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A simple method for simulating the coffee stain effect

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ABSTRACT

Inkjet printing of structures like microscopic electronic circuit paths on thin substrates includes drop wise application and drying of particulate suspensions. The drying of these drops can leave behind a multiplicity of structures of sediment deposit, which to control is a major subject of investigation in the design of the process. In this work we present a simple and efficient simulation method for predicting the three dimensional structure of sediment deposits based on a one way coupled scheme of Brownian dynamics and analytic modeling of the fluid flow inside a drying colloidal drop under presence of Marangoni flow. Aiming for micrometer sized drops with high particle concentrations (up to 20 vol.%), our method takes into account particle diffusion and convection, particle collisions as well as particle staggering at the contact line. The method is validated by experimental results and applied to predict the behavior of a new setup. We find from our simulations that DLVO forces may be neglected for a well stabilized suspension and that the model works well in predicting coffee stain formation.

1. Introduction

The coffee stain effect is well known to everyone who ever spilled a drop of coffee and found it leaving some ring shaped remains after drying. Besides its undesirable appearance in everyday life, this effect is also of interest for many technological applications, e.g., for inkjet printing.

In the production of highly conductive microstructures on a thin substrate via inkjet printing, suspensions of metallic particles are applied drop wise in order to create a layer of metallic sediment, which afterwards is sintered yielding a solid conductive structure [1,2]. The principal regimes in which drops are suitable for inkjet printing (i.e. Reynolds and Weber number) are discussed by Derby and Reis [3]. When drying, these drops can leave behind a multiplicity of structures of sediment deposit [4], ranging from single rings over multiple rings to a uniform layer. The electrical conductivity G of a body can be calculated using Pouillet's law

$$G^{-1} = \int \rho/A \, ds, \tag{1}$$

where ρ is the resistivity of the material, A is the local cross section of the body and s runs over its length. From Eq. (1) it is clear that a high conductivity requires a large cross sectional area of the structure all along its length. Hence, the shape of the dried deposit pattern is very important for the quality of the final product.

Investigating the preferential deposit structures of drying drops, Deegan et al. [5,6] found that ring formation occurs if both the contact line is pinned (i.e. it does not recede during drying) and evaporation from the edge of the drop is possible, both of which is usually valid in practice [3]. The pinning of the contact line leads to a flow towards the edge region to compensate for the evaporation of liquid in this area, which results in a corresponding convective particle transport. Park and Moon [7] further investigated the influence of surface tension and found that ring formation can be prohibited by using a drying agent which slows down the drying process and introduces a gradient of surface tension. This gradient leads to a flow from regions of low to regions of high surface tension, often referred to as Marangoni flow, and can enable particles to travel back into the bulk region, i.e. it reduces the probability of ring formation. Another parameter influencing the pattern of deposit is the drop viscosity, which was studied by Chon et al. [8] by varying particle loads and sizes at constant volume concentration. Here the drops of smaller particles and higher viscosities were found likely to fully cover the substrate whereas drops of larger particles and smaller viscosities tended to form coffee stains. Recently Shen et al. [9] investigated the influence of the proportion of diffusion and convection within the drop and proposed the existence of a minimal droplet size below which diffusion exceeds convection and hence particles do not significantly accumulate at the edge of the drop.

Summarizing the above, the most important parameters favoring ring structures seem to be a pinned contact line, high particle concentration and small drop sizes. In this study, the first is assumed to always be true, the latter two will be considered in more detail in Section 3. Another important parameter can be the presence of Marangoni flow, which can be considered by the model proposed later on in this work. However, its influence on the particle deposition is not studied here.

Numerical investigations of the drying process have been carried out using Finite-Element modeling for both drop and atmosphere flow

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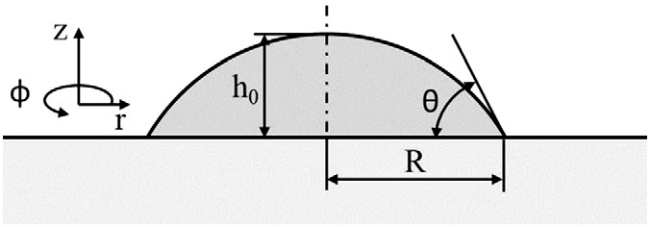

Fig. 1. A liquid drop on a flat solid substrate.

