Joint effect of advection, diffusion and capillary attraction on a spatial structure of particle depositions from evaporating droplets

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A simplified model is developed, which allows us to perform computer simulations of the particles transport in an evaporating droplet with a contact line pinned to a hydrophobic substrate. The model accounts for advection in the droplet, diffusion and particle attraction by capillary forces. On the basis of the simulations, we analyse the physical mechanisms of forming of individual chains of particles inside the annular sediment. The parameters chosen correspond to the experiments of Park and Moon [Langmuir 22, 3506 (2006)], where an annular deposition and snake-like chains of colloid particles have been identified. The annular sediment is formed by advection and diffusion transport. We find that the close packing of the particles in the sediment is possible if the evaporation time exceeds the characteristic time of diffusion-based ordering. We show that the chains are formed by the end of the evaporation process due to capillary attraction of particles in the region bounded by a fixing radius, where the local droplet height is comparable to the particle size. At the beginning of the evaporation, the annular deposition is shown to expand faster than the fixing radius moves. However, by the end of the process, the fixing radius rapidly outreaches the expanding inner front of the ring. The snake-like chains are formed at this final stage when the fixing radius moves toward the symmetry axis.

I. INTRODUCTION

The processes of heat and mass transfer occurring in droplets and films are of interest in various applications such as fuel droplet evaporation and combustion in engines [1, 2], interaction of droplets with surfaces of varying wettabilities in ink-jet printing [3], obtaining stable ultrathin film surfaces on the basis of polar liquids [4], removing nanoparticles from a solid surface [5], and many other applications.

One of the most important and actively discussed problems is connected to studying structures of nanoparticles, which emerge on the surface of an evaporating sessile colloidal droplet and remain on the substrate after drying [6–13]. One of the examples is the effect of evaporative contact line deposition, the so-called coffee-ring effect [14, 15]. While a droplet is drying on the substrate, capillary flows carry the colloid particles toward the three-phase boundary. In this case, formation of an annular deposition is observed if the contact line was pinned throughout the entire process. According to the experimental results, coffee-rings may have an inner structure [16], and colloid particles can also merge into chains and other geometric shapes [17]. However, the existing models which describe this phenomenon [14, 18–20] do not allow predicting the inner structure and location of the particles relatively to each other.

Effects of this kind are studied experimentally in [16, 17, 21–29]. Marín et al. primarily explained the mechanism of these effects by convective transfer and diffusion [16]. Park and Moon obtained circular depositions and stains as a result of evaporating picoliter droplets based on water ink and different solvent mixtures [17]. Such depositions are characterized by a well-ordered hexagonal structure of particles. In case of the annular deposition, the images show the presence of independent chains of particles within the ring.

The role of the Marangoni flow in case of a heated substrate is discussed in [21]. Yunker et al. studied the influence of particle shape on the resulting structure of deposition [22, 23]. Depositions of microgel soft particles are characterized by a gradual order-to-disorder transition, that is not abrupt like the hard colloid depositions [24]. Li et al. used solvents with dendrimers and obtained annular structures of a periodic thickness [25]. Callegari et al. studied the influence of active matter (moving bacteria) on the dynamics of the coffee-rings growth [26]. A series of papers is dedicated to the formation of nanoparticle chains along the contact line of micron-size droplets [27–29].

There are several discrete models, which explicitly describe the dynamics of each particular particle. These models are usually based on Monte Carlo or molecular dynamics methods [30–35]. Some Monte Carlo based models are lattice models [36–38], and some are not [26, 39]. The flow velocity is often calculated analytically for simple particular cases [32, 37–40]. The obtained velocity field is taken into account for calculations of the particles dynamics. Lebdev-Stepanov and Vlasov took account of the adhesion of particles and roughness of the substrate [32]. The formation of branched nanoparticle aggregates in the drying sessile droplet is modeled in [36]. The models [37, 40] describe the formation of annular depositions in the process of droplet evaporation.

