 \phi_1 \right)} \right] \right. \\ &\quad \left. (1 - \phi_1 - \phi_2) \frac{d}{dX} \left[\left(\phi_2 + \left(\frac{\text{Pe}_2}{\text{Pe}_1} \right)^3 \phi_1 \right) Z(\phi_1, \phi_2) \right] \right]. \end{aligned} \quad (\text{S2.14})$$

Integrating once, from the bottom of the film to a point in the film, using boundary conditions (S2.3)–(S2.5), gives

$$\begin{aligned} \frac{\phi_m(\phi_1 - \phi_{1,\tau=0})}{\phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0})} &= \left(\frac{\text{Pe}_2}{\text{Pe}_1} \right) \left(\frac{1}{1-\tau} \right) \left[\frac{\phi_1 K_{11}(\phi_1, \phi_2)}{\left(\phi_1 + \left(\frac{\text{Pe}_1}{\text{Pe}_2} \right)^3 \phi_2 \frac{d\mu_2/dX}{d\mu_1/dX} \right)} + \frac{\phi_1 \phi_2 K_{12}(\phi_1, \phi_2)}{\left(\phi_1 \frac{d\mu_1/dX}{d\mu_2/dX} + \left(\frac{\text{Pe}_1}{\text{Pe}_2} \right)^3 \phi_2 \right)} \right] \\ &\quad (1 - \phi_1 - \phi_2) \frac{d}{dX} \left[\left(\phi_1 + \left(\frac{\text{Pe}_1}{\text{Pe}_2} \right)^3 \phi_2 \right) Z(\phi_1, \phi_2) \right] \end{aligned} \quad (\text{S2.15})$$

and

$$\begin{aligned} \frac{\phi_m(\phi_2 - \phi_{2,\tau=0})}{\phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0})} &= \left(\frac{1}{1-\tau} \right) \left[\frac{\phi_2 K_{22}(\phi_1, \phi_2)}{\left(\phi_2 + \left(\frac{\text{Pe}_2}{\text{Pe}_1} \right)^3 \phi_1 \frac{d\mu_1/dX}{d\mu_2/dX} \right)} + \frac{\phi_1 \phi_2 K_{21}(\phi_1, \phi_2)}{\left(\phi_2 \frac{d\mu_2/dX}{d\mu_1/dX} + \left(\frac{\text{Pe}_2}{\text{Pe}_1} \right)^3 \phi_1 \right)} \right] \\ &\quad (1 - \phi_1 - \phi_2) \frac{d}{dX} \left[\left(\phi_2 + \left(\frac{\text{Pe}_2}{\text{Pe}_1} \right)^3 \phi_1 \right) Z(\phi_1, \phi_2) \right]. \end{aligned} \quad (\text{S2.16})$$

S2.1.4 Solve for $\phi_{1,X \rightarrow \infty}$ and $\phi_{2,X \rightarrow \infty}$

If equations (S2.13) and (S2.14) are instead integrated across the entire domain of X , using boundary conditions (S2.3)–(S2.8), then the resulting equations are

$$\frac{\phi_m(\phi_{1,X \rightarrow \infty} - \phi_{1,\tau=0})}{\phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0})} = \phi_{1,X \rightarrow \infty} \quad (\text{S2.17})$$

and

$$\frac{\phi_m(\phi_{2,X \rightarrow \infty} - \phi_{2,\tau=0})}{\phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0})} = \phi_{2,X \rightarrow \infty}. \quad (\text{S2.18})$$

Upon rearranging,

$$\phi_{1,X \rightarrow \infty} = \frac{\phi_m \phi_{1,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} \quad (\text{S2.19})$$

and

$$\phi_{2,X \rightarrow \infty} = \frac{\phi_m \phi_{2,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})}. \quad (\text{S2.20})$$

The volume fractions of components one and two at the top surface are $\phi_{1,X \rightarrow \infty}$ and $\phi_{2,X \rightarrow \infty}$, respectively, so numerical solutions for these can be compared with the asymptotic solutions.

S2.1.5 Approximate solution for $\phi_1(\phi_2)$

Equations (S2.15) and (S2.16), when $\left(\frac{\text{Pe}_2}{\text{Pe}_1}\right)^3 \gg 1$, can be approximated as

$$\begin{aligned} \frac{\phi_m(\phi_1 - \phi_{1,\tau=0})}{\phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0})} &= \left(\frac{\text{Pe}_2}{\text{Pe}_1}\right) \left(\frac{1}{1-\tau}\right) \left[K_{11}(\phi_1, \phi_2) + \frac{\phi_1 \phi_2 K_{12}(\phi_1, \phi_2)}{\left(\phi_1 \frac{d\mu_1/dX}{d\mu_2/dX}\right)} \right] \\ (1 - \phi_1 - \phi_2) \frac{d}{dX} &\left[\left(\phi_1 + \left(\frac{\text{Pe}_1}{\text{Pe}_2}\right)^3 \phi_2 \right) Z(\phi_1, \phi_2) \right] \end{aligned} \quad (\text{S2.21})$$

and

$$\begin{aligned} \frac{\phi_m(\phi_2 - \phi_{2,\tau=0})}{\phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0})} &= \left(\frac{1}{1-\tau}\right) \left[\frac{\phi_2 K_{22}(\phi_1, \phi_2)}{\left(\phi_1 \frac{d\mu_1/dX}{d\mu_2/dX}\right)} + \phi_2 K_{21}(\phi_1, \phi_2) \right] \\ (1 - \phi_1 - \phi_2) \frac{d}{dX} &\left[\left(\left(\frac{\text{Pe}_1}{\text{Pe}_2}\right)^3 \phi_2 + \phi_1 \right) Z(\phi_1, \phi_2) \right], \end{aligned} \quad (\text{S2.22})$$

respectively.

Considering the case where $K_{12}(\phi_1, \phi_2) = K_{21}(\phi_1, \phi_2) = 0$ gives

$$\frac{\phi_m(\phi_1 - \phi_{1,\tau=0})}{\phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0})} = \left(\frac{Pe_2}{Pe_1}\right) \left(\frac{1}{1-\tau}\right) K_{11}(\phi_1, \phi_2)$$

$$(1 - \phi_1 - \phi_2) \frac{d}{dX} \left[\left(\phi_1 + \left(\frac{Pe_1}{Pe_2}\right)^3 \phi_2 \right) Z(\phi_1, \phi_2) \right] \quad (S2.23)$$

and

$$\frac{\phi_m(\phi_2 - \phi_{2,\tau=0})}{\phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0})} = \left(\frac{1}{1-\tau}\right) \frac{\phi_2 K_{22}(\phi_1, \phi_2)}{\left(\phi_1 \frac{d\mu_1/dX}{d\mu_2/dX}\right)}$$

$$(1 - \phi_1 - \phi_2) \frac{d}{dX} \left[\left(\left(\frac{Pe_1}{Pe_2}\right)^3 \phi_2 + \phi_1 \right) Z(\phi_1, \phi_2) \right]. \quad (S2.24)$$

Equating (S2.23) and (S2.24) results in

$$\frac{(\phi_1 - \phi_{1,\tau=0})}{(\phi_2 - \phi_{2,\tau=0})} = \left(\frac{Pe_2}{Pe_1}\right) \frac{K_{11}(\phi_1, \phi_2)}{K_{22}(\phi_1, \phi_2)} \left(\frac{\phi_1}{\phi_2} \frac{d\mu_1/dX}{d\mu_2/dX}\right). \quad (S2.25)$$

Then, using $d\mu_1/d\mu_2 = d \ln \phi_1 / d \ln \phi_2$ gives

$$\frac{(\phi_1 - \phi_{1,\tau=0})}{(\phi_2 - \phi_{2,\tau=0})} = \left(\frac{Pe_2}{Pe_1}\right) \frac{K_{11}(\phi_1, \phi_2)}{K_{22}(\phi_1, \phi_2)} \left(\frac{d\phi_1/dX}{d\phi_2/dX}\right). \quad (S2.26)$$

In order to form a separable differential equation, consider the case where $K_{11}(\phi_1, \phi_2) = K_{22}(\phi_1, \phi_2)$:

$$\frac{d\phi_1/dX}{d\phi_2/dX} = \left(\frac{Pe_1}{Pe_2}\right) \frac{(\phi_1 - \phi_{1,\tau=0})}{(\phi_2 - \phi_{2,\tau=0})}. \quad (S2.27)$$

Integrating, and using the results in equations (S2.19) and (S2.20), gives

$$\frac{\phi_1 - \phi_{1,\tau=0}}{\frac{\phi_m \phi_{1,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{1,\tau=0}} = \left[\frac{\phi_2 - \phi_{2,\tau=0}}{\frac{\phi_m \phi_{2,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{2,\tau=0}} \right]^{\frac{Pe_1}{Pe_2}}, \quad (S2.28)$$

as is presented in the main text (equation (5.2)).

S2.1.6 Solve for $X(\phi_1, \phi_2)$

Equation (S2.28) can be substituted into either equation (S2.23) or equation (S2.24) to find either $X(\phi_1)$ or $X(\phi_2)$, depending on which variable is eliminated. Arbitrarily, equation

(S2.28) is used to eliminate ϕ_2 from equation (S2.23), to find $X(\phi_1)$. Rearranging equation (S2.28) for ϕ_2 gives

$$\phi_2 = \left[\frac{\phi_1 - \phi_{1,\tau=0}}{\frac{\phi_m \phi_{1,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{1,\tau=0}} \right]^{\frac{Pe_2}{Pe_1}} \left[\frac{\phi_m \phi_{2,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{2,\tau=0} \right] + \phi_{2,\tau=0}. \quad (S2.29)$$

This is substituted into equation (S2.23).

