Simulation of desolvated self-assembly in a picoliter drop of colloidal solution by dissipative particle dynamics

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ABSTRACT

A number of papers devoted to heat and mass transfer of evaporating drops on a flat substrate have been published over the last years, mainly due to the importance of the evaporating drop problem for fundamental and applied sciences. The physical and computational model of selfassembly in an evaporating picoliter drop of solution is described as a further development of dissipative particle dynamics methods for systems with a changeable volume. The calculation starts with generating the initial particle distribution in the drop with a uniform volume concentration of particles in the solution. Particle trajectories are then calculated step by step from the initial to the final state. The application includes inkjet technologies and printable electronics fabrications; medical diagnostics by dry pattern analysis, design of microstructures and materials with new properties, and also in the scientific tutoring.

Keywords: self-assembly, self-ordering, dissipative particle dynamics; Langevin equation, colloidal solution.

1 INTRODUCTION

The ordering of colloid nanoparticles ensemble in an evaporating drop of solution deposited on the substrate is a kind of the self-assembly processes in an open dissipative system [1-4]. The development of methods for controlling of the size, form, morphology, and structure of the solid residue (dry pattern) which is formed from the drop of colloidal solution on a flat substrate is an important problem in the modern physics and chemistry.

The theoretical and experimental investigations of the role of various physicochemical properties of solution, surface properties, capillary forces, hydrodynamic flows, environmental conditions, interparticle potentials on the processes of self-assembly allow predicting the dry pattern properties by computer modeling. A number of papers devoted these problems (for example, [5-11]) have been published over the last years.

The detail information about ordering of colloids can be obtained only by an explicit description of particles trajectories during the drop evaporation process. The maximal number of colloidal particles in computer simulations usually has to less than fifty thousands. This number limits the volume of droplet of solution (as a rule, no more than several hundred picoliters) which can be investigated in numeric experiments. The optimal physical model of self-assembly of such a system is a further development of dissipative particle dynamics (DPD) [4, 12] adapted to the systems with a changeable (reduced by evaporation) volume.

The proposed method takes into account the roughness of substrate surface, sorption of the particles to the substrate, triple line depinning with account of the certain outflow angle of the droplet, laminar solvent microfluidics, etc. The model allows us to investigate in a detail the ordering of colloids in evaporating droplet and a dry pattern formation stages.

2 MODEL

2.1 Dissipative particle dynamics

The physical and computational model of self-assembly in an evaporating picoliter drop of solution is described as a further development of dissipative particle dynamics methods for systems with a changeable volume [4]. The calculation starts with generating the initial particle distribution in the drop with a uniform volume concentration of particles in the solution. Particle trajectories are then calculated step by step from the initial to the final state. To generate the uniform initial distribution, a repulsive Coulomb-type potential is introduced and the assemblage energy is then optimized by particle positions inside the drop. After the initial particle distribution is achieved, a step by step integration algorithm

is run for each particle. The *i*-th particle acceleration $\frac{d\mathbf{v}_i}{dt}$ is

calculated by the following Langevin equation:

$$m_{i} \frac{d\mathbf{v}_{i}}{dt} = m_{i} \left(\frac{\partial \mathbf{V}}{\partial t} + (\mathbf{v}_{i}, \nabla) \mathbf{V} \right) - \nabla \sum_{i \neq j}^{N} U(r_{ij}) + \mathbf{F}_{Si}(r_{Si}) + \mathbf{F}_{Li}(r_{Li}) + \mathbf{F}_{Ri}(r_{Ri}) - 6\pi a \eta (\mathbf{v}_{i} - \mathbf{V}) + \mathbf{F}_{Bi}$$
(1)

where m_i is an effective mass of *i*-th particle with the 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 $U(r_{ij})$ acting on the *i*-th particle from other *j*th particles, $\mathbf{F}_{Si}(r_{Si})$ is the interaction force between the th particle and substrate, $\mathbf{F}_{Li}(r_{Li})$ is the capillary force, $\mathbf{F}_{Ri}(r_{Ri})$ is a friction force acted due to roughness of the substrate surface, $-6\pi a \eta(\mathbf{v}_i - \mathbf{V})$ is a Stokes' viscous force, where \mathbf{V} is a field of hydrodynamic flow in the solution, and the Brownian force is \mathbf{F}_B (Fig.1). The selfassembled pattern morphology dependence on the model parameters is investigated.



