

# Binary-Mixture Droplet Evaporation: Lubrication Approximation and Coffee Ring Formation

Moussa TEMBELY<sup>1,\*</sup>, Anne-Gaëlle MERCIER<sup>2</sup>, Christine NAYOZE<sup>2</sup> and Arthur SOUCEMARIANADIN<sup>1</sup>

\*Corresponding author: Tel.: (00)33-456-521-120 ; Fax: (00)33-475-561-620;

Email: [moussa.tembely@ujf-grenoble.fr](mailto:moussa.tembely@ujf-grenoble.fr)

1: UJF-Grenoble 1 / Grenoble-INP / CNRS, LEGI UMR 5519, Grenoble, F-38041, France

2: Atomic Energy and Alternative Energies Commission (CEA)/DRT/LITEN, Laboratory of Components for Fuel Cells and Electrolysers and of Modeling (LCPEM), 38054 Grenoble, France

## Abstract

In this paper the dynamics of an evaporating sessile droplet spreading on a horizontal substrate is reported. A mathematical model based on the lubrication approximation is developed accounting for Marangoni effect, contact line motion, and multi-component fluid. After validating the model through pure liquid spreading and evaporation, an extension of the model is performed on a binary component liquid in which composition changes occur during the drying process. Furthermore, the presence of particles in the fluid enables to retrieve the coffee-ring formation. A good qualitative and quantitative agreement between the model and experimental observations is found.

**Keywords:** Modeling, Drop evaporation, Lubrication approximation, Marangoni effect, Coffee Ring

## 1. Introduction

Drop impact and the subsequent spreading and evaporation on an heated substrate has attracted renewed interest in the past decade due to the large number of applications involved in microfluidics or ink jet printing [1, 2]. The underlying hydrodynamics is a complex problem involving three phases (liquid, vapor, and solid) interaction through coupling by conduction with the substrate, the convection/conduction inside the drop and the convection/diffusion in the vapor phase. Multiphase flow coupled with heat transfer still poses challenges for numerical simulations.

We report in this work an experimental and theoretical modeling of the evaporation of sessile drops. The liquid is a suspension with a solvent component which evaporates during the process. The model is based on the lubrication approximation taking into account the contact line motion, the solvent evaporation, Marangoni effect as well as the particle effects. This study is undertaken for

better understanding the process and control in the so-called coffee ring formation [3]. We propose here a simplified model to account for binary-mixture evaporation. Within this model, the deposition patterns are investigated as functions of the substrate temperature, the solid content, as well as the solvent characteristics. The model uses the lubrication approximation, which reduces the Navier-Stokes equations to a single nonlinear fourth order partial differential equation describing time evolution of the free surface of the drop.

## 2. Model Equation of Motion

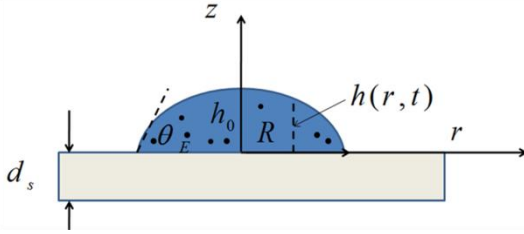
### 2.1 Basic modeling requirements

We propose to model the sessile drop evaporation in the case of fluids containing particles. The Marangoni effect on the drop evaporation seems to limit the coffee ring phenomenon with the particles deposit, depending on the fluid, not only at the contact line but at the center of the drop [4]. For our modeling, the contact line is not necessarily assumed pinned, as traditionally admitted [3],

since moving contact line could happen especially with low concentration of particles. We propose to establish a first model taking into account all the relevant physical processes involved. This modeling will be based on the lubrication approximation which has shown its relevance to deal with droplet spreading or evaporation [5, 6]. We perform our analysis for a more general situation where the drop is constituted of a binary mixture: a solvent and a solute in addition to the solids particles.