based on the Navier–Stokes equations and a continuum advection–diffusion approach to track the particle concentration within the drop [4,10]. While a gradient in surface tension was neglected by Widjaja and Harris [10] it was considered by Bhardwaj et al. [4], both leading to good agreement with experimental findings. Explicit modeling of the particle trajectories was carried out by Hu and Larson [11] who coupled their analytically derived flow field with Brownian dynamics simulations for very light suspensions (<1 vol.% of solid content) where particle collisions where neglected and the particles were fixed upon contact with the substrate. A similar approach was used in two dimensions by Petsi et al. [12] who successfully simulated the deposit patterns of a variety of drops by coupling Brownian particles and an analytically derived flow field for which Marangoni flows were assumed to be absent. Masoud and Felske [13] used their own fluid flow model in combination with a Lagrangian simulation method for the particles and neglected particle diffusion, Marangoni flows and particle collisions. Considering two dimensional drops of constant particle volume fraction, they studied both hydrophobic and hydrophilic cases with both pinned and freely moving contact lines and also found a pinned contact line to highly favor ring formation. All the reported studies using explicit tracking of particle motion neglect the effect of the particles onto the fluid flow (i.e. they all use the so called one way coupling).

In this work we present a simple and efficient simulation method for predicting the three dimensional structure of the deposits. The method is based on a coupled scheme of Brownian dynamics [14] and an analytic model of the fluid flow inside a drying colloidal drop under the presence of Marangoni flow. The model aims to account also for higher particle concentrations and, therefore explicitly simulates particle collisions. The analytic flow model of Hu and Larson [11] which we use, however, remains unchanged. In contrast to [11] we use a no-slip boundary condition for the particles on the substrate and fix them only at the contact line or at other fixed particles to allow for particle staggering. The method is implemented in the SimPARTIX software package for particle based simulations [15].

2. Methods

2.1. Macroscopic model: fluid flow

The macroscopic drying model predicts both the velocity field within the drop and the evolution of the drop surface. In this work we adapted the analytic model by Hu and Larson [11], which is based on the assumption that the drop is always in equilibrium. Hence, the drop surface always maintains a spherical cap shape

$$h(r,\Theta) = \sqrt{R^2/sin^2\Theta - r^2} - R/tan\Theta, \tag{2}$$

where r is the radial component of the cylindrical coordinate system (r, ϕ, z), h is the height of the surface over the substrate, Θ is the contact angle and R is the radius of the contact line (see Fig. 1). The model further assumes a pinned contact line, i.e. it does not recede, which is usually valid until the final stage of the drying process [5].

Under realistic process parameters, most of the inks used in practice feature low evaporation rates. Hence, the vapor concentration c at the phase boundary can be assumed to be almost constant

$$\nabla^2 c = 0. \tag{3}$$

Hu and Larson [16] showed that both evaporation rate as well as a decrease of drop height are almost constant until the end of the drying period t_e. Hence, the rate of change of the drop height can be represented by the constant

$$\frac{dh_{(r=0)}}{dt} \approx -\frac{h_0}{t_e}, \tag{4}$$

where h_0 is short for $h(r=0, \Theta_0)$ and refers to the initial height of the drop at its axis of rotational symmetry. Recently it has been shown that this assumption only holds for drops with contact angles up to approximately 50 ° and pinned contact lines [17].

Under these conditions, the velocity profile $\mathbf{v}$ within the drop can be expressed analytically in the form [18,11]