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tion using a cubic lattice. Petsi et al. compared the Monte Carlo and lattice Boltzmann equation methods for a semi-cylindrical geometry of the droplet and also provided a numerical description of the process of particles deposition on the substrate as a result of the transfer by the compensatory fluid flow and their Brownian motion [39]. The computational experiment was carried out for different wetting angles and three-phase boundary modes. Jung et al. used a model with a circular lattice to describe the coffee-ring effect mathematically [38].

The capillary attraction of the particles in liquid films was studied in [35, 41–45]. Based on such interaction between the particles, a lithographic method of self-assembly of nanostructures was developed [46].

The objective of the present work is to analyse physical mechanisms of the formation of standalone particle chains located within an annular monolayer deposition [17]. Our hypothesis is that this effect is caused by the particles’ capillary attraction, which occurs at different times in those areas of the droplet where the thickness of the liquid layer reduces to the size of particles. To verify this mechanism, we employ a simplified mathematical model, which accounts for joint consideration of advection, diffusion, and capillarity and allows us to perform computer simulations of the transport of particles.

II. METHODS

A. Problem formulation

Let us consider an evaporating sessile droplet of colloid solution (Fig. 1). The diameter of the spherical particles of SiO$_2$ $d_p \approx 0.7 \ \mu$m [17]. We assume that the particles remain suspended for a long time due to their small size. For this reason, we do not take account of sedimentation, because of the small volume of liquid (approximately 72 pl [17]). Such geometry facilitates working with a cylindrical coordinate system ($r, \varphi, z$). The direction of axis $r$ is parallel to the substrate. The symmetry center of the droplet corresponds to $r = 0$. Axis $z$ is perpendicular to the substrate. The surface of the solid base corresponds to $z = 0$. The three-phase boundary is fixed throughout the entire process at $r = R$. Radius of the droplet base is $R \approx 60 \ \mu$m (the droplet base is the region of the substrate contacting with the liquid). The substrate is made from a hydrophilic material, and the droplet is flattened. Its contact angle $\theta \leq 10^\circ$ [17]. In such cases, one or two layers of particles are formed [17]. In this work, we only consider the case with a monolayer formation from particles. We do not take account of circulating flows of the liquid, because the liquid layer is thin. Also, Marangoni flows may be suppressed in some cases, for example as an effect of surface surfactants. We only account for radial flow of the liquid, directed from the symmetry axis toward the droplet periphery. This compensatory flow is a result of intense evaporation near the contact line (Fig. 1).

B. Description of the model

1. Capillary attraction

It is convenient to use both polar ($r, \phi$) and Cartesian coordinates ($x, y$). Since thickness of the liquid layer $h$ in the flattened droplet is much smaller than $R$, the dynamics of the particles can be described in a horizontal plane, $xy$. Despite the fact that we study the case with a fixed three-phase boundary, the $xy$ plane also has a movable boundary, $R_f$. Let the fixing radius $R_f$ define a boundary, where the particle size and the local droplet height are comparable ($d_p \approx h$), provided that $R_f < R$. In a thin droplet, the particles cannot reach the contact line, because the local droplet height is very small in the vicinity of the contact line. The particles will not move farther than $R_f$, since beyond this boundary $h < d_p$. The surface tension forces will restrain them. Let us write the approximate expression for the shape of the droplet surface [47]

$$h(r, t) = \theta(t) \frac{R^2 - r^2}{2R},$$  \hspace{1cm} (1)

where radial coordinate is $r = \sqrt{x^2 + y^2}$. From (1) we derive the dependence of the fixing radius on time

$$R_f(t) = \sqrt{R^2 - \frac{4r_p R}{\theta(t)}}.$$  \hspace{1cm} (2)

The movement of boundary $R_f$ results from the reducing the height of the droplet in process of evaporation and, hence, the contact angle also reduces (Fig. 1).