## 2.2 Lubrication approximation

We consider a droplet of a volatile liquid on a uniformly heated horizontal substrate as sketched in Figure 1. The liquid vapor interface is given by  $h(r,t)$  with contact angle  $\theta_E$ , the evaporative mass flux through the interface is  $J$ . The drop liquid is assumed to be composed of a catalyst ink dissolved in a volatile solvent with the associated concentration equation.



**Figure 1:** Geometry of the physical system and problem statement.

The model accounts for two partial differential equations solved simultaneously for the drop non-volatile ‘solute’ fraction  $c$  and droplet height  $h$ . In fact we consider the liquid used to be consisted of a solvent phase, which evaporates, and a solute phase containing particles which does not. For simplicity, we neglect gravity, which is a good approximation for drops smaller than the capillary length  $l_c = (\sigma/(\rho g))^{1/2}$  since also in this case the Bond number  $Bo = \rho g r_0^2 / \sigma < 0.05$  is much smaller than 1.

Assuming the drop as a paraboloid of revolution, the different equations are made dimensionless based on the initial radius ( $r_0$ ) and height ( $h_0$ ) based on the drop volume ( $V_0$ )

and contact angle ( $\theta_0$ ):

$$r_0 = \left( \frac{4V_0}{\pi \tan \theta_0} \right)^{1/3} \quad (1)$$

$$h_0 = \frac{\tan \theta_0}{2} \left( \frac{4V_0}{\pi \tan \theta_0} \right)^{1/3} \quad (2)$$

where  $\tan \theta_0 = 2\varepsilon$  with  $\varepsilon = h_0 / r_0 < 1$

The dimensionless equation in cylindrical coordinates for  $h(r,t)$  of the problem could be rewritten in the following form [5]:

$$\frac{\partial h}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \left\{ rh^3 \frac{\partial P}{\partial r} + rh^2 \frac{\partial \tilde{T}}{\partial r} \right\} + EJ = 0 \quad (3)$$

where  $P$  and  $\tilde{T}$  express respectively:

$$P = \frac{1}{r} \frac{\partial}{\partial r} \left[ r \frac{\partial h}{\partial r} \right] + \Pi \quad \text{and} \quad \tilde{T} = \frac{M_a}{P_r} (h + W)J$$

The dimensionless number,  $E = (k_l \Delta T / \rho \varepsilon L_{sat} h_0 U_0)$  which represents the ratio of the viscous time scale to the evaporative time scale, enables to impose the temperature variation of the substrate.  $\Delta T = T_{sub} - T_{sat}$  is the temperature increase of the substrate with respect to the saturation temperature ( $T_{sat}$ ). The liquid is of density  $\rho$ , kinematic viscosity  $\nu$ , thermal conductivity  $k_l$ , and latent heat of vaporization  $L_{sat}$ .  $\Pi$  corresponds to the dimensionless disjoining pressure modeling the wettability. Since we assume a linear variation in the surface tension  $\sigma$  due to temperature  $T$ , we have  $M_a = \gamma \Delta T h_0 / (2\mu \kappa U_0 r_0)$  and  $P_r = \nu / \kappa$ , the thermo-capillary Marangoni and Prandtl numbers, respectively. The time scale being  $T_c = 3\mu r_0^4 / (\sigma_0 h_0^3)$ , the velocity scale  $U_0 = r_0 / T_c$ .  $\gamma = -d\sigma / dT$ ,  $\kappa = k_l / \rho c_p$ , where  $c_p$  is the heat capacity.  $W = k_l d_s / k_s h_0$ , where  $k_s$ ,  $k_l$ ,  $d_s$ ,  $h_0$  are the substrate and liquid thermal conductivities, the substrate thickness and droplet height, respectively.

For simplicity purpose, we use the assumption that the concentration of the solute depends only on the radial position  $c(r,t)$ . The solute conservation leads to satisfy the following equation:

$$\frac{\partial(hc)}{\partial t} + \frac{\partial}{\partial r} [rh^2 c Q] = 0 \quad (4)$$

where  $Q = h \frac{\partial P}{\partial r} + \frac{\partial \tilde{\Gamma}}{\partial r}$ .

