

Modeling evaporation and ring-shaped particle deposition of a colloidal microdroplet, with applications in biological assays

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ABSTRACT

Biological microarrays can be manufactured by spotting colloidal drops and evaporating them. The remaining deposits, however are not always homogeneous and often exhibit ring-like patterns. In this work, a numerical modelling is made for the evaporation of a colloidal nanoliter drop on a solid, non-isothermal substrate. The equations governing fluid, heat and mass transport are expressed in a Lagrangian framework. The boundary conditions at the drop free surface are the mass and energy jump conditions. The diffusion of vapor in the gas surrounding the drop is solved numerically, determined by the drop-substrate geometry and thermodynamic conditions. The formation of a peripheral ring is observed during the evaporation of the drop. The proposed modeling will allow the determination of optimum processing conditions to make spot arrays from drying colloidal drops.

Keywords: evaporation, colloidal drop, ring formation, particle deposition

1 INTRODUCTION

Colloidal drops evaporating on a solid substrate can be used to deposit or organize small particles. The pattern left after the evaporation often looks like the ring-like structure of the dried DNA drop [1] in Figure 1a. Transport phenomena during the evaporation of a colloidal drop evaporation are complex and coupled: the fluid dynamics is transient and severely influenced by the shrinking free surface and wetting conditions; heat transfer occurs by evaporation, convection and conduction to the substrate; mass transfer takes place by the diffusion of liquid vapor in the atmosphere and diffusion of particles in the bulk liquid. Deegan and co-workers made a significant contribution to the understanding of the deposit formation [2]. They explained the formation of a peripheral ring-pattern or “coffee ring” by showing that the diffusion equation predicts the evaporative flux to be highest near the wetting line. This phenomenon, together with a pinned wetting line, results in a radially outward flow inside the drop so that most particles are convected towards the wetting line. Recently, Maenosono et al [3] studied the growth of a nanoparticle-ring during the evaporation of pyridine and

water drops. They observed two stages of ring evolution, a ring buildup followed by a receding of the wetting line. They predicted ring growth dynamics and found a reasonable agreement with experiments for both the ring growth and the final width. Researchers have also looked the formation of multiple rings during the drying of the colloidal drop. Adachi et al. [4] suggested that the “stick slip motion” of the wetting line caused the formation of stripe patterns (since particles accumulate at the wetting line when it sticks) and they proposed a model for the stick slip motion. Due to the complex, coupled physics involved, most theoretical models reported are based on relatively crude assumptions such as fluid flow with negligible inertia [5-8], negligible gravity [5-8], small wetting angle [2, 8], a spherical cap shape of the free surface [2, 5-10], pinned wetting line throughout the evaporation [5-8, 10-14] and negligible heat transfer between the drop and the substrate [2, 6, 8, 14, 15]. However, the ring formation kinetics depends upon the evaporation rate, flow and thermal fields. Thus a full numerical solution for the fluid flow, temperature field and particle diffusion is highly desirable to predict particle deposition and pattern growth. In this paper, we present a two-dimensional axisymmetric finite element model that solves the mass conservation, Navier-Stokes, energy equations, diffusion equation for particle transport and diffusion equation for the vapor concentration outside the drop for the evaporation of a nanoliter colloidal drop.

2 NUMERICAL MODEL

We extend a mathematical modeling for drop deposition [16, 17] to account for the evaporation and particle transport in the colloidal drops. The 2D axisymmetric finite element model solves the unsteady equations of mass, momentum and heat transfer. All governing equations are expressed in a Lagrangian framework, which provides accurate modeling of the free surface motion. The boundary conditions at the free surface are the mass and energy jump conditions. While the equations for mass conservation, Navier-Stokes and heat transfer equations are given in [16, 17], we describe here the mathematical model for particle transport and evaporation: The value of evaporative mass flux j at the free surface is obtained by solving the quasi-steady diffusion equation for the water vapor concentration

$c: \nabla^2 c = 0$. The boundary conditions for the above governing equation are:

