Supporting information for: Role of vapor mass transfer in flow coating of colloidal dispersions in the evaporative regime

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Diffusion evaporation flux for an infinite stripe domain

Formulation of the problem; Imposed concentration at $y = a$

We want to solve the Laplace equation for concentration field in 2D geometry, see Figure S1. Consider a thin liquid film sitting on a solid substrate (in fact we will treat film of zero thickness). All lengths have been scaled by the evaporation length L_{ev}. The liquid film now extends from $x = -1$ to $x = 1$, and the boundary layer thickness is $a = \Lambda/L_{ev}$.

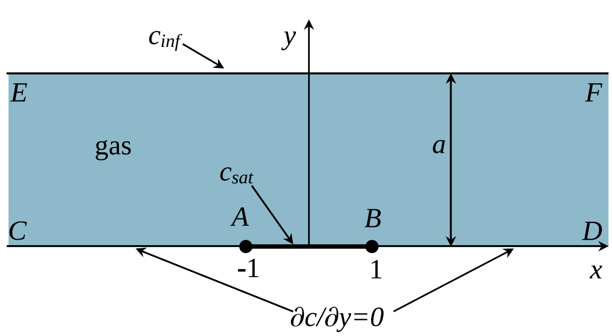

Figure S1: Geometry of the problem in the z-plane.

The stationary concentration field is a solution of Laplace equation:

$$\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} = 0, \tag{S1}$$

where $-\infty < x < \infty$ and $0 < y < a$. The boundary conditions corresponding to our problem are

1. $c(x, a) = c_{inf}$ for $-\infty < x < \infty$,
2. $c(x, 0) = c_{sat}$ for $|x| \leq 1$,
3. $\dfrac{\partial c(x, 0)}{\partial y} = 0$ for $|x| > 1$.

Oy is axis of symmetry. This problem is thus equivalent to the configuration addressed in the main paper (cf. Figure 2 and eqs (5-8) in the main paper).

Solution of the problem

It is advantageous to reformulate problem as:

$$\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} = 0, \tag{S2}$$

where $C = c - c_{inf}$ and the boundary conditions reduce to

1. $C(x, a) = 0$ for $-\infty < x < \infty$,
2. $C(x, 0) = \delta C \equiv c_{sat} - c_{inf}$ for $|x| \leq 1$,
3. $\dfrac{\partial C(x, 0)}{\partial y} = 0$ for $|x| > 1$.

To solve eq (S2), the following conformal transform[S1] is introduced:

$$\exp \frac{\pi(z+1)}{2a} = \mathrm{sn}(w, k), \tag{S3}$$

where $\mathrm{sn}(\cdot, k)$ is the Jacobi elliptic sine of modulus k, $w = u + iv$, $z = x + iy$, and k is defined by

$$k = \exp\left(-\frac{\pi}{a}\right). \tag{S4}$$

Note that $0 < k < 1$ so it can be indeed the Jacobi modulus. The transformation (S3) can be seen as two sequential transformations:

$$t = r + is = \exp \frac{\pi(z+1)}{2a} \tag{S5}$$

and

$$t = \mathrm{sn}(w, k). \tag{S6}$$

The transform (S5) can be seen as a mapping

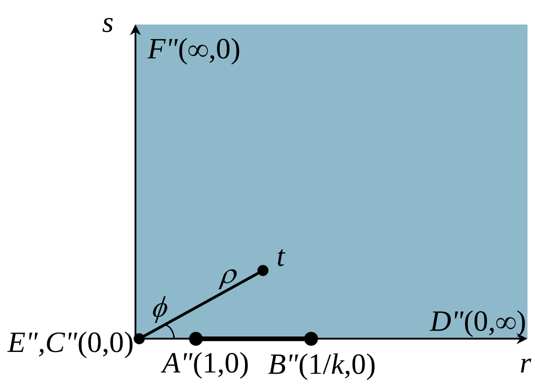

Figure S2: Conformal mapping: t-plane. The points corresponding to those of Figure S1 are denoted by the double prime.

of the region $-\infty < x < \infty$, $0 \leq y \leq a$ to the first quarter $r > 0, s > 0$ where $\rho = \exp[\pi(1 + x)/(2a)]$ is the polar radius and $\phi = \pi y/(2a)$ is the polar angle in the plane t (Figure S2). The second transform (S6) maps this region into the rectangle $0 \leq u \leq K$, $0 \leq v \leq K'$ (Figure S3), where $K \equiv K(k)$ is the complete elliptic integral of the first kind, $K' = K(k')$, and $k' = \sqrt{1 - k^2}$. The dimensions of the rectangle are $K \times K'$.