We neglect the surface tension variation of the mixture, assuming the surface to be a linear function of solute concentration

$$\sigma = \sigma_s + (\sigma_r - \sigma_s)c \approx \sigma_s \quad (5)$$

where  $\sigma_s$  and  $\sigma_{st}$  are respectively the solvent and solute surface tension. We also neglect the solute flux changes due to diffusion.

We take into account the variation of the viscosity of the fluid due to the evaporation of the solvent. The effect of evaporation could be expressed using [7] as follows:

$$\frac{\mu}{\mu_0} = \exp[a_v(c - c_0)] \quad (6)$$

where  $c_0$  is the initial solute fraction and  $a_v$  a constant.

To account for the presence of particles, we make use of the Krieger-Doherty equation:

$$\mu_0 = \mu_s (1 - \varphi / \varphi_m)^{-B\varphi} \quad (7)$$

$\mu_s$  is the liquid viscosity without particles,  $\varphi_m$  the maximum packing fraction,  $B$  a constant close to 2.5.

Furthermore we assume that the particle fraction is proportional to the solute fraction,  $\varphi \propto c$ , therefore, we have:

$$\varphi = \left( \frac{\varphi_0}{c_0} \right) c \quad (8)$$

where  $c_0$ ,  $\varphi_0$  are the initial solute and particle fraction, respectively.

And the flux writes as:

$$J = J_0 (1 - c) \quad (9)$$

where  $J_0$  is the initial flux.

We use the following expression for the evaporative flux mainly due to the temperature increase imposed by the substrate:

$$J_0 = \frac{1}{h + W + K} \quad (10)$$

with  $K = \frac{(2\pi R_g)^{1/2} k_{th} T_{sat}^{3/2}}{\alpha h_0 \rho_v L_{at}^2}$  and  $W = k_l d_s / k_s h_0$

where  $R_g$  is the ratio of the universal gas constant and molar mass,  $\alpha$  the accommodation coefficient, and  $\rho_v$  vapor density.

This relation is chosen preferentially to the one deduced by Deegan et al. [3, 8]  $J_0 = 1/H^\alpha$  which accounts only on the vapor phase and assuming a pinning contact. It is unclear to which extend this assumption is valid, when contact evolves. In general this may not be true. This form will be investigated in future work.

To solve the problem, we adopt the following formulation for the disjoining pressure ( $n=9$ ,  $m=3$ ):

$$\Pi = A(1 - \sigma \cos \theta_E) \left[ \left( \frac{h^*}{h} \right)^n - \left( \frac{h^*}{h} \right)^m \right] \quad (11)$$

where  $A = (1-n)(1-m) / \varepsilon^2 h^* (n-m)$  and  $h^*$  are constants accounting for the precursor film.

Note that the disjoining pressure term is zero for a fully wetting substrate where  $\theta_E = 0$ .

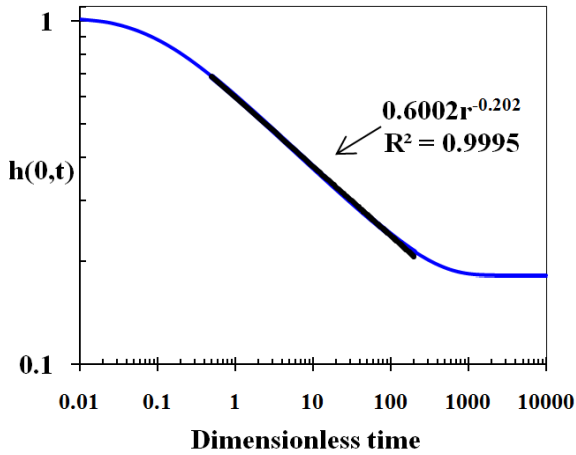
### 3. Model Validation

#### 3.1 Spreading

We first consider for validation purpose of the lubrication model the drop spreading on a horizontal wetted substrate. It is well-known that the centerline height follows a power law behavior referred to as Tanner's law

$$h = at^\alpha \quad (12)$$

We carry out the modeling of the water drop spreading from deposit contact angle of 50° to an equilibrium contact angle of 5° for 50μl drop. Figure 2 shows the center height evolution during the spreading.