Figure 1: The major forces in a droplet are (a) the liquid–air boundary (ball segment) interactions and displacement of particles during evaporation, (b) the interaction force between the particles and surface layer of the drop, and (c) interaction between the particles and substrate, V is a hydrodynamic compensation flow which can be a reason of a coffee ring effect if the drop contact line is pinned.

The pair interparticle potential $U(r_{ij})$ is expressed, accordingly to the Derjaguin–Landau–Verwey–Overbeek (DLFO) theory, as a sum of two contributions $U_{ij}(r_{ij}) = U_{C,ij}(r_{ij}) + U_{vdW,ij}(r_{ij})$ namely the Coulomb repulsion and van der Waals force respectively. (In order to prevent the particles coagulation, the surface of selfassembling particles is modified by functional groups of atoms, which dissociate in the aqueous solution and thereby become charged.)

Other terms of Eq. (1) were described in detail in Ref. [4].

2.2 Droplet evaporation

The most important driving force that initiates ordering of colloids in droplet of the solution is the evaporation of the solvent into the surrounding atmosphere. It results in a displacement of the drop boundaries, which causes the solution to move inside the droplet. External parameters (the temperature and pressure of the solvent vapor in the surrounding atmosphere) are the major factors that affect the dynamics of the drop evaporation and, hence, the value of the capillary driving force. The slowly diffusion controlled evaporation of liquid drop of small capillary size at each moment of time can be approximately described as a ball segment whose geometric parameters are determined by the solution volume and contact angle ϕ only (Fig.2).

We use the approximate model suggested by Hu and Larson [9-10] to calculate of evaporation of such a droplet. An expression of the evaporation flux density with the contact angle ϕ taken from can be written as follows:

$$J(r,t) = J_0(\phi) \left(1 - \frac{r}{R}\right)^{-\lambda(\phi)},$$

where $\lambda(\phi) = \frac{1}{2} - \frac{\phi}{\pi},$
$$J_0(\phi) = \frac{D(n_s - n_0)}{R} \times \left[0.27\phi^2 + 1.30\right)(0.6381 - 0.2239\left(\phi - \frac{\pi}{4}\right)^2\right]^2$$





Figure 2: The droplet of capillary size has a ball segment form, if, as it takes place here, the gravitation forces can be negligible; r and z are the cylindrical coordinates, ϕ is the contact (wetting) angle, R and R_d are the droplet radius and the ball segment radius respectively, $\mathbf{J}(r,t)$ is a density of evaporation flux which is directed along the outer normal to the drop surface; $\mathbf{V}(r,z,t)$ is a rate of the hydrodynamic flow in a bulk liquid.

2.3 Hydrodynamic flows

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 [6]. This flow has a pure laminar structure without the vortex component when the Marangoni number is small [4], as it takes place in the case of a little droplet (with a volume of 10-100 picoliters) of water solution at normal conditions.

In frameworks of incompressible fluid approximation the laminar hydrodynamic flow inside the drop of axisymmetric form can be described in cylindrical coordinates by the radial vector component $v_r(z,r)$ and vertical $v_z(z,r)$ projection of the rate of liquid flow $\mathbf{v}(z,r)$. In the case of laminar nonviscous flow approximation we can write the next representation of rate of the flow: $\mathbf{v} = \nabla \varphi$, where φ is a scalar function of coordinates. With account of flow equation of continuity $(\nabla, \mathbf{v}) = 0$ or

 $\nabla^2 \varphi = 0.$

The boundary conditions of rate of flow on the top of drop surface (Fig. 2) are

$$V_z(\theta, t) = \frac{J(r(\theta), t)}{\rho} \cos \theta - \frac{dZ(\theta, t)}{dt},$$
 (2)

$$V_r(\theta, t) = \frac{J(r(\theta), t)}{\rho} \sin \theta - \frac{dR(\theta, t)}{dt},$$
(3)

where ρ 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 shift of

the point on a drop surface, shift which takes place due to the evolution of the form and size of the evaporating drop with account of the triple line motion. The boundary condition on the bottom of drop surface is

$$V_z(\theta, t) = 0. \tag{4}$$

We used the next simple model solution for the rate of flow which met the equations (2)-(4)