The forms of $K_{11}(\phi_1, \phi_2)$ and $Z(\phi_1, \phi_2)$ used here are $K_{11}(\phi_1, \phi_2) = (1 - \phi_1 - \phi_2)^{6.55}$ and $Z(\phi_1, \phi_2) = \phi_m(\phi_m - \phi_1 - \phi_2)^{-1}$. The resulting equation is

$$\begin{aligned} \frac{\phi_m}{\phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0})} &= \left(\frac{Pe_2}{Pe_1} \right) \left(\frac{1}{1-\tau} \right) \frac{1}{(\phi_1 - \phi_{1,\tau=0})} \\ &\left(1 - \phi_1 - \left\{ \left[\frac{\phi_1 - \phi_{1,\tau=0}}{\frac{\phi_m \phi_{1,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{1,\tau=0}} \right]^{\frac{Pe_2}{Pe_1}} \left[\frac{\phi_m \phi_{2,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{2,\tau=0} \right] + \phi_{2,\tau=0} \right\} \right)^{7.55} \\ &\frac{d\phi_1}{dX} \frac{d}{d\phi_1} \left[\left(\phi_1 + \left(\frac{Pe_1}{Pe_2} \right)^3 \left\{ \left[\frac{\phi_1 - \phi_{1,\tau=0}}{\frac{\phi_m \phi_{1,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{1,\tau=0}} \right]^{\frac{Pe_2}{Pe_1}} \left[\frac{\phi_m \phi_{2,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{2,\tau=0} \right] + \phi_{2,\tau=0} \right\} \right) \right. \\ &\left. \phi_m \left(\phi_m - \phi_1 - \left\{ \left[\frac{\phi_1 - \phi_{1,\tau=0}}{\frac{\phi_m \phi_{1,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{1,\tau=0}} \right]^{\frac{Pe_2}{Pe_1}} \left[\frac{\phi_m \phi_{2,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{2,\tau=0} \right] + \phi_{2,\tau=0} \right\} \right)^{-1} \right]. \end{aligned} \quad (S2.30)$$

Separating the variables and integrating gives

$$\begin{aligned} (1 - \tau) \int_{X, \text{boundary}}^X dX &= \left(\frac{Pe_2}{Pe_1} \right) \{ \phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0}) \} \int_{\phi_{1, \text{boundary}}}^{\phi_1} \frac{1}{(\phi_1 - \phi_{1,\tau=0})} \\ &\left(1 - \phi_1 - \left\{ \left[\frac{\phi_1 - \phi_{1,\tau=0}}{\frac{\phi_m \phi_{1,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{1,\tau=0}} \right]^{\frac{Pe_2}{Pe_1}} \left[\frac{\phi_m \phi_{2,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{2,\tau=0} \right] + \phi_{2,\tau=0} \right\} \right)^{7.55} \\ &\left[\left(\phi_1 + \left(\frac{Pe_1}{Pe_2} \right)^3 \left\{ \left[\frac{\phi_1 - \phi_{1,\tau=0}}{\frac{\phi_m \phi_{1,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{1,\tau=0}} \right]^{\frac{Pe_2}{Pe_1}} \left[\frac{\phi_m \phi_{2,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{2,\tau=0} \right] + \phi_{2,\tau=0} \right\} \right) \right. \end{aligned}$$

$$\begin{aligned}
& (-1) \left(\phi_m - \phi_1 - \left\{ \left[\frac{\phi_1 - \phi_{1,\tau=0}}{\left[\frac{\phi_m \phi_{1,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{1,\tau=0} \right]^{\frac{Pe_2}{Pe_1}}} \left[\frac{\phi_m \phi_{2,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{2,\tau=0} \right] + \phi_{2,\tau=0} \right\} \right)^{-2} \\
& \left(-1 - \frac{\left(\frac{Pe_2}{Pe_1} \right) [\phi_1 - \phi_{1,\tau=0}] \left(\frac{Pe_2}{Pe_1} - 1 \right) \left[\frac{\phi_m \phi_{2,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{2,\tau=0} \right]}{\left[\frac{\phi_m \phi_{1,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{1,\tau=0} \right]^{\frac{Pe_2}{Pe_1}}} \right) \\
& + \left(\phi_m - \phi_1 - \left\{ \left[\frac{\phi_1 - \phi_{1,\tau=0}}{\left[\frac{\phi_m \phi_{1,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{1,\tau=0} \right]^{\frac{Pe_2}{Pe_1}}} \left[\frac{\phi_m \phi_{2,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{2,\tau=0} \right] + \phi_{2,\tau=0} \right\} \right)^{-1} \\
& \left(1 + \left(\frac{Pe_1}{Pe_2} \right)^2 \frac{\left\{ [\phi_1 - \phi_{1,\tau=0}] \left(\frac{Pe_2}{Pe_1} - 1 \right) \left[\frac{\phi_m \phi_{2,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{2,\tau=0} \right] \right\}}{\left[\frac{\phi_m \phi_{1,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{1,\tau=0} \right]^{\frac{Pe_2}{Pe_1}}} \right) \Bigg] d\phi_1. \tag{S2.31}
\end{aligned}$$

For the boundary condition, arbitrarily set $X = 0$ at $(\phi_{1,X=0} + \phi_{2,X=0}) = [(\phi_{1,\tau=0} + \phi_{2,\tau=0}) + (\phi_{1,X \rightarrow \infty} + \phi_{2,X \rightarrow \infty})]/2$, where $(\phi_{1,X \rightarrow \infty} + \phi_{2,X \rightarrow \infty})$ is found using equation (S2.6):

$$(\phi_{1,X=0} + \phi_{2,X=0}) = \frac{(\phi_{1,\tau=0} + \phi_{2,\tau=0}) + \phi_m}{2}. \tag{S2.32}$$

By using equation (S2.32) to eliminate $\phi_{2,X=0}$ from equation (S2.30), the following equation for $\phi_{1,X=0}$ is obtained:

$$\frac{\phi_{1,X=0} - \phi_{1,\tau=0}}{\frac{\phi_m \phi_{1,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{1,\tau=0}} = \left[\frac{\frac{(\phi_{1,\tau=0} + \phi_{2,\tau=0}) + \phi_m}{2} - \phi_{1,X=0} - \phi_{2,\tau=0}}{\frac{\phi_m \phi_{2,\tau=0}}{(\phi_{1,\tau=0} + \phi_{2,\tau=0})} - \phi_{2,\tau=0}} \right]^{\frac{Pe_1}{Pe_2}}. \tag{S2.33}$$

This can be solved numerically, or algebraically in special cases, for $\phi_{1,X=0}$. Hence equation (S2.31) can now be numerically integrated to find the left-hand side, $X(1 - \tau)$, as a function of ϕ_1 .

S2.2 Diffusiophoresis

S2.2.1 Find $P(\tau)$

Using the same method as in Sections S2.1.1–S2.1.2, $P(\tau)$ can be shown to have the same form as for the diffusion-only case, equation (S2.12): Using the same change of variable as before, $X = [\xi - P(\tau)]\text{Pe}_2$, to expand around this transition, to leading order in Pe_2 , analogous equations to equations (S2.1) and (S2.2) are obtained, with the inclusion of the diffusiophoretic flux. The boundary conditions around $P(\tau)$ are as in equations (S2.3)–(S2.8), but with the flux terms also including enhanced diffusiophoresis. Similar equations to (S2.9)–(S2.12) can be written to obtain the same expression for $P(\tau)$. Physically, this is because the front's position is again governed by the overall mass balance.

S2.2.2 Form differential equations for $X(\phi_1, \phi_2)$

This section forms differential equations for $X(\phi_1, \phi_2)$, which can be solved to give the profile in the film region around $P(\tau)$, from the bottom of the film up to just beneath $Q(\tau)$.

Similarly to Section S2.1.3, equation (S2.11) is substituted into the equations formed from changing the variables in equations (3.3) and (3.4). Analogous equations to (S2.13) and (S2.14), but including the diffusiophoresis terms, result. Integrating once, from the bottom of the film to a point in the film, and using the boundary conditions, gives

$$\begin{aligned} \frac{\phi_m(\phi_1 - \phi_{1,\tau=0})}{\phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0})} &= \left(\frac{\text{Pe}_2}{\text{Pe}_1}\right) \frac{1}{(1-\tau)} (1 - \phi_1 - \phi_2) \\ &\quad \left[\frac{[\phi_1 K_{11}(\phi_1, \phi_2) - 3\pi(\phi_1)^2 \phi_2 K_P(\phi_1, \phi_2)]}{\left(\phi_1 + \left(\frac{\text{Pe}_1}{\text{Pe}_2}\right)^3 \phi_2 \frac{d\mu_2/dX}{d\mu_1/dX}\right)} + \frac{\phi_1 \phi_2 K_{12}(\phi_1, \phi_2)}{\left(\left(\frac{\text{Pe}_2}{\text{Pe}_1}\right)^3 \phi_1 \frac{d\mu_1/dX}{d\mu_2/dX} + \phi_2\right)} \left(\frac{\text{Pe}_2}{\text{Pe}_1}\right)^3 \right] \\ &\quad \frac{d}{dX} \left[\left(\phi_1 + \left(\frac{\text{Pe}_1}{\text{Pe}_2}\right)^3 \phi_2 \right) Z(\phi_1, \phi_2) \right] \end{aligned} \quad (\text{S2.34})$$

and

$$\begin{aligned} \frac{\phi_m(\phi_2 - \phi_{2,\tau=0})}{\phi_m - (\phi_{1,\tau=0} + \phi_{2,\tau=0})} &= \frac{1}{(1-\tau)} (1 - \phi_1 - \phi_2) \\ &\quad \left[\left(\frac{\text{Pe}_1}{\text{Pe}_2}\right)^3 \left[\frac{\phi_1 \phi_2 K_{21}(\phi_1, \phi_2) + 3\pi\left(\frac{\text{Pe}_2}{\text{Pe}_1}\right) \phi_1 \phi_2 (1 - \phi_2) K_P(\phi_1, \phi_2)}{\left(\phi_1 + \left(\frac{\text{Pe}_1}{\text{Pe}_2}\right)^3 \phi_2 \frac{d\mu_2/dX}{d\mu_1/dX}\right)} \right] + \frac{\phi_2 K_{22}(\phi_1, \phi_2)}{\left(\left(\frac{\text{Pe}_2}{\text{Pe}_1}\right)^3 \phi_1 \frac{d\mu_1/dX}{d\mu_2/dX} + \phi_2\right)} \right] \end{aligned}$$

$$\frac{d}{dX} \left[\left(\left(\frac{Pe_2}{Pe_1} \right)^3 \phi_1 + \phi_2 \right) Z(\phi_1, \phi_2) \right]. \quad (S2.35)$$

