# LAYER THICKNESS DISTRIBUTION OF THIN-FILM INK-JET PRINTED STRUCTURES

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Summary We studied the layer formation process of sessile droplets of a colloidal silver suspension, deposited by ink jet printing. An approximate numerical model was developed, and associated scaling laws. The numerical prediction and underlying assumptions of the model were compared with experimental results. They were found to be in reasonable agreement with each other, showing the practical value of the approach.

## INTRODUCTION

The drying of ink-jet printed droplets that form thin films of solute is a process that can show various hydrodynamical phenomena, such as Marangoni flow and hydrodynamic instabilities (e.g. [1]). However, even in a relatively simple form that still has practical significance, the description of the drying process already poses significant difficulties. In the case considered here, the processes involved are convective and diffusive transport of solute, coupled with the evolution of the free surface, the evaporation of the solvent, and the viscosity increase of the solution (see figure 1).

Significant work on drying has been performed by Deegan (e.g. [2]), quantifying the surface-tension driven mechanism of convective solute transport initiated by evaporation of droplets of order 1 mm radius. However, for smaller size particles and droplets than Deegan studied, diffusion established by advectively induced concentration gradients can become important. Also, the increase of viscosity as the concentration of the solute increases can become important.

In this study we present a practical and approximate approach towards the drying of an ink-jet printed droplet containing colloidal particles, together with experimental validation. Applications for which this approach is useful are e.g. in the field of printable electronics for displays [3].

## MODEL DESCRIPTION

We make the assumption that the solution is well-mixed in the vertical direction, so that the solute concentration only depends on the radial position (valid when $V_cH_c/D<<1$ with $V_c$ and $H_c$ being a characteristic respectively evaporation rate and wet layer thickness, and $D$ being the solute's diffusion coefficient). We then write the convection-diffusion equation integrated over the droplet height as:

$$\frac{\partial}{\partial t}(ch)=H\left(1-\frac{c}{c_{cr}}\right)\cdot\left(\frac{1}{r}\frac{\partial}{\partial r}\left(Dhr\frac{\partial c}{\partial r}\right)-\frac{1}{r}\frac{\partial}{\partial r}(rchv)\right) \qquad (1)$$

where $t$ is time, $c$ is the solute volume concentration, $h$ is the wet layer thickness of the droplet, $H$ is the Heaviside step function, $r$ is the radial coordinate, and $v$ is the radial velocity averaged over the droplet height. The use of $H$ expresses a sudden prevention of further solute transport at a critical concentration $c_{cr}$, as a result of increased viscosity that develops during drying. This approach is motivated by considering a capillary number $Ca$ giving the order of magnitude of the proportion between viscous forces and forces generated by surface-tension in an evaporating sessile droplet:

$$Ca=\frac{\eta v_{e,av}}{\sigma}\left(\frac{r_0}{h_0}\right)^4 \qquad (2)$$

where $r_0$ and $h_0$ are the radius and central layer thickness of the droplet during drying, $v_{e,av}$ is the average evaporation rate (defined as evaporating volume per unit of time divided by $\pi r_0^2$), $\eta$ is the viscosity and $\sigma$ the surface tension of the solution. For practical ink-jet printable fluids and substrates, we usually have $Ca<<1$ at the start of drying. For the materials used in this study we found that the viscosity increases sharply with concentration around a critical concentration $c_{cr}$, so that we can assume that $Ca<<1$ if $c<c_{cr}$ and$Ca>>1$ if $c>c_{cr}$ and no solute transport occurs.

We assume that the surface evolves as a spherical cap and that the contact line remains pinned, which is the case for many practical situations. Assuming a spherical cap neglects profile changes by gellation or solidification of the material, and unknown development of evaporation rate and material density [4]. Experiments on droplets of 1 mm radius show that this assumption is good for times <80% of the total drying time for the materials in this study.

The continuity equation and evaporation rate model – based on diffusive transport of solvent vapour [2] – read:

$$\frac{d(rvh)}{dr}=-r\left(\frac{dh}{dt}+v_e\right), \qquad v_e=v_{e,av}(1-\lambda)\left(1-\left(\frac{r}{r_0}\right)^2\right)^{-\lambda} \qquad (3), (4)$$

where $v_e$ is the evaporation rate,$\lambda=(\pi-2\theta)/(2\pi-2\theta)$ and $\theta$ is the contact angle between fluid and substrate.

We can numerically solve equation (1), (3), (4) and the spherical-cap description for $h$. We can also infer that the problem is described by three dimensionless numbers and a parameter describing the evaporation rate profile:

$$N_H = \frac{H_0}{R_0}, \qquad N_D = \frac{H_0 D}{v_{e,av} R_0^2}, \qquad N_c = \frac{c_0}{c_{cr}}, \qquad \lambda_0 \tag{5}$$

where $H_0$, $R_0$ and $\lambda_0$ are the central layer thickness, droplet radius and $\lambda$ at the start of drying.

