Drying droplet deposited on poor wetting substrate: beyond the lubrication approximation

P Lebedev-Stepanov¹², S Efimov¹ and A Kobelev²

¹ Photochemistry Center of FSRC Crystallography & Photonics RAS Novatorov St., 7a/1, Moscow, 119421, Russia
² National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 31 Kashirskoeshosse, 115409, Moscow, Russia

E-mail: petrls@yandex.ru

Abstract. Evaporating sessile droplet of aqueous solution deposited on hydrophobic surface is an urgent object of theoretical modeling (evaporation dynamics, microfluidics inside the drop, particle dynamics in evaporating drop, etc) and applied researches (printing technologies, nanoparticle ensemble self-assembly processes, hydrophobic coatings, etc). Although self-assembly investigation in evaporating droplet of colloidal solution on smooth surfaces with quite acute contact angles has been widely studied recently for liquids of different properties, nanoparticles ensemble self-assembly processes in droplet deposited on hydrophobic and superhydrophobic surfaces has not received much attention up to date. This work includes the analysis of application of existing droplet evaporation models, the boundary conditions for the hydrodynamic flows on the drop surface, as well as the nanoparticle dynamics in the volume of aqueous solution droplet deposited on hydrophobic flat surface, and the dried pattern formation processes modelling.

1. Introduction
There are three basic problems to estimate the colloidal particles self-assembly in evaporating droplets: 1) solute evaporation from the droplet surface to surrounding air (outer problem), 2) hydrodynamic flows in droplet volume (inner problem), 3) particle dynamics into droplet with account of interparticle interactions, particle-surfaces interactions, particle-flow interactions, solvation effects [1,2]. Although self-assembly investigation in evaporating droplet of colloidal solution on smooth surfaces with quite acute contact angles has been widely studied recently for liquids of different properties including binary solute mixtures [3-8], nanoparticles ensemble self-assembly processes in droplet deposited on hydrophobic and superhydrophobic surfaces has not investigated up to date.

A hydrodynamic flow occurs inside the drop as a result of the drop volume change and chemical potential gradients on surface or into volume of the liquid drop. The flow dramatically depends on character of the triple line movement during drop evaporation. Temperature gradient on drop surface can lead to arising of the toroidal vortex flow if Marangoni number is reached a value more than 100 approximately [9]. On the contrary, the flow has the simplest structure without the vortex component when the Marangoni number is small, as it takes place in the case of a little aqueous droplet (with a volume of 10-100 picoliters) at normal conditions [1]. Such a flow, i.e. the Deegan flow, which leads to coffee ring effect [4] we consider for illustration of the 3D generalization approach of 1D
approximation of the boundary conditions that are used in the lubrication theory framework to
describe not only the droplets with acute contact angles but also in case of obtuse ones. Thus, we
neglect the temperature gradient effects and Marangoni convection due to the volume of considered
droplet is quite small and Marangoni number is less than 100.

2. Spherical drop evaporation models
The contact angle of aqueous droplet deposited on hydrophobic surface has a value in interval from
about 90° to about 180°. In this case, evaporation flow density has no the integrable singularity at
contact line, unlike a drop with an acute angle (figure 1). Deegan [4], Hu and Larson [5,6], Popov [7]
have elaborated the useable models of evaporation of sessile drop of single liquid based on Maxwell
diffusion model.

This model is useful for calculation of the evaporation flow for the contact angle interval from 0° to
90°. In framework of this model, the evaporation flow density on the droplet surface is given by

\[ J(r) = J_0(\lambda) \left(1 - \frac{r^2}{R^2}\right)^{-\lambda(0)} , \quad \lambda(\theta) = \frac{1}{2} - \frac{\theta}{\pi}. \]

where \( \theta \) is a contact angle; \( R \) is a droplet radius (figure 2).

Figure 1. Evaporative flux density (evaporation rate) on a surface of sessile droplet with acute contact angle (left) and with obtuse angle (right); the pictures were estimated by Comsol

To increase the computation speed, computer modeling of self-assembly of an ensemble of
nanoparticles in drying droplet requires the using of simple analytic approximation for evaporation
flow. A good example of such approximation is the Hu-Larson’s [5] solution given by equation 1. But, up to date, such a solution for droplet on solvatophobic substrate is absent.

Figure 2. Geometry of liquid capillary-sized droplet on a flat substrate.
Popov’s model with integral for the evaporation flux [7] can be used for whole open interval of contact angles from about 0° to 180°:

\[
W = -\pi R D (n_x - n_w) \left[ \frac{\sin \theta}{1 + \cos \theta} + 4 \int_0^{\pi} \frac{1 + \cosh 2\theta \tau}{\sinh 2\pi \tau} \tanh[(\pi - \theta)\tau] \right],
\]

but the numerical approximation of the evaporation flux given by Picknett and Bexon [3] is more applicable for computer modelling.