S2.2.3 Approximate solution for $\phi_1(\phi_2)$ around $P(\tau)$

As explained in the main text, the denominators of the right-hand sides of equations (S2.34) and (S2.35) should not be approximated further. Considering the case $K_{12}(\phi_1, \phi_2) = K_{21}(\phi_1, \phi_2) = 0$ and $K_{11}(\phi_1, \phi_2) = K_{22}(\phi_1, \phi_2) = K_P(\phi_1, \phi_2)$, equating equations (S2.34) and (S2.35) results in

$$\frac{[\phi_1 - \phi_{1,\tau=0}]}{[\phi_2 - \phi_{2,\tau=0}]} = \frac{[\phi_1 - 3\pi(\phi_1)^2\phi_2]}{\left[3\pi\phi_1\phi_2(1-\phi_2) + \frac{\left(\frac{Pe_2}{Pe_1}\right)^2\phi_2\left(\phi_1 + \left(\frac{Pe_1}{Pe_2}\right)^3\phi_2\frac{d\mu_2/dX}{d\mu_1/dX}\right)}{\left(\left(\frac{Pe_2}{Pe_1}\right)^3\phi_1\frac{d\mu_1/dX}{d\mu_2/dX} + \phi_2\right)} \right]}. \quad (S2.36)$$

Then, using $\partial\mu_1/\partial\mu_2 = \partial \ln \phi_1 / \partial \ln \phi_2$ gives

$$\frac{[\phi_1 - \phi_{1,\tau=0}]}{[\phi_2 - \phi_{2,\tau=0}]} = \frac{[1 - 3\pi\phi_1\phi_2]}{\left[3\pi\phi_2(1-\phi_2) + \frac{\left(\frac{Pe_2}{Pe_1}\right)^2\left(1 + \left(\frac{Pe_1}{Pe_2}\right)^3\frac{d\phi_2}{d\phi_1}\right)}{\left(\left(\frac{Pe_2}{Pe_1}\right)^3\frac{d\phi_1}{d\phi_2} + 1\right)} \right]}. \quad (S2.37)$$

This rearranges to yield a quadratic in $d\phi_1/d\phi_2$:

$$\begin{aligned} & \left(\frac{d\phi_1}{d\phi_2} \right)^2 \left(\frac{Pe_2}{Pe_1} \right)^3 \left[[1 - 3\pi\phi_1\phi_2] - \frac{[\phi_1 - \phi_{1,\tau=0}]}{[\phi_2 - \phi_{2,\tau=0}]} 3\pi\phi_2(1 - \phi_2) \right] \\ & + \left(\frac{d\phi_1}{d\phi_2} \right) \left[- \left\{ 3\pi\phi_2(1 - \phi_2) + \left(\frac{Pe_2}{Pe_1} \right)^2 \right\} \frac{[\phi_1 - \phi_{1,\tau=0}]}{[\phi_2 - \phi_{2,\tau=0}]} + [1 - 3\pi\phi_1\phi_2] \right] \\ & + \left[- \left(\frac{Pe_1}{Pe_2} \right) \frac{[\phi_1 - \phi_{1,\tau=0}]}{[\phi_2 - \phi_{2,\tau=0}]} \right] = 0. \end{aligned} \quad (S2.38)$$

Note that equation (S2.38) is independent of $K_{ij}(\phi_1, \phi_2)$, $K_P(\phi_1, \phi_2)$, $Z(\phi_1, \phi_2)$ and τ . The quadratic can be solved for $d\phi_1/d\phi_2$, taking the positive root. The constant term in the quadratic needs to be included, despite its coefficient of Pe_1/Pe_2 , in order to obtain accurate results. The resulting solution for $d\phi_1/d\phi_2$ can be integrated numerically, with a boundary condition.

S2.2.4 Find ϕ_1 and ϕ_2 around $Q(\tau)$

Finding the values of ϕ_1 and ϕ_2 either side of the transition $Q(\tau)$ will provide a boundary condition for integrating $d\phi_1/d\phi_2$ around $P(\tau)$, as well as allowing the asymptotic solution for the upper part of the film to be constructed. Using the change of variable $Y = [\xi - Q(\tau)]Pe_2$ to expand about this transition obtains analogous equations to equations (S2.1) and (S2.2), with the inclusion of the diffusiophoretic flux, Y replacing X and $Q(\tau)$ replacing $P(\tau)$. The boundary conditions are analogous to equations (S2.3)–(S2.8), but including the diffusiophoresis terms and replacing X with Y .

It is assumed that $Q(\tau)$ takes the form given in equation (5.3) in the main text. Then, integrating from $Y = -\infty$ to a point in the film gives

$$\begin{aligned} [\phi_1 - \phi_{1,\tau=0}]v &= \left(\frac{Pe_2}{Pe_1}\right) \frac{1}{(1-\tau)} (1 - \phi_1 - \phi_2) \\ &\quad \left[\frac{[\phi_1 K_{11}(\phi_1, \phi_2) - 3\pi(\phi_1)^2 \phi_2 K_P(\phi_1, \phi_2)]}{\left(\phi_1 + \left(\frac{Pe_1}{Pe_2}\right)^3 \phi_2 \frac{d\mu_2/dY}{d\mu_1/dY}\right)} + \frac{\phi_1 \phi_2 K_{12}(\phi_1, \phi_2)}{\left(\left(\frac{Pe_2}{Pe_1}\right)^3 \phi_1 \frac{d\mu_1/dY}{d\mu_2/dY} + \phi_2\right)} \left(\frac{Pe_2}{Pe_1}\right)^3 \right] \\ &\quad \frac{d}{dY} \left[\left(\phi_1 + \left(\frac{Pe_1}{Pe_2}\right)^3 \phi_2 \right) Z(\phi_1, \phi_2) \right] \end{aligned} \quad (S2.39)$$

and

$$\begin{aligned} [\phi_2 - \phi_{2,\tau=0}]v &= \frac{1}{(1-\tau)} (1 - \phi_1 - \phi_2) \\ &\quad \left[\left(\frac{Pe_1}{Pe_2}\right)^3 \left[\frac{\phi_1 \phi_2 K_{21}(\phi_1, \phi_2) + 3\pi\left(\frac{Pe_2}{Pe_1}\right) \phi_1 \phi_2 (1 - \phi_2) K_P(\phi_1, \phi_2)}{\left(\phi_1 + \left(\frac{Pe_1}{Pe_2}\right)^3 \phi_2 \frac{d\mu_2/dY}{d\mu_1/dY}\right)} \right] + \frac{\phi_2 K_{22}(\phi_1, \phi_2)}{\left(\left(\frac{Pe_2}{Pe_1}\right)^3 \phi_1 \frac{d\mu_1/dY}{d\mu_2/dY} + \phi_2\right)} \right] \\ &\quad \frac{d}{dY} \left[\left(\left(\frac{Pe_2}{Pe_1}\right)^3 \phi_1 + \phi_2 \right) Z(\phi_1, \phi_2) \right]. \end{aligned} \quad (S2.40)$$

Considering the case $K_{12}(\phi_1, \phi_2) = K_{21}(\phi_1, \phi_2) = 0$ and $K_{11}(\phi_1, \phi_2) = K_{22}(\phi_1, \phi_2) = K_P(\phi_1, \phi_2)$, and dividing equation (S2.39) by equation (S2.40), gives the same equation as (S2.35), but with Y replacing X . Then, using $d\mu_1/d\mu_2 = d \ln \phi_1 / d \ln \phi_2$ gives the same equation as (S2.36).

In the upper region of the film, $\phi_1 + \phi_2 \approx \phi_m$. Substituting $\phi_2 = \phi_m - \phi_1$ into equation (S2.36) results in a quadratic equation for ϕ_1 . The solution is

$$\begin{aligned}
\phi_1 = & - \left[\frac{\left(\frac{Pe_1}{Pe_2} \right)}{\left(\frac{d\phi_1}{d\phi_2} \right)} + 1 + 3\pi [\phi_{1,\tau=0} + \phi_m(1 - \phi_{2,\tau=0} - 2\phi_{1,\tau=0})] \pm \left[\left[\frac{\left(\frac{Pe_1}{Pe_2} \right)}{\left(\frac{d\phi_1}{d\phi_2} \right)} \right]^2 \right. \\
& + 6\pi \frac{\left(\frac{Pe_1}{Pe_2} \right)}{\left(\frac{d\phi_1}{d\phi_2} \right)} \{ 2\phi_{1,\tau=0} [\phi_{1,\tau=0} + \phi_{2,\tau=0} - \phi_m] + [\phi_m(1 - \phi_{2,\tau=0}) - \phi_{1,\tau=0}] + 2 \} \\
& + 9\pi^2 \{ [\phi_{1,\tau=0}^2 + \phi_m^2(1 + \phi_{2,\tau=0}^2)] + 2\phi_m [\phi_{2,\tau=0}(\phi_{1,\tau=0} - \phi_m) - \phi_{1,\tau=0}] \} \\
& \left. + 6\pi \{ [\phi_{1,\tau=0} + \phi_m(\phi_{2,\tau=0} - 1)] + 2\phi_{20}[1 - \phi_{1,\tau=0} - \phi_{2,\tau=0}] \} + 1 \right]^{\frac{1}{2}} \\
& / [6\pi(\phi_{1,\tau=0} + \phi_{2,\tau=0} - 1)]. \tag{S2.41}
\end{aligned}$$

Figure S1 plots the resulting root values as a function of $d\phi_1/d\phi_2$, for $Pe_2/Pe_1 = 2$, $\phi_{1,\tau=0} = \phi_{2,\tau=0} = 0.10$ and $\phi_m = 0.64$.