![Figure 1](image-url)
The droplet height and the contact angle reduce during the evaporation process, and, hence, the fixing radius is changed as well. It should be noted that \( R_f \) is changed insignificantly for the majority of time. Only at the end of the process, this radius starts shrinking. At \( t \to t_{\text{max}} \) the value of \( R_f \to 0 \). Contact angle \( \theta \) decreases linearly over time, \( \theta \to 0 \) at \( t \to t_{\text{max}} \) [48], where \( t_{\text{max}} \) is the time of full evaporation. This dependence can be expressed as follows:

\[
\theta(t) = \theta_0 \left(1 - \frac{t}{t_{\text{max}}} \right), \tag{3}
\]

where \( \theta_0 \) is the initial value of the contact angle [47]. The exact value of \( \theta_0 \) is not determined in the experiment [17]. It is only known that it does not exceed 10° for the case of the hydrophilic substrate. For the calculations, we will use \( \theta_0 = 10° \).

In the region of boundary \( R_f \), the particles are subject to the capillary attraction [41, 42, 45]

\[
F \approx \frac{2\pi\sigma Q_1 Q_2}{L}, \tag{4}
\]

where \( L \) is the distance between particles, \( Q_k \) is the capillary charge of the \( k \)-th particle, and \( \sigma \) is the surface tension coefficient of the liquid. Expression (4) resembles Coulomb’s law. Here, \( Q_k \) characterizes the ability of a particle to deform the free surface of the liquid, \( Q_k = r_p \sin \psi_k \). The radius of any particle is assumed to be constant value \( r_p \). The meniscus slope angle may vary depending on the location of a particle. To carry out assessment, let us consider the average of \( \psi \). In this case, \( Q_1 = Q_2 = Q \), where \( Q = r_p \sin \psi \). Then, expression (4) can be written as follows:

\[
F \approx \frac{2\pi\sigma Q^2}{L}. \tag{5}
\]

Let us assume that angle \( \psi = 1^\circ \). Let us study a three-particle system as an example (Fig. 2).

![Figure 2: A schematic of particles capillary attraction](image)

FIG. 2. A schematic of particles capillary attraction

We assume that the left and the right particles are attached to the substrate. Let us determine the displacement of the central particle over a time step of \( \Delta t = 10^{-4} \) s. The choice of the time step value is discussed in Sec. II C. Let the distance between the 1st and 2nd particles be \( L_{12} = 11 r_p \), and the distance between the 2nd and 3rd particles be \( L_{23} = 12 r_p \). Now, let us determine the values of \( F_{12} \) and \( F_{23} \) by substituting \( L_{12} \) and \( L_{23} \) in (5). The second particle displacement caused by capillary forces,

\[
\Delta l_{\text{cap}} = \frac{F_{23} - F_{12} \Delta t^2}{m_p}. \tag{6}
\]

Mass of a particle \( m_p = V_p \rho_p \approx 0.5 \) pg, where \( V_p \) is the volume of a spherical particle, and \( \rho_p \) is the density of silicon dioxide. We obtain the value of relation \( \Delta l_{\text{cap}}/L_{12} \approx -1 \). This means that the second particle shifts tightly to the first particle, since the distance between them is smaller and the capillary effect is stronger. It will occur more rapidly at a larger angle \( \psi \).

2. Advection

Based on the mass conservation law [14] and taking consideration of the lubrication approximation \( \sqrt{1 + (\partial h/\partial r)^2} \approx 1 \) we express the height-averaged velocity of radial flow of the liquid \( \vec{v}_r(r,t) \),

\[
\vec{v}_r \approx -\frac{1}{rh} \int_0^r \left( \frac{J}{\rho_l} + \frac{\partial h}{\partial t} \right) r \, dr, \tag{6}
\]

where density of the liquid \( \rho_l \approx 10^3 \) kg/m\(^3\), and \( J = J(r,t) \) is the local evaporation flux with a dimension of kg/(m\(^2\)s).