One can verify that the following (Cauchy) relations

$$\frac{\partial u}{\partial y} = -\frac{\partial v}{\partial x}, \quad \frac{\partial v}{\partial y} = \frac{\partial u}{\partial x} \tag{S7}$$

hold for the $z(w)$ function given by eq (S3), which means that it is analytical. Such a transform is thus indeed conformal. By using

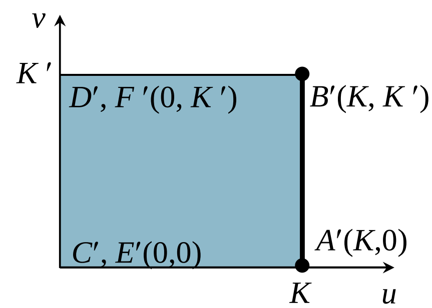

Figure S3: Geometry and coordinate system in the w-plane. The points corresponding to those of Figure S1 are denoted by the prime.

eqs (S7), the boundary-value problem (S2) can be reformulated for the function $C = C(u, v)$ in the w-plane as

$$\frac{\partial^2 C}{\partial u^2} + \frac{\partial^2 C}{\partial v^2} = 0, \tag{S8}$$

1. $C(0, v) = 0$ for $0 \leq v \leq K'$,
2. $C(K, v) = \delta C$ for $0 \leq v \leq K'$,
3. $\dfrac{\partial C(u, K')}{\partial v} = \dfrac{\partial C(u, 0)}{\partial v} = 0$ for $0 \leq u \leq K$.

It is evident that the solution of the problem (S8) is

$$C(u, v) = u \frac{\delta C}{K}. \tag{S9}$$

Let us find the evaporation flux defined by the y derivative of C along AB in Figure S1,

$$\frac{\partial C}{\partial y} = \frac{\partial C}{\partial u}\frac{\partial u}{\partial y} = -\frac{\partial C}{\partial u}\frac{\partial v}{\partial x} = -\frac{\delta C}{K}\frac{\partial v}{\partial x}, \tag{S10}$$

where the solution (S9) and the first of eqs (S7) is used. To find the $\partial v/\partial x$ one can use the transformation (S3) and write the relation between x and v along AB,

$$\exp\left(\frac{\pi(1+x)}{2a}\right) = \mathrm{sn}(K+iv,k) = \frac{1}{\mathrm{dn}(v,k')}, \tag{S11}$$

where dn is a Jacobi elliptic function.[S2] Eq (S11) can be rewritten as

$$x = -\frac{2a}{\pi}\ln \mathrm{dn}(v,k') - 1. \tag{S12}$$

$\partial v/\partial x$ in (S10) can be obtained from (S12)

$$\frac{dx}{dv} = \frac{2a}{\pi}\frac{k'^2}{\mathrm{dn}(v,k')}\mathrm{sn}(v,k')\mathrm{cn}(v,k'). \tag{S13}$$

From eq (S11), $\mathrm{dn}(v,k') = b$, where we denote $b \equiv \exp[-\pi(1+x)/(2a)]$, with $k \le b \le 1$. Let us now express $\mathrm{sn}(v,k')$ and $\mathrm{cn}(v,k')$ with b. The elliptic functions are related to each other through the equations[S2]

$$\begin{aligned} \mathrm{sn}(v,k') &= \sin\phi, \\ \mathrm{cn}(v,k') &= \cos\phi, \\ \mathrm{dn}(v,k') &= \sqrt{1-k'^{\,2}\sin^2\phi}. \end{aligned}$$

Note that both $\mathrm{sn}(v,k')$ and $\mathrm{cn}(v,k')$ are non-negative when $0 \le v \le K'$. Therefore,

$$\begin{aligned} \mathrm{sn}(v,k') &= \frac{\sqrt{1-b^2}}{k'}, \\ \mathrm{cn}(v,k') &= \frac{\sqrt{b^2-k^2}}{k'}. \end{aligned}$$

Finally,

$$\begin{aligned} \frac{\partial C}{\partial y} &= -\frac{\delta C}{K(k)}\frac{\pi}{2a}\frac{b}{\sqrt{(1-b^2)(b^2-k^2)}} \\ &= -\frac{\delta C}{K(k)}\frac{\pi}{2a}\left\{\left[\exp\left(\frac{\pi(1+x)}{a}\right)-1\right]\right. \\ &\left.\left[\exp\left(-\frac{\pi(1+x)}{a}\right)-\exp\left(-\frac{2\pi}{a}\right)\right]\right\}^{-1/2}, \end{aligned} \tag{S14}$$

where k is defined by eq (S4). Note that this function is even, in agreement with the x-mirror symmetry of the problem.

