Horizontal drying fronts in films of colloidal dispersions: influence of hydrostatic pressure and collective diffusion

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# **Electronic Supplementary Information**

Schemes of drying fronts



Schematic (above) of a drying colloid showing normal (vertical, z direction) and lateral (horizontal, x direction) drying fronts moving at speeds  $S_N$  and  $S_L$ , respectively.  $S_L >> S_N$ . For clarity, lateral drying fronts in the y direction are not represented but also exist.

In the case of rigid particles, when one zooms onto a horizontal drying front (below) one sees that two fronts can be distinguished: a compaction front where particles agglomerate and a water front separating the wet and dry gel regions.



#### Fluid velocity in the fluid domain tacking hydrostatics into account

In the following, we derive the fluid velocity in the fluid domain within the lubrication approximation in presence of hydrostatic pressure, for a simple case (1D) of a film spreading on a substrate with  $P_A$ ,  $P_B$ ,  $P_C$ ,  $P_D$  the pressures at different points in the film:



$$P_{A} - P_{B} + P_{B} - P_{C} + P_{C} - P_{D} + P_{D} - P_{A} = 0$$

Schematic of a sample during drying. Each point on the schematic has a specific pressure.

Where:

•  $P_A - P_D \sim 0$ ,

• 
$$P_A - P_B \sim \gamma \frac{d^2 h(x)}{dx^2}$$
,  $h(x) = height of the film at position x.$ 

• 
$$P_B - P_C \sim \int_C^B \vec{\nabla} p. \vec{dl} = \int_{x_C}^{x_B} \frac{dp}{dx}. dx_d$$

•  $P_C - P_D \sim + \rho g(h_\infty - h_C) = \rho g(h_\infty - h_B) = \rho g(h_\infty - h(x_B))$  here  $h_\infty$  represents the maximum height of the film.

The characteristic time of establishment of hydrostatic pressures is  $\sim H_0/C_s$ . Where  $H_0$  is the initial height of the sample and  $C_s$  is a constant.

The integral of the pressure circuit gives:

$$\gamma \frac{d^2 h(x_B)}{dx^2} + \int_{x_C}^{x_B} \frac{dp}{dx} dx + \rho g(h_{\infty} - h(x_B)) = 0$$

Within the lubrication approximation, the profile of horizontal fluid velocity is given by Poiseuille's law. The mean velocity in the horizontal direction is

$$< u > = -K \frac{dP}{dx}$$

The characteristic time of Poiseuille is:

$$\frac{{H_0}^2}{\mu} = \frac{\rho H_0^2}{\eta} = \tau_P$$

With  $\mu$  the kinematic viscosity and  $\eta$  the dynamic viscosity. It has to be noted that every relaxation faster than  $\tau_P$  is likely not to be well described using the lubrication approximation.

$$K = \frac{h^2}{3\eta}$$
$$\tau_P = 3\rho K = \frac{\rho h^2}{\eta}$$

Using these equations in the pressure circuit gives:

$$\gamma \frac{d^2 h(x_B)}{dx^2} + \int_{x_C}^{x_B} -\frac{\langle u \rangle (x)}{K(x)} dx + \rho g(h_{\infty} - h(x_B)) = 0$$
$$\gamma \frac{d^3 h(x_B)}{dx^3} - \frac{\langle u \rangle (x_B)}{K(x_B)} - \rho g \frac{dh}{dx_B} = 0$$

Therefore:

$$h < u >= K \left[ \gamma \frac{d^3 h}{dx^3} - \rho g \frac{dh}{dx} \right] h = \frac{h^3}{3\eta} \left[ \gamma \frac{d^3 h}{dx^3} - \rho g \frac{dh}{dx} \right]$$

The variation of h within an elementary volume with respect to time is given by:

$$dx(h(x,t+dt) - h(x,t))dt = dt(h < u > (x+dx,t) + h < u > (x,t)) - \dot{E}dtdx$$