If we consider the evaporation as only a diffusion of vapor into air and assume the process is quasi-stationary, then, by solving the Laplace equation for the distribution of vapor concentration \( \Delta c = 0 \), we find \( J \). In this approximation, \( J \) only depends on \( r \). Boundary condition at the liquid-vapor interface is \( J(r,t) = D_v (\vec{n} \cdot \nabla c)|_{z=h} \), where \( \vec{n} \) is the normal vector to the droplet surface, and \( D_v \) is the coefficient of vapor diffusion. Analytical solution

\[
J(r) \approx \frac{2}{\pi} \frac{D_v(c_s - c_{\infty})}{\sqrt{R^2 - r^2}}. \tag{7}
\]

had been obtained earlier for \( \theta \to 0 \) [14, 47, 49]. Here \( c_s \) is the concentration of saturated vapor, and \( c_{\infty} \) is the concentration of vapor in the surrounding air far from the droplet surface.

Let us substitute (1), (3) and (7) in (6) and then integrate. Considering the fact that mass of the droplet \( m \) is equal to the mass of the entire evaporated liquid [47],

\[
m = \frac{\pi \rho_l R_i^2 \theta_0}{4} = 2\pi \int_0^{t_{\text{max}}} \int_0^R J r \, dr \, dt = 4D_v(c_s - c_{\infty}) R t_{\text{max}},
\]

we find

\[
\vec{v}_r = \frac{R}{4\rho_l(t_{\text{max}} - t)} \left[ \frac{1}{\sqrt{1 - r^2}} - (1 - r^2) \right], \tag{8}
\]

where \( \tilde{r} = r/R \) [47, 49]. Displacement of the particle by the radial fluid flow over one time step is \( \Delta l_{\text{adv}} = \vec{v}_r \Delta t \).
Eq. (8) is a rough approximation for an actual fluid velocity, so the suggested model is only of a phenomenological nature. The process can be considered as quasi-stationary when $R^2/D_v \ll t_{\text{max}}$ [47]. In order to further refine the suggested model, one has to consider $J$, which depends on time $t$, as well. For example, dependencies $J(r, t)$ are suggested in [50–53].

3. Diffusion

The diffusion coefficient of the particles is determined by Einstein formula $D = kT/(6\pi \eta p_r)$, where $k$ is Boltzmann’s constant, and $T$ is the temperature of the liquid. Substituting the value of water viscosity $\eta$ at room temperature, we find $D \approx 2 \times 10^{-13}$ m$^2$/s. The diffusion displacement distance is $\Delta l_{\text{diff}} = \sqrt{2D\Delta t} \approx 6$ nm. We obtain the relation: $\Delta l_{\text{cap}}/\Delta l_{\text{diff}} \approx 615$. Hence, capillary attraction of the particles prevails over diffusion, which can be neglected on achievement of fixing radius $R_f$ by the particle. The characteristic time of diffusion-based ordering of particles is $t_d = r^2/D \approx 2.45$ s. The precise value of evaporation time $t_{\text{max}}$ is not given in [17]. For a pure liquid, there is an approximation:

$$t_{\text{max}} \approx \frac{\rho_n h(0, 0) R}{\pi D_v \rho_v (1 - H) (0.27 \theta + 1.3)} \approx 1 \text{ s},$$

where coefficient of diffusion $D_v \approx 2.4 \times 10^{-5}$ m$^2$/s, density of saturated vapor is $\rho_v \approx 17.3 \times 10^{-3}$ kg/m$^3$ [6]. The value of the contact wetting angle is $\theta = \pi/18$. Height of the flattened droplet $h(0, 0) \approx R \tan(0.5\theta) \approx 10$ μm. In the experiment [17], relative humidity of the surrounding air $H \approx 0.4$. Obviously, evaporation occurs slower in presence of particles, since they cover a part of the air–liquid interface. Therefore, the time of evaporation can be substantially larger. We consider $t_{\text{max}}$ as a parameter. In calculations, we will use $t_{\text{max}} = 1 \text{ s} < t_d$ and $t_{\text{max}} = 10 \text{ s} > t_d$.