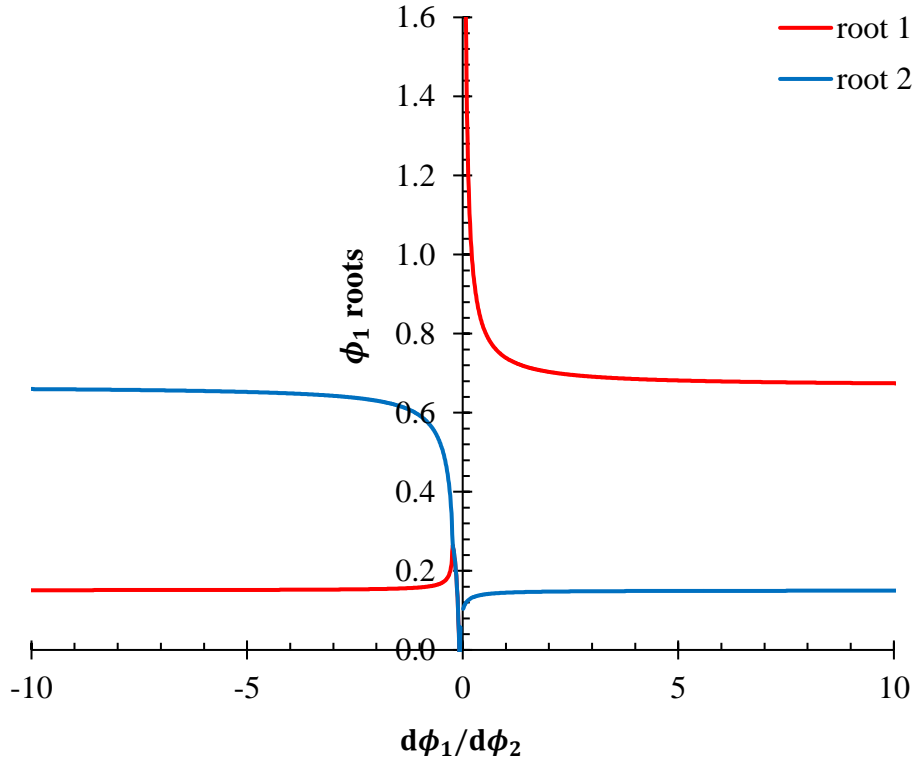


Figure S1: Plot of the roots for ϕ_1 of equation (S2.36) as a function of $d\phi_1/d\phi_2$, with $Pe_2/Pe_1 = 2$, $\phi_{1,\tau=0} = \phi_{2,\tau=0} = 0.10$ and $\phi_m = 0.64$.

Note that there is little change in the root values with $d\phi_1/d\phi_2$, except where $d\phi_1/d\phi_2$ is close to zero. This can be seen from equation (S2.41), which for small $(Pe_1/Pe_2)/(d\phi_1/d\phi_2)$ becomes

$$\begin{aligned} \phi_1 \sim & - \left[1 + 3\pi[\phi_{1,\tau=0} + \phi_m(1 - \phi_{2,\tau=0} - 2\phi_{1,\tau=0})] \right. \\ & \pm \left[9\pi^2\{[\phi_{1,\tau=0}^2 + \phi_m^2(1 + \phi_{2,\tau=0}^2)] + 2\phi_m[\phi_{2,\tau=0}(\phi_{1,\tau=0} - \phi_m) - \phi_{1,\tau=0}]\} \right. \\ & \left. \left. + 6\pi\{[\phi_{1,\tau=0} + \phi_m(\phi_{2,\tau=0} - 1)] + 2\phi_{2,\tau=0}[1 - \phi_{1,\tau=0} - \phi_{2,\tau=0}]\} + 1\right]^{\frac{1}{2}} \right] \\ & / [6\pi(\phi_{1,\tau=0} + \phi_{2,\tau=0} - 1)]. \end{aligned} \quad (S2.42)$$

When $\phi_{1,\tau=0} = \phi_{2,\tau=0} = 0.10$ and $\phi_m = 0.64$, the two roots are $\{0.151, 0.667\}$. This suggests that when the model is run for large Pe_2/Pe_1 , a constraint should be added to the model to prevent ϕ_1 from becoming larger than ϕ_m at the top surface. As equations (3.3)–(3.4) are written, only $(\phi_1 + \phi_2)$ is prevented from exceeding ϕ_m , via $Z(\phi_1, \phi_2)$, not ϕ_1 and ϕ_2 individually.

By comparison with the numerical results, it can be seen that the smaller root for ϕ_1 , denoted by ϕ_{1-} , corresponds to the region below $Q(\tau)$, whilst the larger root, denoted by ϕ_{1+} , corresponds to the region above $Q(\tau)$. Above $Q(\tau)$, a reasonable choice of $\partial\phi_1/\partial\phi_2$ appears to be around -1 . For $\phi_{1,\tau=0} = \phi_{2,\tau=0} = 0.10$, $\phi_m = 0.64$ and $Pe_2/Pe_1 = 2$, this suggests that $\phi_{1+} \sim 0.593$ above $Q(\tau)$. For the root below $Q(\tau)$, there is considerably less variation in its value with $d\phi_1/d\phi_2$ as $d\phi_1/d\phi_2$ approaches 0. Therefore, it is considered reasonable to take the solution for small $(Pe_1/Pe_2)/(d\phi_1/d\phi_2)$. The numerical simulation gives values of $\phi_{1+} \sim 0.60$ and $\phi_{1-} \sim 0.15$ above and below $Q(\tau)$, respectively, so the roots from the asymptotic solution are in good agreement.

S2.2.5 Solve for $X(\phi_1, \phi_2)$ around $P(\tau)$

The root ϕ_{1-} , and corresponding value of ϕ_2 , $\phi_{2-} = \phi_m - \phi_{1-}$, can be used as the boundary condition to numerically integrate $d\phi_1/d\phi_2$ from equation (S2.38). The resulting numerical solution for $\phi_1(\phi_2)$ can be directly compared with numerical results, or it can be used with either equation (S2.34) or equation (S2.35) to find $X(\phi_1)$. For example, rearranging equation (S2.34) gives

$$\begin{aligned}
(1 - \tau) \int_{X, \text{boundary}}^X dX &= [\phi_m - (\phi_{1, \tau=0} + \phi_{2, \tau=0})] \left(\frac{\text{Pe}_2}{\text{Pe}_1} \right) \int_{\phi_{1, \text{boundary}}}^{\phi_1} \frac{(1 - \phi_1 - \phi_2)}{\phi_m(\phi_1 - \phi_{1, \tau=0})} \\
&\left[\frac{[\phi_1 K_{11}(\phi_1, \phi_2) - 3\pi(\phi_1)^2 \phi_2 K_P(\phi_1, \phi_2)]}{\left(\phi_1 + \left(\frac{\text{Pe}_1}{\text{Pe}_2} \right)^3 \phi_2 \frac{d\mu_2/dX}{d\mu_1/dX} \right)} + \frac{\phi_1 \phi_2 K_{12}(\phi_1, \phi_2)}{\left(\left(\frac{\text{Pe}_2}{\text{Pe}_1} \right)^3 \phi_1 \frac{d\mu_1/dX}{d\mu_2/dX} + \phi_2 \right)} \left(\frac{\text{Pe}_2}{\text{Pe}_1} \right)^3 \right] \\
&\frac{d}{d\phi_1} \left[\left(\phi_1 + \left(\frac{\text{Pe}_1}{\text{Pe}_2} \right)^3 \phi_2 \right) Z(\phi_1, \phi_2) \right] d\phi_1, \tag{S2.43}
\end{aligned}$$

where ϕ_2 is a numerical function of ϕ_1 . The derivative term on the right-hand side of equation (S2.43) can either be evaluated numerically, or by using the chain rule and the result for $d\phi_1/d\phi_2$ from equation (S2.38).

As for the diffusion-only case, for the boundary condition, set $X = 0$ at $(\phi_{1, X=0} + \phi_{2, X=0}) = [(\phi_{1, \tau=0} + \phi_{2, \tau=0}) + (\phi_{1, X \rightarrow \infty} + \phi_{2, X \rightarrow \infty})]/2$. The value of ϕ_1 which, in conjunction with its corresponding value of ϕ_2 , meets this condition with the smallest error is selected numerically as the point where $X = 0$. The whole right-hand side of equation (S2.43) can then be numerically integrated, giving the left-hand side, $X(1 - \tau)$, as a function of ϕ_1 .

S2.2.6 Find v for $Q(\tau)$

Now that $X(\phi_1, \phi_2)$ around $P(\tau)$ has been found, this can be used to calculate the velocity of the other transition, $Q(\tau)$. This is a sharp transition in ϕ_1 and ϕ_2 , so v can be found by integrating either equation obtained from the changing the variables in equations (3.3) and (3.4) to Y across this transition. For example, integrating equation (3.3) with the change of variables and the top boundary condition gives

$$\begin{aligned}
[\phi_{1+} - \phi_{1-}]v &= \phi_{1+} - \left\{ \left(\frac{\text{Pe}_2}{\text{Pe}_1} \right) \frac{1}{(1-\tau)} [(1 - \phi_1 - \phi_2)] \right. \\
&\left[\frac{[\phi_1 K_{11}(\phi_1, \phi_2) - 3\pi(\phi_1)^2 \phi_2 K_P(\phi_1, \phi_2)]}{\left(\phi_1 + \left(\frac{\text{Pe}_1}{\text{Pe}_2} \right)^3 \phi_2 \frac{d\mu_2/dY}{d\mu_1/dY} \right)} + \frac{\phi_1 \phi_2 K_{12}(\phi_1, \phi_2)}{\left(\left(\frac{\text{Pe}_2}{\text{Pe}_1} \right)^3 \phi_1 \frac{d\mu_1/dY}{d\mu_2/dY} + \phi_2 \right)} \left(\frac{\text{Pe}_2}{\text{Pe}_1} \right)^3 \right] \\
&\left. \frac{d}{dY} \left[\left(\phi_1 + \left(\frac{\text{Pe}_1}{\text{Pe}_2} \right)^3 \phi_2 \right) Z(\phi_1, \phi_2) \right] \right\}_{\phi_{1-}}. \tag{S2.44}
\end{aligned}$$

The values $\{\phi_{1-}, \phi_{1+}\}$ were found in Section S2.2.4. The value of the second term on the right-hand side of equation (S2.44) can be numerically evaluated using the solution for $X(\phi_1, \phi_2)$ around $P(\tau)$ from Section S2.2.5. This term should be evaluated as $\phi_1 \rightarrow \phi_{1-}$

from below. The non-derivative part of this term can be found directly from $\phi_1(\phi_2)$, with the denominators requiring the value of $d\phi_1/d\phi_2$ from equation (S2.38). The derivative part of this term can be found by noting that, at constant τ , $d/dY = d/dX$. The derivative term can then be evaluated either numerically, or using the chain rule and the value of $d\phi_1/d\phi_2$. Note that equation (S2.44) is equivalent to a mass balance on ϕ_1 across $Q(\tau)$.

