Manufacturing self-assembled coatings of micro- and nano-particles by controlled evaporation of drops and thin films

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ABSTRACT

The engineered deposition of self-assembled coatings of micro- and nano-particles on solid surfaces has applications in photonic crystals, optoelectronic devices, sensors, waveguides and antireflective coatings. Besides lithographic, etching or vapor deposition methods, these coatings can be self-assembled on small (<O(1mm²)) circular surfaces by the deposition and drying of drops on surfaces, or on larger (O(cm²)) rectangular surfaces by pulling an evaporating meniscus, in a process called convective deposition. Both processes involve multiscale phenomena such as transient fluid dynamics with wetted regions, DLVO forces, heat and mass transfer in the deforming geometry of a complex fluid. These competing phenomena control the self-assembly of micro- and nano-particle deposits. A simple phase diagram is presented, that describes the mechanisms governing the transition between different patterns during the evaporation of a drop. A multiphysics modeling of the convective deposition process is also presented, which provides insight on ways to improve the reliability of the deposition process. Finally, an outlook is given on technical applications related to the use of convective deposition techniques in manufacturing.

Keywords: thermofluids, convective deposition, self-assembly, colloidal crystals, optical coatings

1. INTRODUCTION

Deposition of micro- and nano-particles on a substrate is relevant to the manufacturing of conductive and antireflective functional coatings, surface-enhanced Raman scattering substrate and photolithography 1. Colloidal deposition and crystallization 2 8 can also be used to manufacture micro- and nanowires 9, 10, nanocrystals 11, cosmetics and explosive crystalline layers 12. In biology, spotting and evaporation of drops containing colloidal particles is used for depositing and organizing biological materials such as proteins and DNA 13 19. Several techniques are used to fabricate particle coatings, such as dip coating, sedimentation, electrostatic assembly, covalent attachment and convective deposition. Drop evaporation and convective deposition are convenient way to deposit coatings of micro- and nano-particles 20; they minimize the amounts of fluids, which might induce economic advantages. In this paper, we discuss two mechanism based on evaporation of complex fluids to create layers of micro-and nanoparticles on a surface: drop evaporation and convective deposition, and describe theoretical tools to understand and control the deposition process.

2. SELF-ASSEMBLY DURING DROP EVAPORATION

2.1 Process description and current physical understanding

Typical inkjet processes 21, 22 are either driven by impulse boiling or piezoelectric squeezing in a small fluidic reservoir. They can be used to dispense colloid and dispersion particles on flat, solid surfaces with volumes ranging from picoliter to microliter. Figure 1 shows that the deposit patterns left by an evaporating drop containing colloidal particles can exhibit a multiplicity of structures, such as a ring-like structure 23, a central bump 24, a uniform deposit 25, 26, complex patterns involving multiple rings, a network of polygons 27, hexagonal arrays 11 or Marangoni tongues. This variety of patterns reflects the complex, coupled and multi-scale nature of the transport phenomena occurring during the droplet evaporation. The fluid dynamics involved in droplet evaporation is transient. It depends on the Reynolds and Weber number of the droplet impact, on the impact angle and associated interfacial deformation or break-

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Figure 1: A multiplicity of deposits can be obtained after the drying of a drop containing colloidal particles: (a) ring-like pattern from an aqueous drop containing 60 nm polystyrene spheres on titanium substrate (with permission from ACS); (b) central bump obtained after the drying of a 38 nL isopropanol drop on PDMS at ambient temperature; (c) multiple rings from a μL water drop containing 1 μm polystyrene microspheres on glass (our work); (d) fingering at wetting line obtained from a μL isopropanol drop with 1μm polystyrene microspheres on glass (our work); (e) uniform deposition pattern of 60 nm hydroxyapatite particles from aqueous drop on titanium disk (with permission from ACS); (f) hexagonal cells from surfactant-laden aqueous drop containing polystyrene microspheres on hydrophobic OctadecylTrichlorosilane (OTS) substrate (with permission from ACS).

up, on the Marangoni and wetting stresses, and on the evaporation at the free surface. Heat transfer occurs by convection inside the drop and conduction in the substrate, driven by a latent heat contribution at the evaporating free surface. Mass
transfer occurs through diffusion of liquid vapor in the atmosphere, advection-diffusion of particles in the drop and long range interactions between the charged particles and substrate surfaces.