(a) at $r > R_{cap}, z = 0; \partial c / \partial z = 0$

(b) at $r = 0; \partial c / \partial r = 0$

(c) at $r = \infty, z = \infty; c = Hc_\infty$

(d) at free surface $c = c_{int}$

where R_{cap} is the wetted radius, c_{int} is the saturated density (kg/m^3) of water vapor near the interface and c_∞ is density of water vapor in the far-field (ambient). These densities are calculated using data in [18]. At the free surface of the drop, we assume 100% of relative humidity H , while in the far-field H is measured. In these calculations, the far field ($r = \infty, z = \infty$) is considered at $r = 20R_{cap}, z = 20R_{cap}$. The evaporative mass flux j at the free surface can be expressed as:

$$\mathbf{j}(r, T) = D_{LG}(T) \left[\frac{\partial c}{\partial r} \mathbf{n}_r + \frac{\partial c}{\partial z} \mathbf{n}_z \right] \Bigg|_{free_surface}$$

where D_{LG} is the diffusion coefficient of liquid in surrounding gas. At the free surface of the drop, the hydrodynamic and thermodynamic vapor-liquid jump conditions [10, 19] are applied:

$$\mathbf{j} \cdot \mathbf{n} = \rho(1 - X_f)(\mathbf{v} - \mathbf{v}_f) \cdot \mathbf{n} \quad \text{and} \quad jL = -k\nabla T \cdot \mathbf{n}$$

where, \mathbf{v} is velocity of the liquid at the free surface, \mathbf{v}_f denotes the velocity of the free surface, \mathbf{j} is the evaporative mass flux at the free surface ($\text{kg/m}^2\text{-s}$), \mathbf{n} is the outward normal unit vector at the liquid-air interface ρ is the density of the liquid. X_f is the volume concentration of particles at the free surface and L is the latent heat of evaporation of the liquid (J/kg). We assume that the particles have same density as water. The governing equation for particles transport is given by [20-22]: $D_X / Dt = D_{PL} \nabla^2 X$ where D_{PL} is the diffusion coefficient of particles in the fluid. Boundary conditions are given by:

@ $r = 0, \partial X / \partial r = 0$ (Axisymmetry).

@ $z = 0$, one of the following two cases is possible:

1. Non-sticky substrate, like silicon: $\partial X / \partial z = 0$
2. Sticky substrate, like silicone: $X = 0$ (Perfect sink boundary condition).

Physically, the perfect sink boundary condition means that all particles approaching the surface deposit instantaneously [23]. The mathematical model presented is solved using the Galerkin finite element method [16]. The computational domain (Figure 1b) is discretized with a mesh of linear, triangular elements. The unsteady solution for the fluid dynamics is based on the scheme given by Bach and Hassager [24]. The time step is constrained to the smallest time scale of the problem (free surface oscillations, about 15 ns) so that a whole evaporation simulation (2 minutes for a 20nL drop) would involve 8 billion time steps, implying a prohibitive computing time. To resolve this issue, a two-step temporal integration scheme is developed for this problem. This scheme is described as follows: first, a converged, instantaneous solution of the

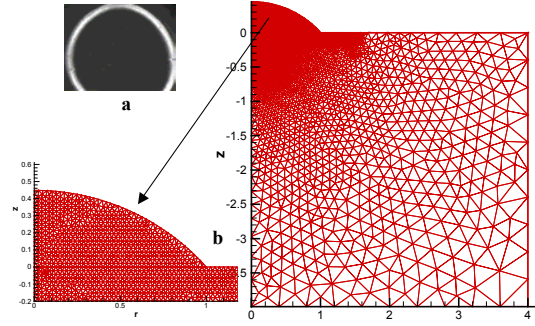


Figure 1: (a) Ring-like pattern formation during the drying of a DNA drop. Drop wetted radius is about 500 micrometer [1] (b) Typical mesh in the computational domain.