In this manner, for the case in Figure 9 in the main text, the second term on the right-hand side of equation (S2.44) is calculated to be 0.074, giving a value for ν of 1.17. This is in excellent agreement with the numerical results, which gave $\nu = 1.16$. Having found asymptotic solutions for ϕ_{1-} , ϕ_{1+} and ν completes the construction of the solution around $Q(\tau)$. Combined with the asymptotic solution around $P(\tau)$ from Section S2.2.5, this completes the construction of the whole film profile.

S3 Functional forms for the sedimentation coefficients

Sections S3, S4 and S5 explore the effects of varying the sedimentation coefficients, initial concentration, and close-packing volume fraction, respectively.

S3.1 Region of applicability

The functional form used for the sedimentation coefficients in the examples in the main text is $K_{ii}(\phi_1, \phi_2) = (1 - \phi_1 - \phi_2)^{6.55}$. To explain the concentration range in which this functional form is valid, Figure S2 is plotted. Note that, as mentioned in Section 4 of the main text, in a bidisperse mixture, ϕ_m will generally be a function of composition, and this will in turn change where the solution becomes fully hydrodynamically hindered. For this reason, and also because ϕ_m is taken as constant in the examples in this work, Figure S2 is plotted for a one-component solution.

From equations (2.13) and (2.22) in the main text, it can be seen that the particle flux for a one-component solution will contain a factor of $Kd(\phi Z)/d\phi$. This is a function of the particle concentration, ϕ , so Figure S2 plots $Kd(\phi Z)/d\phi$ for different example combinations of functions for $K(\phi)$ and $Z(\phi)$.

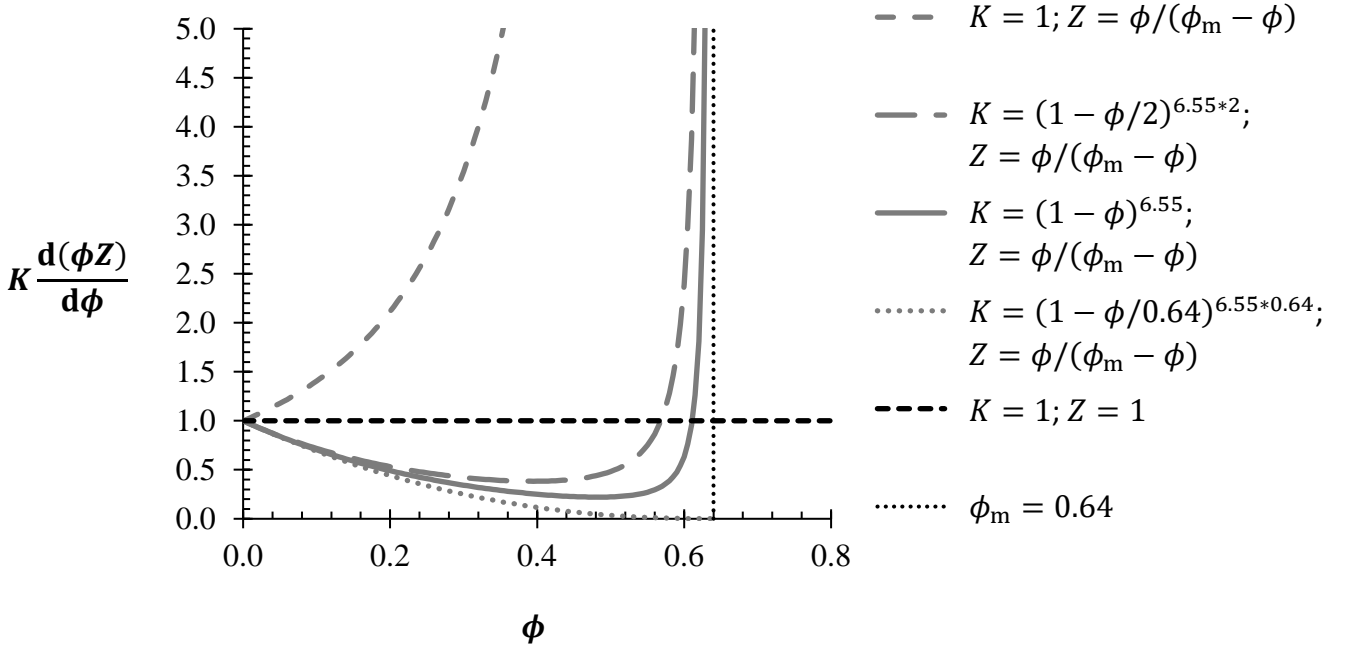


Figure S2: Plot of $Kd(\phi Z)/d\phi$ against ϕ for different forms of $K(\phi)$ and $Z(\phi)$. The solid line represents the forms used in this present work, and is an improvement over $K = 1; Z = 1$ where $Kd(\phi Z)/d\phi$ is less than one.

The corresponding plots of $K(\phi)$ against ϕ are shown in Figure S3.

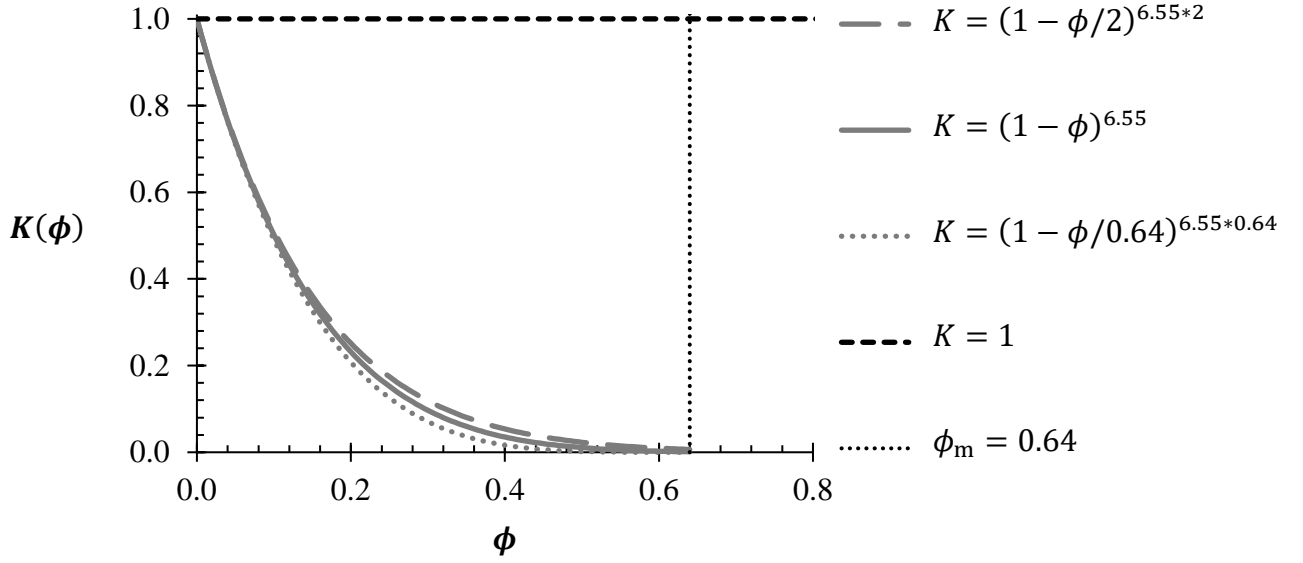


Figure S3: Plot of $K(\phi)$ against ϕ for different forms of $K(\phi)$.

The functional form used in this work is not applicable near to close-packing, since as $\phi_1 + \phi_2 \rightarrow \phi_m$, the functional forms used produce $K_{ii}(\phi_1, \phi_2)Z(\phi_1, \phi_2) \rightarrow \infty$. This is not physical since one expects the particle motion to cease as $\phi_1 + \phi_2 \rightarrow \phi_m$. Apart from near to close-packing, where capturing the exact particle behaviour is not so important, the expressions used are otherwise intended to be valid for concentrated solutions, which is important. Hence results are not shown for late drying times in Figures 3–9 in the main text. However, due to increased hydrodynamic hindrance near close-packing, it is expected that the latest results shown would reflect those at the end of drying.

The functional form chosen for $K_{ii}(\phi_1, \phi_2)$ otherwise fits the required physical constraints, which are equalling unity for an infinitely dilute solution, and then decreasing monotonically. The analytical expressions for dilute multicomponent solution provided by Batchelor (1983) support that the expressions used for $K(\phi_1, \phi_2)$ in this work are reasonable. As was stated by Trueman *et al.* (2012a), the sedimentation coefficients could be obtained experimentally for concentrated solution, but not analytically.

Shown for comparison in Figure S2, the model of Zhou *et al.* (2017) corresponds to the line for $K = 1$; $Z = 1$. With this model, $Kd(\phi Z)/d\phi$ does not fall as the solution becomes more concentrated, as would be expected physically. Whilst the form used for K in this present

work is not applicable quite up to close-packing, it does allow a more realistic model to be run to higher concentrations than the model of Zhou *et al.* The concentration correction factor $Kd(\phi Z)/d\phi$ continues to decrease until the turning point at $\phi = 0.48$, at which $Kd(\phi Z)/d\phi = 0.014$. However, this model is still an improvement over the model of Zhou *et al.* whilst $Kd(\phi Z)/d\phi < 1$. This is the case for $\phi < 0.61$, beyond which this model is not physical.

Since the diffusiophoretic flux has extra factor of (ϕ_1, ϕ_2) compared to the diffusive flux, it is important to be able to model beyond the dilute region in order to probe the effect of diffusiophoresis. This is a motivation for extending the model of Zhou *et al.* to higher concentrations. The numerical solutions of Zhou *et al.* are not presented beyond early stages of drying, with the largest concentrations shown being around $\phi = 0.15$. Nevertheless, Figure S2 shows that even by this concentration, hydrodynamic hindrance would already have reduced K to significantly less than 1.