Over the last decade, theoretical and experimental efforts have been made to explain the mechanisms responsible for two of the most common deposits, the peripheral ring and the central bump. In 1997, Deegan et al. found that a ring forms at the periphery of the wetted area 23, 30, 31 because a strong radial flow carries particles towards the pinned wetting line, where evaporation flux is the highest due to the wedge geometry. A second structure, the formation of a central bump, i.e. a hilly accumulation with a diameter much smaller than the initial wetted diameter of the drop, was explained by Hu and Larson 26 as the result of recirculation loops due to thermal Marangoni stresses along the free surface. The self-assembly of a structure with area about two orders of magnitude smaller than the initial wetted area of the deposited drop is a feature interesting for miniaturization purposes. For applications such as bio-arrays 13-19, 28, a uniform deposit with diameter equivalent to the initial wetted diameter might be desired in place of a ring or a central bump. While the mechanisms responsible for ring and central bumps are well understood, several mechanisms and explanations have however been put forth to explain the formation of uniform deposit 32, 29, 33, 34, 35.

Besides experiments showing deposit patterns and their qualitative interpretations, few numerical and analytical studies have been reported to quantitatively analyze the formation of colloidal deposits. One reason is that modeling drop deposition and evaporation is challenging, given the wide range of transport phenomena, time scales and length scales. The explanation of the coffee-ring pattern, or ring deposition, in Deegan et al. 23, 30, 31 was based on the lubrication approximation, with an analytical expression for the local evaporative flux. Hu and Larson 26 computed the deposition of PMMA particles by combining an analytical flow field with Brownian dynamics simulations. Using potential flow, Petsi and Burganos 36 analytically showed that the radially outward flow during the evaporation of a drop was slower on a hydrophobic surface than on a hydrophilic surface. They used this finding to explain the formation of multiple rings seen in experiments on hydrophobic surfaces 37.

The work presented here describes the role of Derjaguin-Landau-Verwey-Overbeek (DLVO) interactions between the particles and the substrate on the shape of the patterns left by evaporated drops. To do so, we experimentally control the DLVO forces by varying the pH of the drop containing colloidal particles. This way, the value of the attractive or repulsive force between the particles and the substrate can be controlled. If the attraction between particles and substrate dominates over the other transport phenomena, one can expect a uniform pattern.

2.2. Experimental study

The experiments involve Titania or polystyrene particles nanoparticles dispersed in water or isopropanol. Solutions at five pH values from 1.4 to 11.7 were obtained by adding hydrochloric acid (0.1M) or sodium hydroxide (0.01M) to the aqueous solution. The surface charge density of titania particles was determined as a function of the pH by measuring the adsorbed potential-determining ions (here H+) with a back titration method 38. Immediately after sonicating the solutions for five minutes at a power of 200W, nanoliter drops containing colloidal particles were spotted on soda lime glass slides (Fisher Scientific Inc) using a 375 μm diameter stainless steel pin (Telechem International Inc, CA), as in 39. Typically drop volumes were between 4 and 6 nL. The glass slides were previously immersed in freshly prepared Piranha solution for 1 hour at 70°C, thoroughly washed with distilled water and then blown dry with nitrogen to remove residual water. To observe the Marangoni convection, depositions involving isopropanol buffer were made on PDMS substrates, which exhibit larger wetting angles than glass substrates. The droplet evaporation process was visualized from the side using a digital camera (Pixelink, PLA 741, 1.3 Megapixel) and an long-distance zoom objective (Optem), and from the bottom using an inverted microscope (Olympus IX-71). After evaporation, profiles of the deposits were measured using a laser profilometer based on confocal microscopy (Keyence corporation, LT-9010-M, resolution ~ 10 nm). A more exhaustive description of the experiments is given in 40.