Brownian motion of the particles is simulated using a Monte Carlo method. We denote a random angle between a particle displacement and the $x$-axis as $\alpha, \alpha \in [-\pi; \pi]$. Then the brownian displacement of the particle is described by the vector $(\Delta x, \Delta y)^T = (\Delta l_{\text{diff}} \cos \alpha, \Delta l_{\text{diff}} \sin \alpha)^T$.

C. The algorithm

The algorithm for a computer program is given in listing 1. We use the Mersenne Twister generator in order to generate pseudorandom numbers [54]. Efficient implementations for the current computer architectures are contained in modern software libraries for random number generation [55–57].

**Algorithm 1** The algorithm of calculating the dynamics of particles in a drying droplet

1. Set the parameters of the problem: $r_p, R, N_p$, and $t_{\text{max}}$.
2. Randomly generate a uniform distribution of particles and their coordinates $p[i].x$ and $p[i].y$, where $i \in [1, 2, \ldots, N_p]$.
3. By default, all particles are marked green.
4. for $j \leftarrow 1, t_{\text{max}}/\Delta t$ do
5. Calculate $R_f$ according to (2). To avoid dividing by zero (at $t \to t_{\text{max}}$) $R_f \leftarrow r_p$, when $R_f < r_p$.
6. for $i \leftarrow 1, N_p$ do
7. Override the color of the particle with regard to its position relatively to $R_f$.
8. if (the particle is green or yellow) then
9. calculate new coordinates of the particles resulting from the diffusion.
10. if (no collision) then
11. move the particle.
12. end if
13. end if
14. if (the particle is green) then
15. calculate new coordinates of the particles resulting from the advection.
16. if (no collision) then
17. move the particle.
18. end if
19. end if
20. end if
21. if (the particle is black and there is a neighboring particle that is either black or red in its surroundings $R_n$) then
22. calculate new coordinates of the particles resulting from the capillarity.
23. if (no collision) then
24. place the current particle closely to the neighboring one.
25. end if
26. end if
27. end for
28. Write the coordinates of the particles and their colors for the current time step to a file.
29. end for

The particles can be in different states during the calculation. The supplemental video shows results of the simulations and displays the states by different colors. The particles subject to advection and diffusion are marked green. Yellow particles are only subject to diffusion. Black particles are affected by capillarity. Red particles are the ones that stopped their motion and are attached to the substrate. Conventionally, below we use this color notation of the states, because it is identical to the color notation in the supplemental video.

The Monte Carlo method does not allow simulating the mechanical impact of particles as, for example, the discrete element method. That is why we do not consider impact of the particles.

Initially, according to the color designation, the particles are green by default. A particle becomes black on reaching fixing radius $|R_f - r| \leq r_p$. If the particle offsets beyond boundary $R_f$ toward $R$ when $r > R_f + r_p$, it becomes red.
The particles within the forming ring are more affected by diffusion than by fluid flow. Then, we assume that a green particle becomes yellow if its attempt to move was failed due to a collision with a red or black particle. In this context, collision is an overlap of the particles, i.e., in the two-dimensional model representation, an overlap of the circles of radius \( r_p \). The particles are of a solid material and are not deformed. The regions of space occupied by the particles cannot cross even partially.