Also shown for comparison in Figure S2 is $K = 1; Z = \phi/(\phi_m - \phi)$. This line shows that it is essential for a decreasing function for K to be used with the osmotic pressure approach. Otherwise, as demonstrated here with $K = 1$, the flux unphysically increases with ϕ at all concentrations, as the osmotic pressure diverges.”

The functional form used in this work, $K = (1 - \phi)^{6.55}$, is just one example of a form of K which meets the requirements of approximating to $1 - 6.55\phi$ for dilute solution and being monotonically decreasing. More generally, K of the form $K = (1 - \phi/K_{\text{factor}})^{6.55 \cdot K_{\text{factor}}}$, where $K_{\text{factor}} \geq \phi_m$ to ensure non-negativity of K , will meet these requirements. Figure S2 therefore additionally plots examples for $K_{\text{factor}} = 0.64$ and $K_{\text{factor}} = 2$. As K_{factor} is decreased to ϕ_m , the region in ϕ of the form’s applicability increases slightly. However, it also led to increased numerical difficulties (Figure S4), due to decreased stability near close-packing. Furthermore, Figure S3 shows that there is little difference in the plots of K against ϕ as K_{factor} is varied.

S3.2 Model results with different forms of sedimentation coefficients

The model examples with $Pe_1 = 0.70$ and $Pe_2 = 1.40$ from the main text for diffusion only, diffusiophoresis and enhanced diffusiophoresis, were rerun with a range of K_{factor} values.

The results of degree of stratification, as defined in equation (4.1) in the main text, against K_{factor} are plotted in Figure S4.

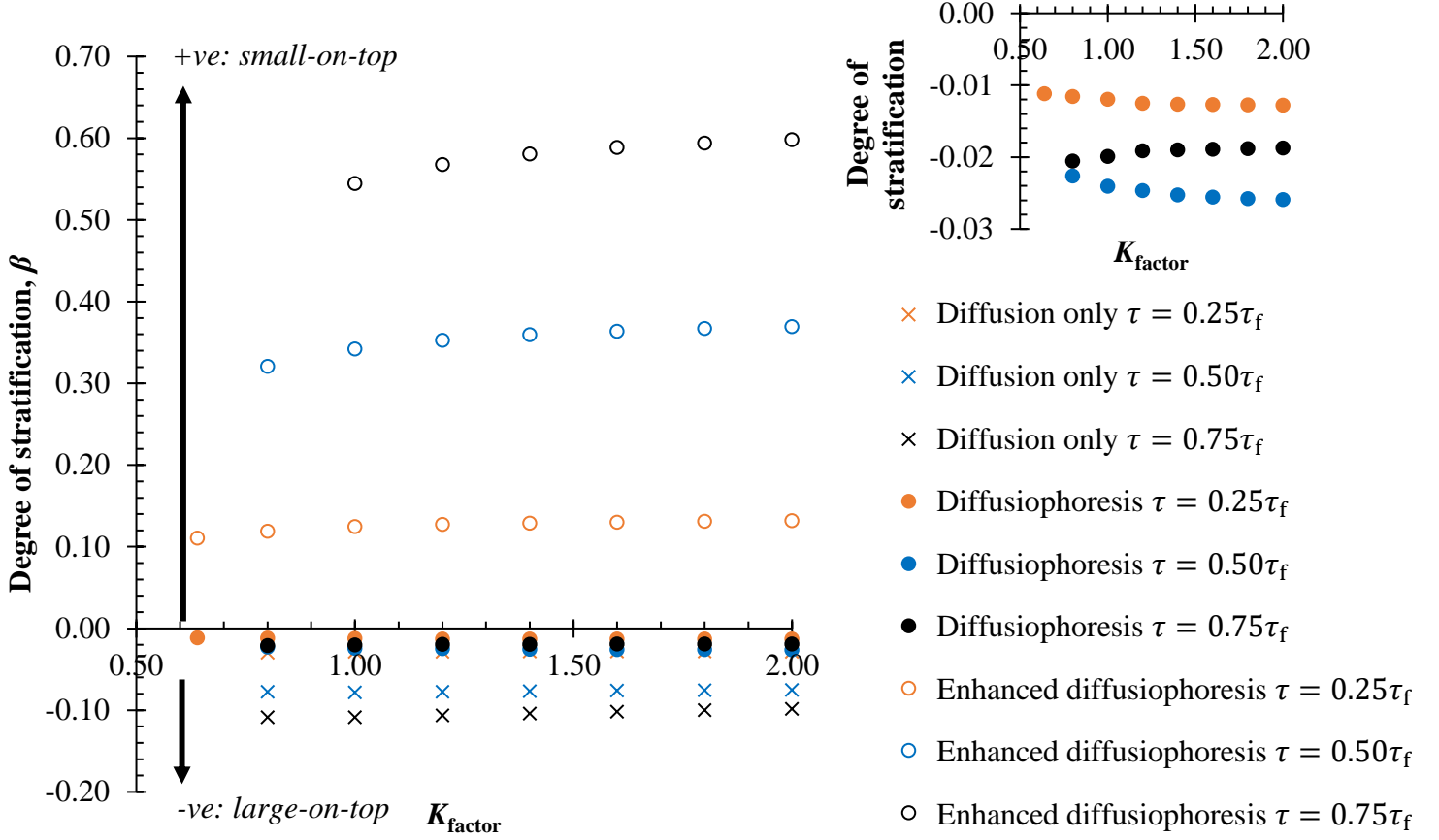


Figure S4: Plot of degree of stratification against K_{factor} for $\text{Pe}_1 = 0.70$ and $\text{Pe}_2 = 1.4$. The data points for $K_{\text{factor}} = 1$ correspond to Figures 3b, 4b and 5b in the main manuscript. Inset: zoom in on the diffusiophoresis model data points. Missing data points are due to numerical difficulties.

The key learning from Figure S4 is that there is little variation in β as K_{factor} is varied. Hence whilst the main text adopted $K_{\text{factor}} = 1$, this has little impact on the results. This is to be expected, since there is little difference between the fluxes in Figure S2 until ϕ approaches close-packing. Therefore, the most notable differences would be expected to occur near the end of drying, if the models were run beyond their region of applicability in ϕ .

Figure S4 clearly demonstrates that the same qualitative behaviour is obtained, independent of K_{factor} : diffusion-only obtains large-on-top stratification, increasing with time; adding diffusiophoresis leads to initial large-on-top stratification, followed by small-on-top stratification as diffusiophoresis overcomes diffusion; and enhanced diffusiophoresis achieves strong small-on-top stratification, increasing with time.

S3.3 Onsager reciprocal relations

This section considers the matrix of Onsager coefficients, L_{ij} , which relates the chemical potential gradients, $\nabla\mu_j$, to fluxes, \mathbf{j}_i (Sear & Warren, 2017):

$$\mathbf{j}_i = L_{ij} \nabla\mu_j. \quad (\text{S3.2})$$

By the Onsager reciprocal relations, the matrix of Onsager coefficients is symmetric, i.e. $L_{12} = L_{21}$ (Demirel, 2007). By comparison with equation (2.13), for the *diffusion-only* model,

$$L_{12} = -\frac{1}{6\pi\eta R_1} \phi_1 \phi_2 K_{12}(\phi_1, \phi_2) \quad (\text{S3.3a})$$

and

$$L_{21} = -\frac{1}{6\pi\eta R_2} \phi_1 \phi_2 K_{21}(\phi_1, \phi_2). \quad (\text{S3.3b})$$

Therefore, in the *diffusion-only* model, whether the Onsager relations are satisfied depends on the functional forms used for $K_{12}(\phi_1, \phi_2)$ and $K_{21}(\phi_1, \phi_2)$. In using $K_{12}(\phi_1, \phi_2) = K_{12}(\phi_1, \phi_2) = 0$ to generate the example results in Figure 3, $L_{12} = L_{21}$, and the Onsager relations are satisfied.

In the *diffusion-diffusiophoresis* model, by comparison with equations (2.36) and (2.37),

$$L_{12} = -\frac{1}{6\pi\eta R_1} \phi_1 \phi_2 K_{12}(\phi_1, \phi_2) \quad (\text{S3.4a})$$

and

$$L_{21} = -\phi_1 \phi_2 K_{21}(\phi_1, \phi_2) + \frac{3\phi_1 \phi_2 (1-\phi_2) K_P(\phi_1, \phi_2)}{8\pi\eta R_1}. \quad (\text{S3.4b})$$

Again, satisfying the Onsager relations is dependent on the functional forms chosen for K_{ij} and K_p . The functional forms adopted for the examples in Figures 4–5 do not satisfy the Onsager reciprocal relations.

S4 Initial concentration

This section presents and discusses additional model results regarding the effect of varying the initial particle concentrations.

The model with diffusiophoresis (as used to obtain Figure 4) was rerun with different combinations of $\phi_{1,\tau=0}$ and $\phi_{2,\tau=0}$, for the sets of Péclet numbers that were used in Figures 3–5. The stratification regimes obtained with each combination are presented in Figure S5. The film is classified as small-on-top stratified if $\phi_1(\xi = 1) > \phi_2(\xi = 1)$ at the end of drying, and vice versa for large-on-top stratified. Since this strength of diffusiophoresis only just overcomes diffusion, outside of the $\phi_{1,\tau=0}$ - $\phi_{2,\tau=0}$ diagonal, the final film regime is determined by whichever species was initially in excess. Therefore, above the diagonal, the film remains large-on-top stratified throughout drying, whilst, below the diagonal, the film remains small-on-top stratified throughout drying.