Thus:

$$\frac{\partial h}{\partial t} dx dt = -dt dx \frac{\partial}{\partial x} (h < u >) - \dot{E} dt dx$$
$$\dot{E} + \frac{\partial h}{\partial t} = \frac{\partial}{\partial t} (h_{\infty} - h(x, t))$$
$$\frac{\partial}{\partial t} (h_{\infty} - h(x, t)) = \frac{\partial}{\partial x} \left( \frac{h^3}{3\eta} \left[ \gamma \frac{d^3 h}{dx^3} - \rho g \frac{dh}{dx} \right] \right)$$

## Front position determination (ImageJ)

ImageJ was used in order to determine the compaction front position. The photograph is first converted into a grey scale image. Then, the intensity along a diameter (for the circular geometry) or along an axis of symmetry (for the rectangular deposit) is computed. An example of such a profile is given in Fig S1 below. From this profile, we determine manually the two compaction fronts (denoted by arrows in Fig S1).



Fig. S1 Example of compaction front position determination using the ImageJ software. Photograph of the circular sample (diameter 4 cm) converted into grey levels (left). Grey level along a diameter (right). Slope changes, indicated by arrows, correspond to compaction fronts. Let us remind the reader that water fronts could not be followed in this work because they corresponded to the apparition of cracks.

Sketch of the principle of the optical profilometry used in this work



A light source projects the image of a grid onto the sample. A CCD camera captures images of this grid reflected by the surface of the suspension. The non-planar surface of the drying film creates a distortion of the image of the grid. An image processing software transforms the deformed grid into quantified information of the local slopes of the surface as well as XYZ coordinate to reconstruct the topography.

#### Routh and Russel model



Fig. S2 Film profile (left) and particle volume fraction (right) versus lateral dimension at different times during drying calculated using our cellular simulation in the conditions of the Routh and Russel (RR) model. Film height scaled on the initial film thickness, lateral dimension (X) scaled on the capillary length in the RR sense, time scaled on the characteristic time  $\frac{H_0}{E}$ . Initial particle volume fraction: 0.3. Volume fraction at close packing: 0.7. Infinite capillary pressure.

Contribution of hydrostatic pressure



Fig. S3 Film profile versus lateral dimension at time = 0.1 for different initial thicknesses (i.e. different  $L_{cap} / L_g$  ratios) when taking hydrostatics into account. Film height and lateral dimension (X) in real dimension (m). time scaled on the characteristic time  $\frac{H_0}{\dot{E}} \cdot L_{cap} / L_g = 1.5$ ; 3; 7.5 for  $H_0 = 100 \mu$ m; 200  $\mu$ m; 500  $\mu$ m, respectively.  $\gamma = 70 \text{ mJ/m}^2$ ,  $\eta_0 = 1 \text{ Pa.s}$ ,  $\dot{E} = 10^{-8} \text{ m/s}$ ,  $\rho = 1000 \text{ kg/m}^3$ ,  $g = 9.81 \text{ m/s}^2$ . Initial particle volume fraction: 0.3. Volume fraction at close packing: 0.7. Infinite capillary pressure (taken at 1000 for calculation).

Particle front position vs time with hydrostatics



Fig. S4 Particle front position versus time for different initial film thicknesses when taking hydrostatics into account. Comparison with RR model (blue curve). Lateral dimension (X) scaled on  $L_{cap}$ , time scaled on  $\frac{H_0}{E}$ . Other parameters like in Fig. S2.

## Taylor diffusion of suspensions in a semi-parabolic flow

The hydrodynamics of drying suspensions is commonly treated in the lubrication approximation. This approximation for Newtonian fluids consists in a locally parabolic velocity profile driven by some pressure gradient. It is analogue to some extent to Poiseuille parabolic flows occurring in pipes of cylindrical section at low Reynolds numbers. When considering the longitudinal diffusion of a solute or suspended particles (*i.e.* parallel to the flow direction) one may be concerned by the fact that the velocity field is not uniform. Suspended particles will be advected faster in the regions close to the free boundary than at the vicinity of the solid surface. Such an heterogeneous advection is known as the Taylor, or Taylor-Aris diffusion problem and has received a satisfactory solution in the case of laminar Poiseuille flows occurring in cylindrical pipes [1, 2]. We outline below an equivalent treatment in the presence of a semiparabolic Poiseuille lubrication flow, and for a concentration independent diffusion coefficient D.