$$\begin{aligned}\tilde{\mathbf{v}} &= \frac{3}{8}\frac{1}{1-\tilde{t}}\frac{1}{\tilde{r}}\left[\left(1-\tilde{r}^2\right)-\left(1-\tilde{r}^2\right)^{-\lambda}\right]\left(\frac{\tilde{z}^2}{\tilde{h}^2}-2\frac{\tilde{z}}{\tilde{h}}\right)+\frac{\tilde{r}h_0{}^2\tilde{h}}{R^2}\left(\tilde{J}\lambda\left(1-\tilde{r}^2\right)^{-\lambda-1}+1\right)\\ &\times\left(\frac{\tilde{z}}{\tilde{h}}-\frac{3\tilde{z}^2}{2\tilde{h}^2}\right)+\frac{Ma\ h_0\tilde{h}}{4R}\frac{d\tilde{T}}{d\tilde{r}}\left(2\frac{\tilde{z}}{\tilde{h}}-3\frac{\tilde{z}^2}{\tilde{h}^2}\right)\\ \tilde{\mathbf{v}}_z &= \frac{3/4}{1-\tilde{t}}\left(1+\lambda\left(1-\tilde{r}^2\right)^{-\lambda-1}\right)\left(\frac{\tilde{z}^3}{3\tilde{h}^2}-\frac{\tilde{z}^2}{\tilde{h}}\right)-\frac{3/4}{1-\tilde{t}}\left(\left(1-\tilde{r}^2\right)-\left(1-\tilde{r}^2\right)^{-\lambda}\right)\left(\frac{\tilde{z}^2}{2\tilde{h}^2}-\frac{\tilde{z}^3}{3\tilde{h}^3}\right)\frac{\partial\tilde{h}}{\tilde{r}\partial\tilde{h}^3}\\ &-\frac{h_0{}^2}{R^2}\left(\tilde{J}\lambda\left(1-\tilde{r}^2\right)^{-\lambda-1}+1\right)\left(\tilde{z}^2-\frac{\tilde{z}^3}{\tilde{h}}\right)-\frac{\tilde{r}^2\tilde{h}_0{}^2}{R^2}\tilde{J}\lambda(\lambda+1)\left(1-\tilde{r}^2\right)^{-\lambda-2}\left(\tilde{z}^2-\frac{\tilde{z}^3}{\tilde{h}}\right)-\end{aligned} \tag{5}$$

$$\begin{aligned}&\frac{\tilde{r}^2\tilde{h}_0{}^2}{R^2}\left(\tilde{J}\lambda\left(1-\tilde{r}^2\right)^{-\lambda-1}+1\right)\left(\frac{\tilde{z}^3}{\tilde{h}^2}\right)\frac{\partial\tilde{h}}{\partial\tilde{h}^3}-\frac{Ma\ h_0}{4R}\left(\tilde{z}^2-\frac{\tilde{z}^3}{\tilde{h}}\right)\left(\frac{d^2\tilde{T}}{d\tilde{r}^2}+\frac{1}{\tilde{r}}\frac{d\tilde{T}}{d\tilde{r}}\right)\\ &-\frac{Ma\ h_0}{4R}\left(\frac{\tilde{z}^3}{\tilde{h}^2}\right)\frac{d\tilde{T}}{d\tilde{r}}\frac{\partial\tilde{h}}{\partial\tilde{h}^3}\end{aligned} \tag{6}$$

where the parameter $\lambda = \lambda(\Theta) = 0.5 - \Theta/\pi$ and the dimensionless quantities $\tilde{\mathbf{v}}_r = \mathbf{v}_r t_e/R, \tilde{\mathbf{v}}_z = \mathbf{v}_z t_e/h_0, \tilde{t} = t/t_e, \tilde{r} = R/t, \tilde{z} = z/h_0, \tilde{J} = J(0,\Theta)/\rho\tilde{h}$, and $\tilde{T} = (T-T_c)/(T_e-T_c)$. The temperatures T_e and T_c apply at the edge and the top of the drop, respectively. ρ and μ are the fluid density and kinematic viscosity, $Ma = -\beta(T_e - T_c) - t_e/\mu R$ is the Marangoni number where β is the surface tension–temperature coefficient. For details of the calculation of the surface temperature T and the

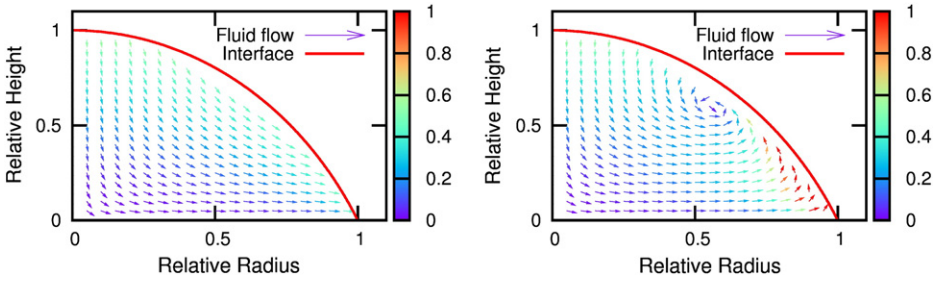

Fig. 2. Analytic description of the fluid flow within the drop without (left) and with (right) Marangoni effect.