Evaporation velocity

By returning to the main text notation, eq (S14) yields the expression for the evaporation velocity:

$$\begin{aligned} v_{ev}(x) &= -\frac{D_v}{\rho}\frac{\partial c}{\partial z} \\ &= \frac{\pi\beta}{2\Lambda K(k)}\left\{\left[\exp\left(\frac{\pi(L_{ev}+x)}{\Lambda}\right)-1\right]\right. \\ &\left.\left[\exp\left(-\frac{\pi(L_{ev}+x)}{\Lambda}\right)-\exp\left(-\frac{2\pi L_{ev}}{\Lambda}\right)\right]\right\}^{-1/2}, \end{aligned} \tag{S15}$$

where $\beta = D_v(c_{sat} - c_\infty)/\rho$. As for the droplet case, there is an integrable divergence at the end of the evaporation region:

$$v_{ev}(x \to L_{ev}) \simeq \frac{J_0}{\sqrt{1-x/L_{ev}}}, \tag{S16}$$

$$\text{where} \quad J_0 = \frac{\beta\sqrt{\pi}}{2K(k)\sqrt{L_{ev}\Lambda(1-k^2)}}. \tag{S17}$$

SEM top view of a coating

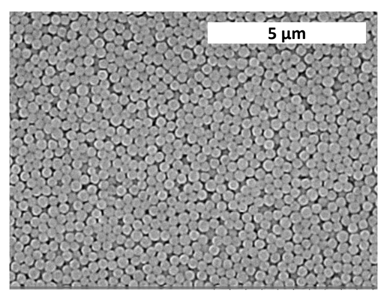

Figure S4: SEM top view of a coating, the particle diameter is 2a = 310 nm.

Driving mechanism of the evaporation flux in the experimental device

A few direct measurements of the overall evaporation rate Q_{ev} have been made under the same conditions as for coating experiments (see section "Experimental results" in main text). These experimental data are compared in Figure S5 with the prediction of main text eq (13), for which evaporation is supposed to be driven by vapor diffusion in a 3D semi-infinite domain of quiescent air. The diffusive model underestimates the experimental data for the largest values of L_{ev}/W. This can be understood by considering the Rayleigh number

$$\mathcal{R}a = \frac{g\Delta\rho L^3}{\mu D_v} \tag{S18}$$

which is indicative of the importance of free convection in the gas phase. For external free convection, the length scale L is defined as the ratio of film area over film perimeter[S3] : $L = L_{ev}W/[2(L_{ev} + W)] \simeq L_{ev}/2$. $\Delta\rho$ is the variation in air density between the liquid/air interface and the ambient air. $\Delta\rho$ depends on both vapor concentration and temperature variations. With the rough approximation of an isothermal problem, we get $\Delta\rho \simeq 5.7 \times 10^{-3}$ kg.m^{-3}. Other parameters are gravity acceleration $g = 9.81$ m.s^{-2}, air dynamic viscosity $\mu = 1.8 \times 10^{-5}$ Pa.s and vapor diffusivity $D_v = 2.5 \times 10^{-5}$ m^2.s^{-1}.

In our experiments, the evaporation length ranges from $L_{ev} \sim 0.1$ to 10 mm. The corresponding Rayleigh number thus ranges from $\mathcal{R}a \sim 10^{-4}$ to 10^2. This indicates a diffusive regime for the lowest values of L_{ev} and a laminar free convection regime for the highest values, with a transition at $L_{ev} \simeq 4$ mm ($L_{ev}/W \simeq 0.08$).

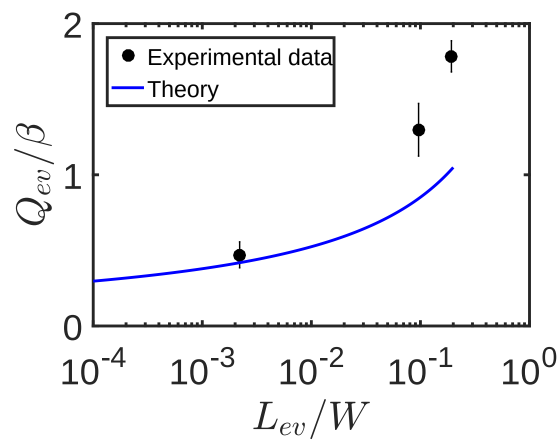

Figure S5: Normalized experimental evaporation rate Q_{ev}/β as a function of the aspect ratio L_{ev}/W: comparison between experimental values and theory based on 3D vapor diffusion in quiescent air [main text eq (13)].

References

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(S2) Abramovitz, M., Stegun, I. A., Eds. *Handbook of Mathematical Functions*; Dover: New York, 1972.

(S3) Rhosenow, W.; Hartnett, J.; Cho, Y. *Handbook of Heat Transfer*, 3rd ed.; McGraw-Hill: New York, 1998.