**The lubrication flow** In the case of drying suspensions, there are two boundary conditions : vanishing velocity at the solid surface and vanishing stress (vanishing velocity gradient) at the free air fluid surface. If one denotes by y the direction normal and x the direction parallel to the surface, the resulting flow displays a semi-parabolic velocity profile

$$\boldsymbol{u} = u(x, y)\boldsymbol{e}_x = \frac{(y - 2h)y}{2\eta_0} \frac{\partial p_h}{\partial x}(x)\boldsymbol{e}_x,\tag{1}$$

 $p_h(x)$  being the total hydrostatic pressure with no y dependence,  $\eta_0$  the dynamic viscosity of the suspension (solvent and particles), h the film thickness.

The local velocity field can also be expressed by means of the average cross-section velocity, obtained by applying a projection operator  $\mathcal{P}$ 

$$\mathcal{P}(u) = \mathcal{P}u = \frac{1}{h} \int_0^h \mathrm{d}y u(x, y).$$
<sup>(2)</sup>

 $\mathcal{P}$  is a linear operator mapping any function of x, y onto a function of x only, and obeys the standard projection rule  $\mathcal{P}(\mathcal{P}) = \mathcal{P}^2 = \mathcal{P}$ . Then, in the lubrication approximation,

$$u(x,y) = \frac{3y(2h-y)}{2h^2} \mathcal{P}u(x) \tag{3}$$

The lubrication approximation is expected to hold if the velocity gradient along the x direction are small compared with the vertical gradient, and the time scales of the problem are long compared with  $\tau_h = \rho H^2/\eta_0$ ,  $\rho$  mass density of the suspension,  $H \sim h$  typical height, which is the characteristic time for stabilizing a Poiseuille parabolic velocity profile.

The transport of a species in the presence of a stream involves explicitly the velocity field u. In the case of an incompressible flow accross a constant section cylindrical pipe, the velocity gradients have the effect of enhancing the diffusion constant of the species along the longitudinal direction.

**Projection of the transport equations** Our notations will be the following ones :

- commas stand for partial differentiation, e.g.  $f(x, y, t)_{,x} = \partial f / \partial x$ .
- $\mathcal{P}$  is the vertical average projection operator, and  $\mathcal{Q} = 1 \mathcal{P}$  its orthogonal complement.

With these notations, one checks the following properties

- $(\mathfrak{P}f)_{,t} = \mathfrak{P}(f_{,t})$  and  $(\mathfrak{Q}f)_{,t} = \mathfrak{Q}(f_{,t})$ ,
- $(\mathfrak{P}f)_{,x} = \mathfrak{P}(f_{,x})$  and  $(\mathfrak{Q}f)_{,x} = \mathfrak{Q}(f_{,x}),$
- $\mathcal{P}(qf) = q\mathcal{P}(f)$  if q is function of x only,

• 
$$\mathcal{P}\mathcal{Q}f = \mathcal{Q}\mathcal{P}f = 0,$$

- $\mathcal{P}(f,y) = \frac{f(y=h) f(y=0)}{h},$   $\mathcal{P}(f,y) = \frac{f_{,y}(y=h) f_{,y}(y=0)}{h},$   $(\mathcal{P}f)_{,y} = 0,$
- $(\Omega f)_{,y} = f_{,y}$

It is expected as a rule that  $\Omega f$  remains smaller than  $\mathcal{P} f$ , and expansions are going to be performed according to this rationale. We assume that the velocity field u and the elevation hare constant and uniform. The starting point is the collective diffusion equation

$$\Phi_{,t} + u\Phi_{,x} = D\Phi_{,xx} + D\Phi_{,yy} \tag{4}$$

This equation expresses the conservation of the latex suspension volume fraction  $\Phi$ , itself proportionnal to the particle number density. Gradients of  $\Phi$  create a current  $-D\nabla\Phi$  which involves the diffusion coefficient D.