If the yellow particle has moved away by a small distance from \( R_f \) due to the Brownian motion toward the symmetry axis (for example, \( r < R_f - 5d_p \)), it becomes green again. In other words, the liquid flow starts moving it toward the periphery again. The capillarity of particles on the basis of assessments using formula (5) in Sec. II B 1 will be simulated as follows. Over one time step, a black particle is attracted and moves closely to the nearest black or red particle in the neighborhood (within the surrounding region of a radius \( R_0 \)). For a calculation, we take \( R_n = 20r_p \) [44]. The value of time step \( \Delta t = 10^{-4} \) s was chosen on the basis of a series of computation experiments to satisfy the Einstein relation for the mean square displacement \( \langle \Delta x^2 \rangle = 2D \Delta t \), where

\[
\langle \Delta x^2 \rangle = \frac{t_{\text{max}}}{\Delta t} \sum_{j=1}^{N_p} \frac{1}{N_p} \sum_{i=1}^{N_p} \left( (x_i^j - x_i^{j-1})^2 + (y_i^j - y_i^{j-1})^2 \right),
\]

\( N_p \) is the number of particles.

III. RESULTS AND DISCUSSION

We chose the number of particles \( N_p = 9000 \) such that the width of the formed annular deposition corresponded to the value from the experiment [17]. The time \( t_{\text{max}} \) was considered as a parameter of the simulations. Figure 3 represents the obtained structures of depositions at the drying time of \( t_{\text{max}} = 1 \) s (left) and 10 s (right). The evaporation time of the droplet depends on the temperature, humidity, air pressure, density of colloidal particles, and other parameters. We studied several variants of the process considering diffusion, capillarity, and advection in different combinations. Density of the particles distribution \( \rho \) along radial coordinate \( r \) for the obtained structures is given in Fig. 4. Here, \( \rho \) is the number of particles per unit area, where the number of particles is normalized to their total number \( N_p \). The calculation error does not exceed the size of the marker. Each calculation was repeated 10 times. The lines connecting the markers are shown for convenience only and do not have a physical meaning.

Based on the simulation results, time \( t_{\text{max}} \) influences the forming structure only in the cases when both diffusion and advection are taken into account (Fig. 3). The fluid flow carries the particles toward the periphery. A ring with unordered particles is formed near the contact line over time \( t_{\text{max}} = 1 \) s. Thus, if \( t_{\text{max}} < t_d \), the particles do not have enough time to densely pack due to the Brownian motion. The coffee rings formed during \( t_{\text{max}} = 10 \) s, are characterized by a hexagonal package of particles. The obtained structure has visible defects and local subdomains. This is due to the annular geometry of the region. Over \( t_{\text{max}} > t_d \), the particles have enough time to densely pack due to diffusive mixing. Thus, as a result of transfer of the particles by the advective flow alone, the total density of the particles near the periphery is not so high (\( \rho \approx 0.56 \)), while under the additional influence of diffusion \( \rho \approx 0.81 \) for \( t_{\text{max}} = 1 \) s and \( \rho \approx 0.86 \) for \( t_{\text{max}} = 10 \) s. When all the three effects are studied in combination, the density values in the ring are the same as in the latter case. The only influence capillarity produces is that, instead of a uniform value of \( \rho \) in the central part of the deposition, the density distribution of the particles grows linearly from the symmetry axis (\( i = 0 \)) toward the ring boundary (\( i \approx 0.7 \)). We find that \( \rho(i = 1) = 0 \), since the particles do not move beyond boundary \( R_f(0) \) toward \( R \).

In the case of studying only advection or its combination with capillarity, tree-like structures of particles are observed within the ring (Fig. 3). Such dendritic shapes are not characteristic to diffusing particles. In absence of the Brownian motion, the particles do not mix within the ring. A particle driven by the fluid flow stops moving when it encounters an obstacle. Then, this particle can represent an obstacle for another particle. This is the essence of the dendritic shape formation mechanism. If the system is only affected by diffusion and capillarity, the depositions also have dendritic structures. The difference is that such structure occupies the entire surface area, which was previously in contact with the liquid layer. Particle density distribution is almost uniform (\( \rho \approx 0.35 \)) in this case. Besides, the ‘tree branches’ turn out sparse, since they are not formed due to advection.