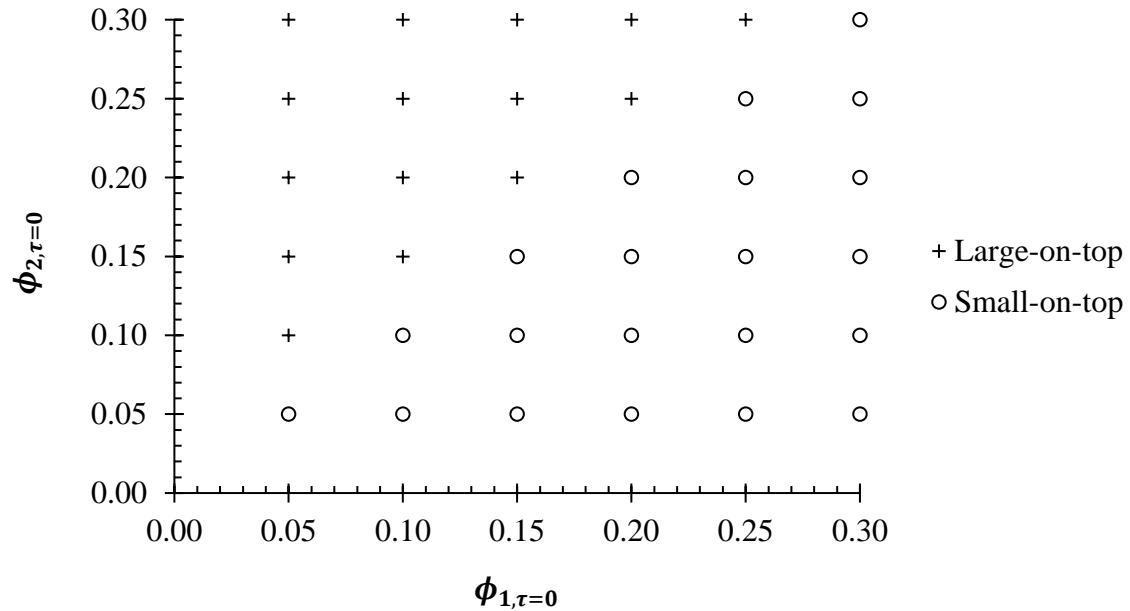


Figure S5: Map of stratification regimes obtained as the initial concentrations are varied. Note that this same map was obtained for $Pe_1 = 0.175$, $Pe_2 = 0.37$; $Pe_1 = 0.7$, $Pe_2 = 1.4$; and $Pe_1 = 2.8$, $Pe_2 = 5.6$.

Along the diagonal, at lower initial concentrations, the film begins large-on-top stratified. However, over the course of drying, diffusiophoresis becomes more important, and the film becomes small-on-top stratified. Figure S6 plots the scaled time at which the film becomes small-on-top stratified against the initial concentration, with $\phi_{1,\tau=0} = \phi_{2,\tau=0}$. The time is normalised by τ_f , which is when all the solvent would have evaporated. From a mass balance on the particles, $\tau_f = 1 - [(\phi_{1,\tau=0} + \phi_{2,\tau=0})/\phi_m]$. This normalisation accounts for the fact that initially more dilute solutions will take longer to dry.

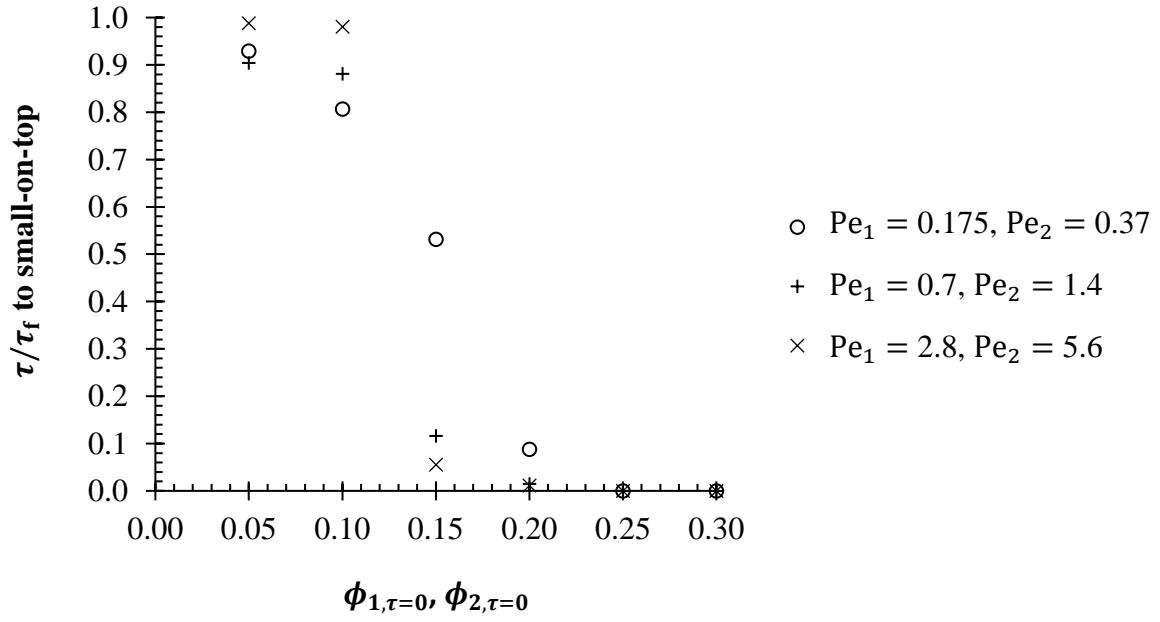


Figure S6: Plot of the normalised time taken to achieve small-on-top stratification against initial solution concentration, where $\phi_{1,\tau=0} = \phi_{2,\tau=0}$.

At each set of Péclet numbers studied, increasing the initial concentration decreases the normalised time taken for the film to become small-on-top stratified. This prediction of increasing concentration favouring small-on-top stratification is in qualitative agreement with the criteria of Sear & Warren (2017) and Sear (2018), which are of the form $Pe_1 \phi_1 \geq C$, where C is a constant. In this present work, this prediction originates from the diffusiophoretic flux containing an extra factor of (ϕ_1, ϕ_2) compared to the diffusional flux.

In Figure S6, as the Péclet numbers are increased, the shape of the plot becomes sharper. The position of the transition in this curve will reflect the concentration at which diffusiophoresis dominates over diffusion. When drying a film with an initial concentration below this, once

the film reaches this critical concentration, diffusiophoresis will still have to reverse the established large-on-top stratification, before it can start to develop the small-on-top stratification.

At all the Péclet number combinations shown in Figure S6, it appears that $\tau/\tau_f \rightarrow 1$ as $\phi_{1,\tau=0}, \phi_{2,\tau=0} \rightarrow 0$, since initially very dilute solutions will take a long time to reach concentrations at which diffusiophoresis becomes significant. Similarly, $\tau/\tau_f \sim 0$ at sufficiently large $\phi_{1,\tau=0}, \phi_{2,\tau=0}$, as diffusiophoresis dominates over diffusion from the very start of drying.

S5 Close-packing volume fraction

A similar study to Section S3.2 is carried out, this time varying the close-packing fraction between 0.52 (simple cubic) and 0.74 (cubic close-packed). Figure S7 shows the results, for $Pe_1 = 0.70$ and $Pe_2 = 1.4$, with $K_{\text{factor}} = 1$, as in the main text.

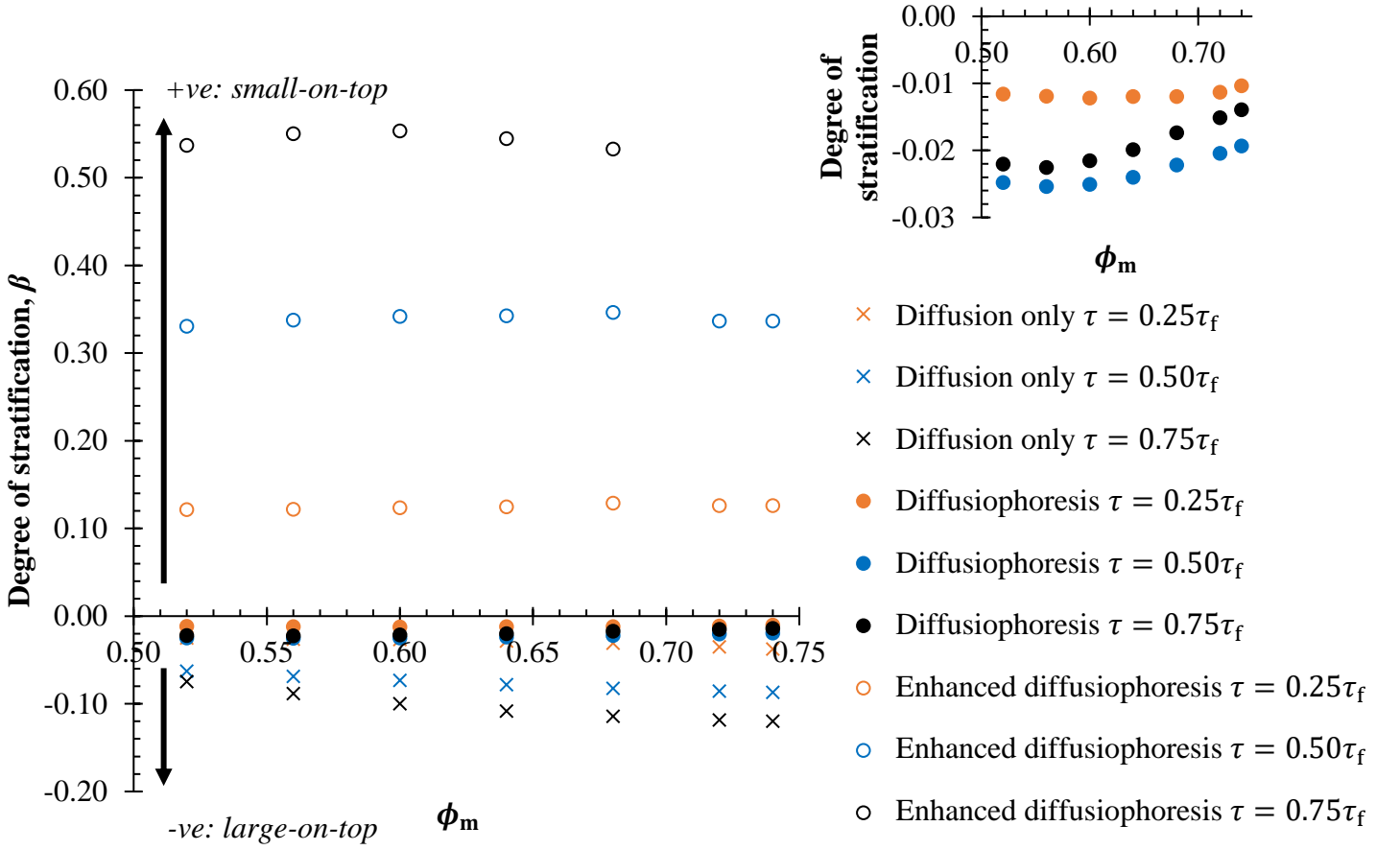


Figure S7: Plot of degree of stratification against ϕ_m for $Pe_1 = 0.70$ and $Pe_2 = 1.4$. The data points for $\phi_m = 0.64$ correspond to Figures 3b, 4b and 5b in the main manuscript. Inset: zoom in on the diffusiophoresis model data points. Missing data points are due to numerical difficulties.