3. Boundary conditions for hydrodynamic flow

The similar situation takes place for inner problem which is concerned the hydrodynamic flows into droplet. Lubrication approximation analysis given by Oron [10], Deegan et al [4] can be applied only for the flow field produced by droplet evaporation under the additional approximation of a flat droplet (small contact angle). Deegan et al. have used the lubrication approximation to calculate the hydrodynamic flow into a droplet with acute angle and pinned contact line.

Hu and Larson have developed such a semi-analytical approximation in their model of hydrodynamic flows in drying drop. The kinematic boundary condition with a phase change is

\[
(n, V) = [n_x, n_z][0, \dot{Z}] + \left(\frac{n, \dot{J}}{\rho}\right),
\]

where \((n, \dot{J})\) is the evaporation flux along the direction normal to the free surface, where \(n\) is a unit vector along the normal direction, and \(n_x\) and \(n_z\) are the \(r\) and \(z\) components of the unit normal vector \(n\), respectively.

![Image](image.png)

**Figure 3.** Trajectories of displacement of the points on liquid surface of drying droplets with acute contact angle during evaporation with a pinned contact line: a) lubrication theory (wrong); b) our model [1,2]; c) geometry of displacement of the stationary point on the surface of the evaporating drop [2].

In our work [1], the boundary conditions of a more general form (three-dimensional) for the rate of flow on the top of drop surface were proposed:

\[
V_z(\theta, t) = \frac{J(\theta, t)}{\rho_m} \cos \theta - \frac{dZ(\theta, t)}{dt}, \quad V_r(\theta, t) = \frac{J(\theta, t)}{\rho_m} \sin \theta - \frac{dR(\theta, t)}{dt},
\]

where \(\rho_m\) is a mass density of a liquid, \(\frac{dZ(\theta, t)}{dt}\) and \(\frac{dR(\theta, t)}{dt}\) are \(z\)- and \(r\)-components of velocity of the geometrical point on a drop surface. Such a shift takes place due to the evolution of the form and size of the evaporated drop with pinned contact line (figure 3).
Figure 4. Trajectories of displacement of the stationary mathematical points (not the particles) on surface of drying droplets with obtuse contact angle during evaporation with a pinned contact line according to our new model.

These boundary conditions were successfully used to simulate the self-assembly of nanoparticles in sessile droplets with contact angles having the value smaller than right angle. However, applicability of equations (4) for hydrophobic droplets still has not been investigated. Until now, the boundary conditions for general three-dimensional case which includes the obtuse contact angles are still absent in scientific publications.

We have analyzed the application of existing droplet evaporation models, the boundary conditions for the hydrodynamic flows on the drop surface (figure 4), as well as the nanoparticle dynamics in the hydrophobic droplet, and the dry pattern formation processes modeling.

4. Dissipative particle dynamics into evaporating drop

Dissipative dynamic model [1,2] was used to estimation of the nanoparticles self-assembly in evaporating aqueous droplet on hydrophobic substrate. The $i$-th particle acceleration $\frac{dv_i}{dt}$ is calculated by the following Langevin equation:

$$m_i \frac{dv_i}{dt} = m_i \left( \frac{\partial V}{\partial t} + (v_i, \nabla)V \right) - \nabla \sum_{j \neq i} U(r_{ij}) + F_{Si}(r_{Si}) + F_{Li}(r_{Li}) + F_{Re}(r_{Re}) - 6\pi\eta(v_i - V) + F_{Bi},$$

where $m_i$ is an effective mass of $i$-th particle with radius of $a$, the first member of the right part is the hydrodynamic force, the second term is the sum of conservative forces with potential $U(r_i)$ acting on the $i$-th particle from other $j$-th particles, $F_{Si}(r_{Si})$ is the interaction force between the $i$-th particle and substrate, $F_{Li}(r_{Li})$ is the capillary force, $F_{Re}(r_{Re})$ is a friction force acted due to roughness of the substrate surface, $- 6\pi\eta(v_i - V)$ is a Stokes viscous force, where $V$ is a field of hydrodynamic flow in the solution, and the Brownian force is $F_{Bi}$.

The calculation result for the pinned drop (included 1000 particles) with initial contact angle of $140^0$ is shown in figure 5.
Figure 5. Three stages of evaporating drop with 1000 particles (side view). The final dried pattern is given in upper right corner of the picture (top view).

5. Conclusion
Analysis of application of the existing droplet evaporation models, the boundary conditions for the hydrodynamic flows on the drop surface, as well as the nanoparticle dynamics in the hydrophobic droplet, and the dried pattern formation processes modeling was carried out. Lubrication theory is valid only for small contact angles and absolutely inapplicable to the angles larger than a right angle. We propose the surface boundary conditions for arbitrary contact angles and tested such a model for simply self-assembly calculations which is applicable for aqueous droplet of picoliter volume and small Marangoni number in normal external conditions.

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