The particles are uniformly distributed in the entire volume and fluctuate chaotically at the beginning of the process (see the supplemental video). As the fixing radius decreases, the particles occurring at the fixing boundary (\( r < R_f \)), are drawn to each other and stop their movement. They are in the state of rest for several reasons. Firstly, the local droplet height is smaller than the particle size, therefore, the particles lie on the substrate. Secondly, the capillary forces press them to the substrate, because a thin film wets these particles.

It should be noted that in cases when advection is taken into account but capillary attraction is not, uniform distribution of the particles is observed in the central region (Fig. 3). These are the particles not yet carried by the flow toward the annular deposition at the droplet periphery. When capillarity is added to the model, we see how these particles form chains (see the supplemental video). Capillarity does not affect the structure inside the forming ring except drawing the particles, which were in the proximity \( R_f \), toward each other. Most of the time, the change of \( R_f(t) \) occurs slower than the growth of ring thickness \( w(t) \). By the end of the process, the situation becomes opposite,
$t_{\text{max}} = 1\, \text{s}$

$\begin{array}{c}
\text{advection} \\
\text{diffusion + capillary attraction} \\
\text{advection + capillary attraction} \\
\text{advection + diffusion} \\
\text{advection + diffusion + capillary attraction}
\end{array}$

$\begin{array}{c}
\text{diffusion + capillary attraction} \\
\text{advection + capillary attraction} \\
\text{advection + diffusion} \\
\text{advection + diffusion + capillary attraction}
\end{array}$

$\text{FIG. 3. Final structures obtained at different combinations of effects taken into account and values of } t_{\text{max}}$
FIG. 4. Density of the particles distribution for the obtained structures
$R_f(t) < R_f(0) - w(t)$ at $t > t_{cri}$. Then the chains start forming from the particles as they appear at fixing boundary $R_f$.

According to the numerical results, critical time $t_{cri} \approx (0.74 \pm 0.06) \times t_{max}$. Considering jointly advection, diffusion, and capillarity for $t_{max} = 10$ s allowed obtaining a numerical result, which is qualitatively consistent with the experimental data [17]. The structure of the deposition shows close-packed particles in the annular part and snake-like chains of particles in the central region. The difference is that these chains are short in the experiment. The numerical results show long chains of particles. It is most likely connected to the used approximation in the simulation of the particles capillarity.

IV. CONCLUSIONS

Formation of both close-packed annular deposition at the periphery of the droplet and the snake-like chains of particles in the central region has been described based on the suggested model. The results obtained qualitatively agree with the experiment [17]. A major part of the colloidal particles is carried towards the periphery due to advection. The fluid flow toward the contact line originates from the non-uniform evaporation rate along the free surface of the droplet. This results in formation of the ring of colloidal particles. The hexagonal structure within the ring is found to be induced by the diffusion-based ordering of the particles when the evaporation time $t_{max}$ exceeds the characteristic time $t_d$. Chains of particles are formed at the final stage in the flattened droplet as a result of the particles capillarity, when the fixing boundary outreaches the inner boundary of the expanding ring, $R_f(t) < R_f(0) - w(t)$.

The presented model jointly takes into account the effects of advection, diffusion, and capillarity on the particle motion. A small contact angle, which is characteristic to a hydrophilic surface, is a substantial assumption of the model developed. We consider only the case when the concentration of colloidal particles and the droplet size allow a formation of a monolayer of particles. The model does not take Marangoni flows into account which can emerge due to a surface tension gradient [58–61]. Stick-slip motion of contact lines can be important in some cases [62, 63]. However, our simplified model and the corresponding numerical simulations allowed us to study some of the effects discovered in the experiment [17] and, in particular, resulted in a qualitative agreement with it. Therefore, we believe that in this case the model accounts for the major physical mechanisms of the deposition microstructure formation.

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