The first step is to apply  $\mathcal{P}$  to eq. (4). The result is

$$\mathcal{P}\Phi_{,t} + \mathcal{P}(u\Phi_{,x}) = \mathcal{P}(D\Phi_{,x})_{,x} \tag{5}$$

where the second term in r.h.s vanishes due to  $\Phi_{,y}(y=0) = 0, \Phi_{,y}(y=h) = 0$ , and one has

$$\mathcal{P}\phi_{,t} + \mathcal{P}u \ \mathcal{P}\Phi_{,x} + \mathcal{P}(u\mathcal{Q}\Phi_{,x}) = D\mathcal{P}\Phi_{,xx} \tag{6}$$

Similar considerations guide the orthogonal projection of the transport equation. The idea is to substract eq.(6) from eq.(4).

$$\mathcal{Q}\phi_{,t} + \mathcal{Q}u\mathcal{P}\Phi_{,x} + \mathcal{Q}(u\mathcal{Q}\Phi_{,x}) = D(Q\Phi)_{,yy} + D(Q\Phi)_{,xx}$$
(7)

Terms in (6) and (7) are not of the same magnitude and must be hierarchized. In order to proceed in a systematic way, it is now necessary to guess which are the relevant scales of the problem and to rescale both equations appropriately.

**Rescaling and effective equations** Let us assume that vertical lengths scale as H and define  $\overline{y} = y/H$ ,  $\overline{h} = h/H$ , that horizontal lengths scale as  $L_{\phi}$  and define  $\overline{x} = x/L_{\phi}$ . One introduces a (yet undetermined) characteristic time scale for horizontal diffusion  $\tau_D$  ( $\bar{t} = t/\tau_D$ ) and a velocity scale V representative of the stream u, with  $\overline{u} = u/V$ .

From V, D and  $L_{\phi}$  can be derived a horizontal Peclet number  $\text{Pe}_h = V L_{\phi}/D$ . An interesting limit emerges when  $L_{\phi}$  is larger than H, with the effect of inhomogeneous flow resulting in the redefinition of the diffusion constant, and the possibility to derive a simple, effective 1d-diffusion equation. We therefore assume  $H/L_{\phi} \ll 1$ .

The two projected equations rescale as

$$\frac{1}{\tau_D} \mathcal{Q}\phi_{,\overline{t}} + \frac{V}{L_{\phi}} \mathcal{Q}\overline{u}\mathcal{P}\Phi_{,\overline{x}} + \frac{V}{L_{\phi}} \mathcal{Q}(\overline{u}\mathcal{Q}\Phi_{,\overline{x}}) = \frac{D}{H^2} (Q\Phi)_{,\overline{yy}} + \frac{D}{L_{\phi}^2} (Q\Phi)_{,\overline{xx}}$$
(8)

$$\frac{1}{\tau_D} \mathcal{P}\phi_{,\overline{t}} + \frac{V}{L_\phi} \mathcal{P}\overline{u}\mathcal{P}\Phi_{,\overline{x}} + \frac{V}{L_\phi} \mathcal{P}(\overline{u}\mathcal{Q}\Phi_{,x}) = \frac{D}{L_\phi^2} \mathcal{P}\Phi_{,\overline{xx}}$$
(9)

The usual treatment of the Taylor diffusion assumes that the second term of lhs and the first term of rhs balance in eq. (8), while other terms are subdominant. Introducing  $\varepsilon = \frac{H^2 V}{DL_{\phi}}$ , one finds

$$\frac{L_{\phi}^2}{D\tau_D} \frac{H^2}{L_{\phi}^2} \mathcal{Q}\phi_{,\bar{t}} + \varepsilon \mathcal{Q}\overline{u}\mathcal{P}\Phi_{,\bar{x}} + \varepsilon \mathcal{Q}(\overline{u}\mathcal{Q}\Phi_{,\bar{x}}) = (Q\Phi)_{,\overline{yy}} + \frac{H^2}{L_{\phi}^2}(Q\Phi)_{,\overline{xx}}$$
(10)

$$\frac{L_{\phi}^{2}}{D\tau_{D}}\mathcal{P}\phi_{,\overline{t}} + \operatorname{Pe}_{h}\mathcal{P}\overline{u}\mathcal{P}\Phi_{,\overline{x}} + \operatorname{Pe}_{h}\mathcal{P}(\overline{u}\mathcal{Q}\Phi_{,x}) = \mathcal{P}\Phi_{,\overline{x}\overline{x}}$$
(11)