## COMPARISON WITH EXPERIMENTS

For experimental verification, we used two colloidal suspensions of silver particles in water stabilised with a polymer, obtained from Merck and Nippon-Paint. We printed these on a glass substrate with modified surface energy using a piezo-electric ink jet head. For both solutions we measured the viscosity and diffusion coeffient at the initial concentration $c_0$, yielding $\eta$=1.0 mPa·s, $D$=2.7·10$^{-11}$ m$^2$s$^{-1}$ and $\eta$=1.9 mPa·s, $D$=1.0·10$^{-10}$ m$^2$s$^{-1}$ respectively. The evaporation rate was measured for droplets with different radius. We also determined the viscosity increase as a function of concentration, at a shear rate of 10 s$^{-1}$. From this we found that we can estimate $c_{cr}$ as 0.05 and 0.03 for initial silver concentrations of 0.017 and 0.0053 respectively. The sessile droplet radius in the various experiments is between 17 and 96 μm. In checking our model assumptions for the materials, we found that solutal Marangoni effects can be neglected.

Figure 2 shows a direct comparison between an experimentally determined layer thickness profile and the numerical model. The uncertainty in the diffusion coefficient (relative error of 50%) and average evaporation rate (relative error of 30%) determine the error boundaries in the simulation, indicated by the dashed lines. The layer thickness profile was measured after curing the material. A fair agreement is obtained, taking into account the relatively large sensitivity of this specific case to variation in the input parameters of the simulation.

Figures 3 and 4 show the transition from convection-dominated drying ($N_D$<<1) towards diffusion-dominated drying ($N_D$>>1), occurring in both the model (for $N_H$=0.3, $N_c$=0.3, $\lambda_0$=0.4) and the experiments. The model shows that the variation of $N_H$ (0.26<$N_H$<0.56)) and $N_c$ (0.18<$N_c$<0.34) in these experiments had a relatively small effect.

## CONCLUSIONS

The model and scaling show agreement with experiments using droplets of suspensions of colloidal silver particles. The number of input parameters in the model was kept to a minimum, still describing the relevant physical phenomena for a wide range of solutions. The approximate model and scaling laws provide useful quantitative insight into the drying process of ink-jet printed structures, which can be used in manufacturing of printable inorganic conductors.

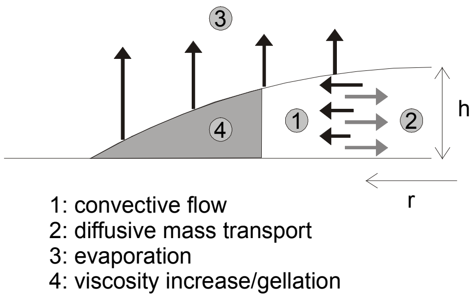

*Figure 1. Schematic representation of the model situation.*

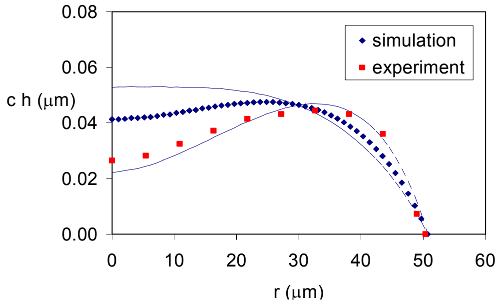

*Figure 2. Comparison of experiment and simulation.*

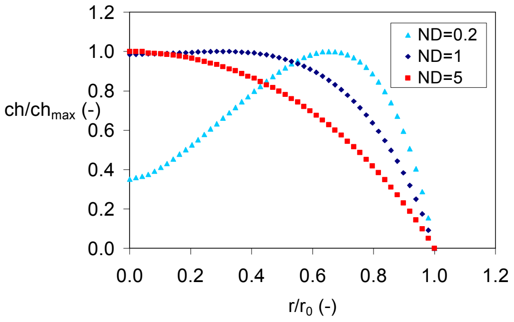

*Figure 3. Effect of $N_D$ on dried layer thickness profile.*

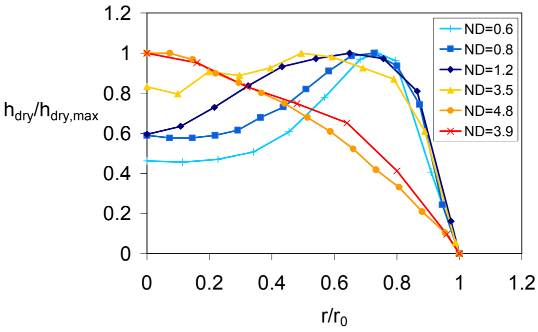

*Figure 4. Varied $N_D$ and normalised dry layer thickness.*

### References

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