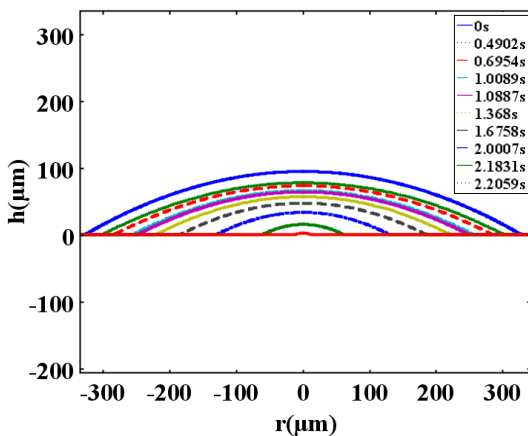


**Figure 2:** Comparison of the drop height evolution in accordance with Tanner’s law.

We observe very good agreement between our numerical results and Tanner’s law. Moreover, the coefficients,  $\alpha=0.202\sim 1/5$ , are very close to those reported elsewhere [5, 6] for water droplets.

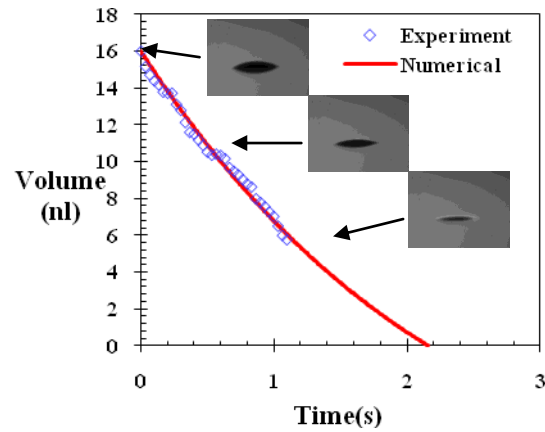
### 3.2 Evaporation

Here we test the model capability to deal with the drop evaporation. We perform both an experimental and numerical modeling of the evaporation of a drop of water of 15nl on a glass substrate of contact angle 30°.



**Figure 3:** Numerical modeling of the drop

evolution during evaporation on a glass substrate at 60°C. The profiles are given for different times



**Figure 4:** Experimental and numerical prediction of drop evaporation.

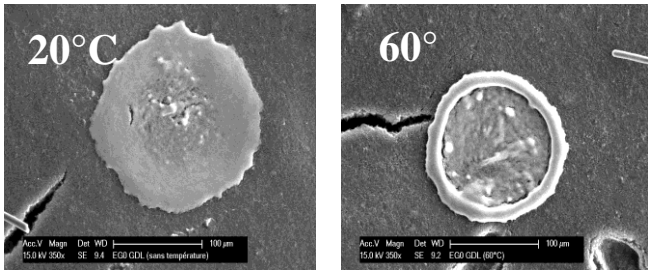
We obtain through our model a quite good prediction of the results. Figure 3 highlights the decreasing drop contact surface during evaporation with the transient profiles and the good agreement regarding the decreasing volume is shown in Figure 4. The experimental limitations prevent to fully measure the volume evolution up to complete disappearance of the drop. The numerical model predicts an evaporation time of almost 2.2s which compares quite well with the characteristic evaporative time.