One expects  $\varepsilon \ll 1$ ,  $\Omega \Phi \sim \varepsilon$  and  $\Omega \Phi \ll \mathcal{P}\Phi$ . The horizontal diffusion time scale is set by the equivalent  $L_{\phi}^2/D\tau_D \sim 1$ , which entails  $H^2/D\tau_D \ll 1$ . The primary balance of the first equation reads

$$\varepsilon \, \mathfrak{Q}\overline{u} \, \mathcal{P}\Phi_{,\overline{x}} = (\mathfrak{Q}\Phi)_{,\overline{y}\overline{y}} \tag{12}$$

Recast in the original, unscaled variables, one finds

$$\mathcal{Q}u(y)\,\mathcal{P}\Phi_{,x} = D(\mathcal{Q}\Phi)_{,yy}\tag{13}$$

As  $\Omega u$  is a known function of y, the above equation reduces to a double quadrature accompanied by the boundary conditions  $\Phi_{,y} = (\Omega \Phi)_{,y} = 0$  at y = h and y = 0, and the integral condition  $\mathcal{P}\Omega \Phi = 0$ . The solution reads

$$\begin{aligned}
\Omega u &= \left( -1 + \frac{3y}{h} - \frac{3}{2} \left( \frac{y}{h} \right)^2 \right) \mathcal{P}u; \\
\Omega \Phi &= \frac{h^2 \mathcal{P} \Phi_{,x} \mathcal{P}u}{8D} \left( \frac{8}{15} - 4\frac{y^2}{h^2} + 4\frac{y^3}{h^3} - \frac{y^4}{h^4} \right).
\end{aligned} \tag{14}$$

Then, one can substitute for the  $\mathcal{P}(u\Omega\Phi_{,x})$  term in eq. (17)

$$u\Omega\Phi_{,x} = \frac{3y(2h-y)}{2h^2} \times \left(\frac{8}{15} - 4\frac{y^2}{h^2} + 4\frac{y^3}{h^3} - \frac{y^4}{h^4}\right) \times \frac{h^2 \mathcal{P}\Phi_{,xx} \mathcal{P}u^2}{8D}$$
$$\mathcal{P}(u\Omega\Phi_{,x}) = -\frac{2}{105} \frac{h^2 \mathcal{P}\Phi_{,xx} \mathcal{P}u^2}{D}$$
(15)

leading eventually to

$$\mathcal{P}\phi_{,t} + \mathcal{P}u\mathcal{P}\Phi_{,x} = \left[D + \frac{2(h\mathcal{P}u)^2}{105D}\right]\mathcal{P}\Phi_{,xx}$$
(16)  
$$\mathcal{P}\phi_{,\bar{t}} + \operatorname{Pe}_{h}\mathcal{P}\overline{u}\mathcal{P}\Phi_{,\bar{x}} = \left[1 + \varepsilon \operatorname{Pe}_{h}\frac{2(\bar{h}\mathcal{P}\overline{u})^2}{105}\right]\mathcal{P}\Phi_{,\bar{x}\bar{x}}$$

It results in an effective enhanced 1-d diffusion coefficient  $D_{\text{eff}} = D + 2h^2 (\mathcal{P}u)^2 / 105D$ , known as Taylor diffusion constant.

**Discussion** It is therefore possible to integrate out the coupled effect of lateral diffusion and lateral shear velocity drift and to obtain an effective 1d transport equation. This can only be done properly if the longitudinal scale  $L_{\phi}$  of the concentration gradient is larger than the thickness of the film H. At large horizontal Peclet number, there is the possibility of a significant enhancement of the effective diffusion constant.

The previous derivation is valid under the assumptions  $H/L_{\phi} \ll 1$ ,  $H^2 V/DL_{\phi} \ll 1$ ,  $\tau_D \sim L_{\phi}^2/D$ .

At the vicinity of the solid (wet gel front) region, the flow has to switch from parabolic to uniform. This is also a region where strong concentration gradients are expected. More likely than not, the above assumptions will break down at the vicinity of the solid front. A comprehensive approach would therefore be needed to deal with a truly 2d problem in variables x and y.

# Références

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