fluid flow and the evaporation flux are obtained using a short time step ($\Delta\tau_{short}$, order of 15 ns) using scheme in [24]. Second, assuming that the fluid flow remains steady, a new location of the free surface due to the evaporation is calculated using a time step 4 orders of magnitude larger ($\Delta\tau_{long}$, order of 150 μs). Then, the first scheme is applied again and so on. In order to avoid losing particles during the shrinkage of the free surface, a source term is added to the diffusion equation for the free surface elements. Increase in the concentration of the particles with time due to the evaporation is given by X_S / ρ where ρ is the density of the liquid and the source term is defined as: $S = j\delta A / \delta V$ where j is the evaporative mass flux [$\text{kg of water m}^{-2}\text{s}^{-1}$], δA is the area from which liquid evaporates [m^2] and δV is the volume of the liquid in which particles accumulate [m^3]. This two-step approach is justified as long as the long time step is small with regard to the evaporation of the drop (quasi-steady approach), so that the fluid flow and the evaporation flux can be considered as steady for the duration of the long time step.

3 RESULTS

Results are presented in this section for the evaporation of a 20 nL water drop with 298 micrometer initial wetted radius and 49° initial contact angle on a flat substrate for four different cases: (a) Drop contains 1 micron particle diameter on sticky or non-sticky substrate (b) Drop contains 10 nm particle diameter on sticky or non-sticky substrate. The value of the diffusion coefficient for 1 micron and 10 nm particles are calculated as $4\text{e-}13$ and $4\text{e-}11 \text{ m}^2/\text{s}$ respectively, assuming spherical particles by Stokes-Einstein equation [25]. The initial temperature of the drop is taken as 25°C (ambient temperature). A relatively high substrate temperature (125°C) was selected to enhance evaporation. A perfect thermal contact is assumed at the drop-substrate interface. The ambient temperature and relative humidity are recorded as 25°C and 40% respectively. The values of dimensionless numbers, Reynolds, Weber, Froude number are 330, 4.1 and 342 respectively. The variation of viscosity with temperature is

taken into account. Initially, the drop contains a uniform 0.5% concentration of particles. The thermophysical properties for water and fused silica used in simulations are presented in [26]. Figure 2 shows streamlines and isotherms (left) during the evaporation of colloidal 20 nL water drop containing 1 micron particles on a non-sticky fused silica substrate heated at 125°C.

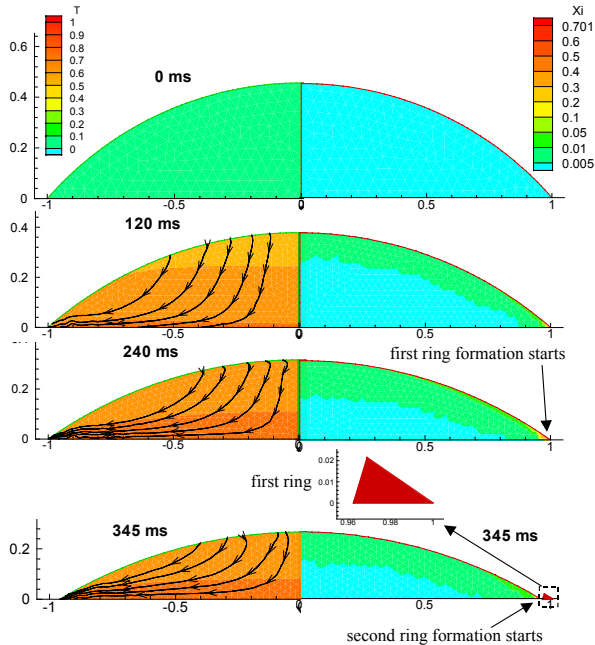


Figure 2: Particle concentrations (right), streamlines and isotherms (left) for the evaporation of a 20 nL water drop for 1 micron particles.