## 4. Model Prediction and Analysis

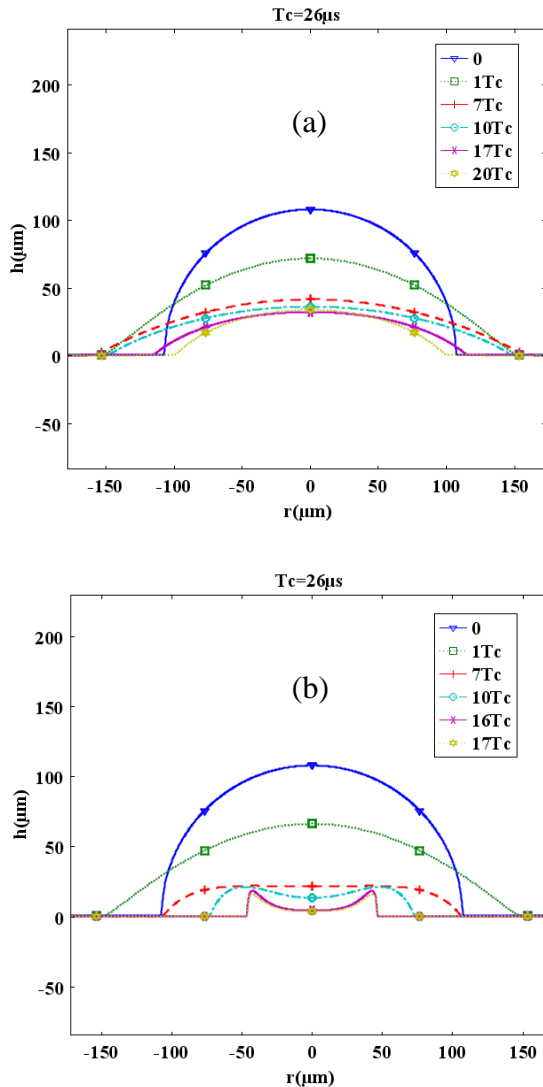
### 4.1 The coffee ring formation

The model established allows modeling the evaporation of a binary component containing particles. The evaporation of such a mixture leads to the formation of the coffee ring. The model is used here for controlling the coffee ring phenomenon involved in applications such as fuel cell manufacturing (Figure 5).

The evaporation of a drop of 2.5nl volume (or 170μm of diameter) containing 3% of solid particle on the PEMFC fuel cell GDL (gas diffusion layer) is performed at 20°C and 60°C.



**Figure 5:** Experimental results of coffee ring formation on PEMFC fuel cell GDL (*Gas diffusion layer*)



**Figure 6:** Temperature effect on the coffee ring formation at (a) 20°C and (b) 60°C.

For this modeling, since the ink on the GDL substrate has a contact angle of around 100°, we use as an initial profile a spherical cap deposited drop which evaporates when spreading from 90° on the heated substrate.

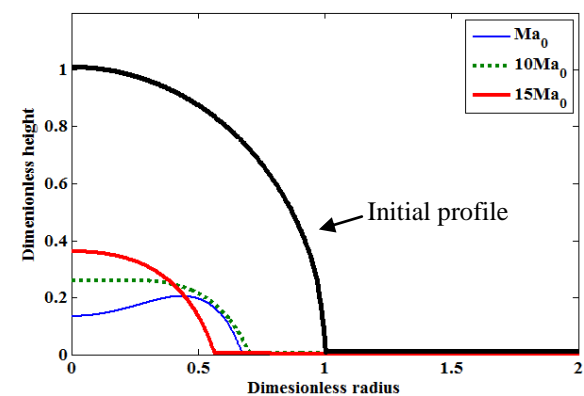
We numerically retrieve the fact that a heated substrate leads to greater evaporation which in turn yields an enhanced coffee ring deposit (Figure 6). We also obtain that the final contact diameter is  $0.5r_0$  which is comparable with the experimental result.

Conversely, a cooled substrate diminishes edge evaporation from the drop and may hinder or even prevent coffee ring formation.

It worth mentioning that the model developed in this work is, to the best of our knowledge, the first 1D model highlighting the formation of the coffee ring.

#### 4.2 Sensitivity to the Marangoni effect

We have also tested the sensitivity of the model concerning the Marangoni effect. One may note that higher is this effect, the lower the coffee ring formation (Figure 7). Indeed, as suggested by [3, 4], flow-induced Marangoni effect counteracts deposition of particles at the triple line. The Marangoni effect being controlled by the rate of change of surface tension with temperature ( $\gamma$ ) and therefore depending on the fluid, its control over the fluid composition may help alleviate the need for the coffee ring. This result is also in agreement with our experimental observation, where the addition of ethylene glycol to the ink tested induces a Marangoni flow preventing the coffee ring deposit.