Figure S7 shows little variation in degree of stratification with ϕ_m , demonstrating that the results in the main text are not qualitatively affected by the assumed value of ϕ_m .

S6 Thermodynamic consistency

This section explains the thermodynamic consistency of the approach in this work with respect to the Maxwell relations. Although equation (2.16) in the main text gives an expression for the osmotic pressure, the drying model takes inputs of the forms of $\nabla\mu_s$ (not Π) and $\nabla\mu_1/\nabla\mu_2$. Note that the derivation of equation (2.16),

$$\Pi = -\frac{\mu_s - \mu_s^0}{v_s} = \left(\frac{\phi_1}{\frac{4}{3}\pi R_1^3} + \frac{\phi_2}{\frac{4}{3}\pi R_2^3} \right) kTZ(\phi_1, \phi_2), \quad (2.16)$$

assumes that v_s does not vary with Π , since the osmotic pressure is derived from a Maxwell relation, as is described below.

The differential relationship for the Helmholtz free energy, F , for a closed system is:

$$dF = -SdT - PdV + \mu_1 dN_1 + \mu_2 dN_2 + \mu_s dN_s. \quad (S6.1)$$

where S denotes the entropy, V denotes the total volume, P denotes the pressure and N_i denotes the number of molecules of component i . Therefore, the forms of μ_1 , μ_2 , μ_s and P are all related to F via:

$$\mu_1 = \left(\frac{\partial F}{\partial N_1} \right)_{T,V,N_2,N_s}, \quad (S6.2a)$$

$$\mu_2 = \left(\frac{\partial F}{\partial N_2} \right)_{T,V,N_1,N_s}, \quad (S6.2b)$$

$$\mu_s = \left(\frac{\partial F}{\partial N_s} \right)_{T,V,N_1,N_2} \quad (S6.2c)$$

and

$$P = -\left(\frac{\partial F}{\partial V} \right)_{T,N_1,N_2,N_s}. \quad (S6.2d)$$

Using equations (S6.2c) and (S6.2d) and the properties of mixed partial derivatives, one obtains the Maxwell relationship

$$\left. \frac{\partial \mu_s}{\partial V} \right|_{T,N_1,N_2,N_s} = - \left. \frac{\partial P}{\partial N_s} \right|_{T,V,N_1,N_2}. \quad (S6.3a)$$

Hence given any form of F , the above Maxwell relationship should be obeyed automatically by the corresponding forms of Π and μ_s .

Likewise, it can be shown that the Maxwell relationships

$$\left. \frac{\partial \mu_1}{\partial V} \right|_{T, N_1, N_2, N_s} = - \left. \frac{\partial P}{\partial N_1} \right|_{T, V, N_2, N_s} \quad (\text{S6.3b})$$

and

$$\left. \frac{\partial \mu_2}{\partial V} \right|_{T, N_1, N_2, N_s} = - \left. \frac{\partial P}{\partial N_2} \right|_{T, V, N_1, N_s} \quad (\text{S6.3c})$$

will be automatically satisfied by any F .

By the triple product and chain rules, equation (6.3a) becomes

$$\left. \frac{\partial N_s}{\partial V} \right|_{T, N_1, N_2, \mu_s} = \left. \frac{\partial P}{\partial \mu_s} \right|_{T, V, N_1, N_2}. \quad (\text{S6.4})$$

Equation (6.4) can be rearranged to give

$$\Pi = - \int_{P^0}^{P^0 - \Pi} dP = - \int_{\mu_s^0}^{\mu_s} \left. \frac{\partial N_s}{\partial V} \right|_{T, N_1, N_2, \mu_s'} d\mu_s' \Big|_{T, V, N_1, N_2}, \quad (\text{S6.5})$$

where P^0 is a reference pressure and the limits are chosen such that Π increases as the solute concentration increases. Note that μ_1 increases with the concentration of solute 1. The osmotic pressure Π likewise increases with solute concentration. Consequently, the solvent chemical potential μ_s decreases with solute concentration.

Assuming that $\partial V / \partial N_s|_{T, N_1, N_2, \mu_s} = \text{constant}$ with μ_s generates equation (2.16). Whilst this is a reasonable assumption for liquids, equation (2.16) should be considered as an approximate estimate for the osmotic pressure, used merely to generate an expression for $\nabla \mu_s$. Without this assumption, the Maxwell relation (S6.3a) would be automatically satisfied.

Note that equation (2.16) can also be derived from the differential relationship for the Gibbs free energy, G :

$$dG = VdP - SdT + \mu_1 dN_1 + \mu_2 dN_2 + \mu_s dN_s. \quad (\text{S6.6})$$

Using the properties of mixed partial derivatives obtains

$$\left. \frac{\partial \mu_s}{\partial P} \right|_{T, N_1, N_2, N_s} = \left. \frac{\partial V}{\partial N_s} \right|_{T, P, N_1, N_2} = \bar{V}_s, \quad (\text{S6.7})$$

where \bar{V}_i denotes the partial molar volume of component i . Assuming that $\bar{V}_s = v_s = \text{constant}$ as pressure is varied, an assumption of incompressibility, leads to equation (2.16).

The chosen rearrangements for $\nabla\mu_1$ and $\nabla\mu_2$ (in terms of $\nabla\mu_s$ and $\nabla\mu_1/\nabla\mu_2$) in equations (2.20) and (2.21), which obey the Gibbs-Duhem equation, could be used to find a corresponding F . The corresponding form of Π will be different to equation (2.16), since we will not assume constant v_s . This leads to a small thermodynamic inconsistency in the expression for Π . However, this does not affect the thermodynamic consistency of the model, viewing it as taking $\nabla\mu_s$ directly as an input.

Alternatively, Π as defined in equation (2.16) could be used to find an expression for F (subject to an arbitrary function of integration), and in turn μ_1 and μ_2 . The resulting expressions for μ_1 from these two approaches can be compared. Any resulting difference would be due to assuming constant v_s when deriving equation (2.16). For clarity, the one-component case is used for this comparison. Following the relationships from Heyes & Santos (2016), when Π is defined as in equation (2.16), the excess chemical potential of component one (compared to an ideal gas), μ_1^{ex} , is given by

$$\mu_1^{\text{ex}}/kT = c(\phi_1), \quad (\text{S6.8})$$

where

$$\phi_1 c'(\phi_1) = Z(\phi_1) - 1. \quad (\text{S6.9})$$

Hence

$$c(\phi_1) = -\ln(\phi_m - \phi_1). \quad (\text{S6.10})$$

Adding on the ideal potential term, μ_1^{id} , gives:

$$\frac{\nabla\mu_1}{kT} = \nabla\mu_1^{\text{id}} + \nabla\mu_1^{\text{ex}} = \left[\frac{1}{(\phi_m - \phi_1)} + \frac{1}{\phi_1} \right] \nabla\phi_1 = \left[\frac{\phi_m}{\phi_1(\phi_m - \phi_1)} \right] \nabla\phi_1 \quad (\text{S6.11})$$

This is plotted in Figure S8.

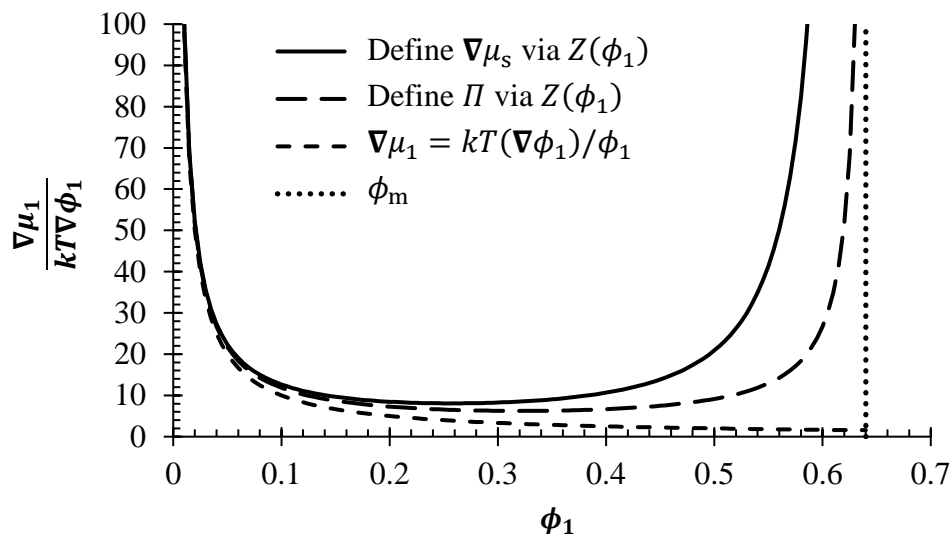


Figure S8: Plot comparing different forms of the gradient of the chemical potential of the solute, for a one-component solution. The method in this work defines $\nabla\mu_s$. An alternative approach of defining Π is also shown, along with a dilute entropic expression.

Both approaches agree well when the solution is dilute. Both diverge at close-packing, but with the approach in this work starting to diverge sooner. More disagreement as the solution becomes more concentrated would be expected, as the solution diverges from ideality, and \bar{V}_s varies more. Note that these two approaches are different thermodynamic models. The difference between them despite being based upon the same Z is due to assuming incompressibility in the derivation for Π .

References

Demirel, Y. (2007). Heat and mass transfer, in *Nonequilibrium thermodynamics*, 2nd ed. (pp. 363–413), Elsevier.