During the evaporation ($t = 0$ to 345 ms), the fluid flow inside the drop is radially outward. This outward flow is due to the fact that the pinning of the wetting line ensures that the liquid evaporating from the edge is replenished by the liquid from the interior [2]. The value of the evaporative flux is also higher near the wetting point. This corresponds to a higher mass loss near the wetting line. This outward flow pattern has maximum velocities on the order of 10 micrometer/sec. The heat transfer is mainly governed by three mechanisms: conduction of heat from the substrate, evaporative cooling along the free surface and convective effects inside the drop. Flat isotherms in Figure 2 show that the conduction heat transfer dominates over convection and evaporative cooling along the free surface. Figure 2 shows the concentration of particles (right) at different times during the evaporation of the drop. The evaporation of the liquid results in build up of concentration along the free surface. The particles accumulate faster near the wetting line than on the top of the drop since the evaporation is highest near the wetting line. As time evolves, more particles are convected to the edge of the drop where they accumulate and start forming a ring (at $t = 240$ ms). A concentration value of 0.7 is considered as the criterion of the ring formation because it corresponds to maximum packing of the particles. When height of the ring formed reaches to 8 micrometer, wetting line is allowed to recede

and pinned to a different location near the first ring. At this time, width of the ring formed is 12 micrometer. The formation of second ring starts at $t = 345$ ms. The mass distribution of the particles in the drop vs. radial distance is shown in Figure 3 for different times during the evaporation of the drop for 10 nm particles.

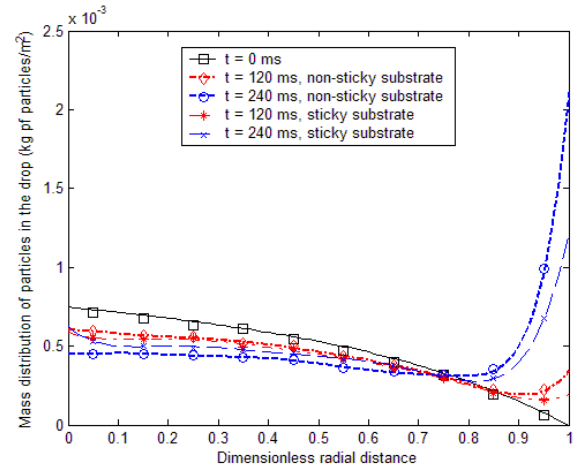


Figure 3: Mass distribution of particles at different radial locations for different times during the evaporation of the drop for the non-sticky and the sticky substrate for 10 nm particles.

Two cases are compared: (a) non-sticky substrate (b) sticky substrate. In case of non-sticky substrate, profile of mass distribution of particles, which is approximately spherical cap initially, develops a spike near the contact line at $t = 240$ ms. This spike is representative of the ring of the particles. At $t = 240$ ms, mass distribution for the sticky substrate shows that the particles have deposited along the drop-substrate interface. Figure 4 shows the mass distribution of the particles in the drop vs. radial distance for 1-micron particles. Two cases are compared for the stick and the non-sticky substrate as explained above. In this case, mass distribution profiles shows that the particles deposition along the drop-substrate interface is negligible.

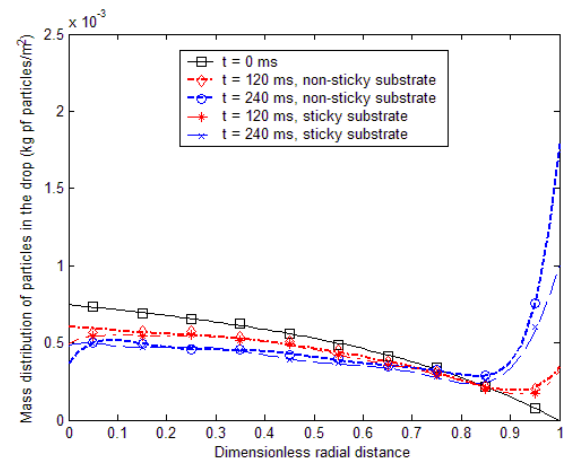


Figure 4: Mass distribution of particles at different radial locations for different times during the evaporation of the drop for non-sticky and sticky substrate for 1-micron particles.

4 CONCLUSIONS

A numerical model for the evaporation of a nanoliter evaporating colloidal drop is presented. Results are presented for the evaporation of colloidal 20 nL water drop on a fused silica substrate heated at 125°C. The flow, thermal and particles concentration fields are shown in the drop. Ring growth and deposition of particles onto the substrate are predicted at different times during the evaporation of the drop.

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