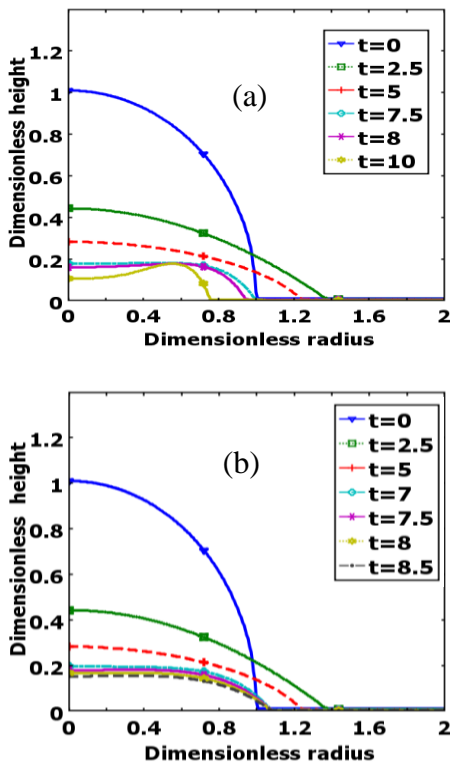


**Figure 7:** Model sensitivity to the Marangoni effect.

#### 4.3 Sensitivity to the liquid particles content

The presence of particles limits the coffee ring

deposit as numerically highlighted (Figure 8). By taking into account this effect, the model retrieves the same trends; an interpretation could be attributed to the increase of the viscosity due to the presence of particles, controlling by the way the coffee ring formation.



**Figure 8:** Sensitivity of the particles content in the solution (a)  $\phi_0$  and (b)  $2\phi_0$

## 5. Conclusion

In this work, a theoretical model based on the lubrication approximation is derived describing the evaporation of multi-component liquid drop on a conductive substrate. The model includes the effect of the moving contact line, fluid and substrate properties, and the operating conditions such as temperature. This model is found to be in good agreement quantitatively with most of the experimental observations.

After validation, the simple 1D model developed enables the prediction of the coffee ring formation and effects such as Marangoni and solid content on binary mixture evaporation.

This work highlights the fact that deposit patterns are influenced by four main parameters: solvent composition, solid content, substrate properties and temperature.

## Acknowledgments

The authors wish to acknowledge financial support from ANR PAN'H 2008 CATIMINHY project.

## References

- [1] M. Singh, H. M. Haverinen, P. Dhagat, G. E. Jabbour, Inkjet Printing—Process and Its Applications, *Adv. Mater.*, 22, 673–685, 2010.
- [2] D. Soltman and V. Subramanian, Inkjet-Printed Line Morphologies and Temperature Control of the Coffee Ring Effect, *Langmuir*, 2007.
- [3] R.D. Deegan, O. Bakajin, T.F. Dupont, G. Huber, S.R. Nagel, T.A. Witten, Capillary flow as the cause of ring stains from dried liquid drops, *Nature*, 389, 827, 1997.
- [4] H. Hu and R. G. Larson, Marangoni Effect Reverses Coffee-Ring Depositions, *J. Phys. Chem. B*, 110, 14, 2006.
- [5] A. Oron, S.H. Davis, and S.G. Bankoff, Long-scale evolution of thin liquid films, *Rev. Mod. Phys.* 69, 931, 1997.
- [6] L.W. Schwartz and R.R. Eley, Simulation of droplet motion on low-energy and heterogeneous surfaces, *J. Colloid Interface Sci.*, 202, 173-188, 1998.
- [7] M. H. Eres, D. E. Weidner, and L. W. Schwartz, Three-Dimensional Direct Numerical Simulation of Surface-Tension-Gradient Effects on the Leveling of an Evaporating Multicomponent Fluid, *Langmuir*, 15, 1859-1871, 1999.
- [8] N. Murisic, L. Kondic Modeling Evaporation of Sessile Drops with Moving Contact Lines, *Phys. Rev. E*, 78, 065301(R), 2008.