$$\begin{aligned} v_r(z,r) &= \frac{V_r(\theta^*)}{r_{\max}}r, \text{ where} \\ \theta^* &= \arccos\left(\frac{z}{R_d} + \cos\phi\right), \ r_{\max} = R_d \sin\theta^*. \\ v_z(z,r) &= \frac{V_z(\theta^*)}{z_{\max}}z, \text{ where } \theta^* = \arcsin\left(\frac{r}{R_d}\right), \\ z_{\max} &= R_d \left(\cos\theta^* - \cos\phi\right) \text{ if } \phi \leq \frac{\pi}{2}. \\ v_z(z,r) &= \frac{V_z(\theta^*)}{z_{\max} - z_{\min}}(z - z_{\min}), \text{ where} \\ \theta^* &= \arcsin\left(\frac{r}{R_d}\right), \ z_{\max} = R_d \left(\cos\theta^* - \cos\phi\right) \text{ if } \phi > \pi - \theta. \end{aligned}$$

In our model, we have introduced the possibility of a single depinning of a pinned contact line where the critical value of contact angle is reached.

3 RESULTS

1. Roughness, adhesion (or particle sorption to substrate) and wettability (defined by the contact angle) in its influence on morphology of solid phase are acting together, contributing and opposing each other.

2. Approaching of the particles to substrate takes out the particles from the area of active radial flows that reduce the particles displacement to the triple line.

3. The role of the roughness is defined by the static friction force, acting on the particles near the substrate. This force is rising with the increase of adhesion.

4. Low of motion of the triple line determines the quantity of radial hydrodynamic flows, which carry the particles to periphery, if this motion is not opposed by roughness and adhesion.



Figure 3: a – Atomic force microscope image of inkjet droplet pattern structure. b – DPD numerically modeling pattern.



Figure 4: Non-domain (a) and domain (b) ordering ensembles in dry patterns (computer modeling).

5. If the triple line is constantly pinned, then radial flows are acting during all the time of droplet evaporation. Hence, in case of small roughness and weak adhesion, the particles move to the border of the droplet and form the ring-shaped pattern in the end of self-assembly process (coffee ring effect) (Fig. 3). With the increase of roughness and adhesion, there are form a pattern with more uniform particles distribution (more wide and diffused ring or spot of round shape).



Figure 5: a - Particles form the agglomerates (colloidal clusters) if there is a week interparticle repulsion into liquid drop solution; b - Strong interparticle repulsion prevents the coagulation of the particles.

6. In the absence of pinning, when during the whole process of evaporation contact angle is a constant, the radial flows are minimum or absences. Triple line is moving during the whole process of droplet evaporation and entraining the particles to the central area. If the roughness of a substrate and adhesion forces are big, then ability of a triple line for carrying the particles by capillarity forces diminishes.

7. The growth of particles size with the same adhesion and roughness leads to weakening of influence of adhesion and roughness on a result of self-assembly, because the ability of particles to get over the roughness of the substrate increases.

8. Domains are the result of the conflicting forces of repulsion between the particles and capillary compression arising by reducing of the evaporating droplet volume. In this case, the hexagonal domain structures are a compromise between a pattern of regular form with total hexagonal close packing of the particles and the pattern of circular form which is energetically favorable for the capillary forces (Fig.4).

9. If interparticle repulsive barrier is small, the particles coagulate in solution and form the colloidal clusters (agglomerates) adsorbed on the substrate surface after solvent evaporation (Fig.5 a). On the contrary, the particles are not formed the agglomerates when the interparticle repulsion barrier is sufficiently high and does not allow to coagulate (Fig. 5 b).

4 CONCLUSION

The physical and computational model of self-assembly in an evaporating microdrop of solution with several hundreds of picoliters in volume is described as a further development of DPD methods used in systems with a changeable volume. Numerical results are in good agreement with experiments on self-assembly in colloidal droplet deposited by inkjet technology (Fig. 3).

The application includes inkjet technologies and printable electronics fabrications; medical diagnostics by dry pattern analysis, design of microstructures and materials with new properties, and also in the scientific tutoring.

We are elaborating the useful software complex to predictive modeling of setup, spreading, evaporation of liquid droplet of inkjet size, as well as self-assembly of solvated nanoparticles or macromolecules from the drop during evaporation.

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