2.3. Theory and Numerical Modeling

Values and sign of the electrostatic and van der Waals forces between the particles and the solid substrate were estimated according to the DLVO theory 41. The total DLVO force between a particle and the substrate is the algebraic sum of the electrostatic and van der Waals forces. A numerical modeling developed and used to simulate the drying and deposit formation, as described in earlier work 24. This model is based on a finite-element code for droplet impact and heat transfer developed by Poulilakos and co-workers in Refs. 42-47, and Attinger and co-workers in Refs. 24, 45, 48. This model has been validated for studies involving impact and heat transfer of molten metal 42, 46 and water drops 48, and for the evaporation of drops containing colloidal particles 24. The flow inside the droplet is assumed to be laminar and axisymmetric. All equations are expressed in a Lagrangian framework, which provides accurate modeling of free surface
deformations and the associated Laplace stresses. This numerical code also models the evaporative flux along the drop-air interface, thermocapillary stresses and Marangoni flow, and wetting line motion. In addition, the code has a dual time-step scheme to handle multiple time scales, which range from nanoseconds for capillary waves or strong deformation during drop impact to several seconds for the whole evaporation. The motion of particles is tracked by solving an advection-diffusion equation for the particle concentration, neglecting buoyancy. In the advection velocity \( v = v_{\text{fluid}} + v_{\text{DLVO}} \) - the symbol \( v_{\text{fluid}} \) stands for the hydrodynamic velocity of the fluid. The velocity \( v_{\text{DLVO}} \) is estimated by balancing the DLVO and the hydrodynamic drag force for a particle. The interaction of the free surface of the drop with the growing deposit is modeled using wetting angles criteria to predict the detachment of the drop liquid from the ring, or depinning.

![Diagram](http://example.com/diagram.png)

**Figure 2:** Phase diagram for the deposit formation. The ratio of three characteristic velocities \( (V_{\text{rad}}, V_{\text{DLVO}}, \text{and } V_{\text{Ma}}) \) determines the final pattern shape. \( V_{\text{rad}} \) is the radial flow velocity scale caused by the maximum evaporation rate at the pinned wetting line, \( V_{\text{DLVO}} \) is the velocity scale caused by an attractive DLVO force and \( V_{\text{Ma}} \) is the Marangoni velocity scale. Cases A, B, C and E are experiments performed in this work, while case D is an experiment performed in another study.
2.4. Experimental results

Inserts in Figure 2 show linear profilometry measurements of deposit patterns obtained at pH values of 1.1 and 11.7. The deposit structure at pH=1.1 is a thin uniform layer with a thicker ring at the periphery. The deposit at the highest pH value, 11.7, is a ring with almost no particles at the center of the deposit. The type of structure of deposited profiles corresponding to intermediate pH values are also described in Figure 2. They exhibit a uniform or ring shape in agreement with calculations that determined an attractive DLVO force for pH ≤ 5.8 and a repulsive force for pH > 5.8. In the former case, the particles are attracted to the substrate and self-assemble in a relatively uniform layer. In the latter case, the particles are repelled from contacting the substrate and follow the general flow pattern, which is radially towards the wetting line, to form a ring. More data on the deposit scans are given in 40. Deposit structure for pH values close to the transition value show agglomerated particles sparsely spread over the entire initial wetted area. This might be explained by the fact that near the point of zero charge of the particles, the DLVO force between the particles and the substrate becomes smaller than the van der Waals forces between the particles, which causes flocculation.

2.5. Phase diagram

Figure 3 describes three convective flow patterns, each associated with a structure for the self-assembled deposit. The first flow pattern is the radial flow caused by the maximum evaporation rate at the pinned wetting line, and the corresponding deposit is a peripheral ring. An analytical expression for the radial velocity is provided by Hu and Larson 50, which scales as $V_{\text{rad}} \sim j/\rho$, the ratio of the evaporation flux over the volumic mass of the liquid. The second relevant flow pattern, shown by our group above in 24, is the transport of particles normally towards the substrate, occurring in the case of an attractive DLVO force. The corresponding deposit pattern is a uniform layer with diameter equal to the initial wetted diameter. This velocity scales as $V_{\text{DLVO+}} \sim 2F_{\text{DLVO+}}/6\pi\mu d_p$, where $F_{\text{DLVO+}}$ is the magnitude of the attractive DLVO force calculated at the Debye length. The third flow pattern is a Marangoni recirculation loop, and the corresponding deposit is a central bump, i.e., a hilly accumulation with a diameter much smaller than the initial wetted diameter of the drop. The typical loop velocity is given analytically by Hu and Larson 51 and scales as $V_{\text{Ma}} \sim (1/32)(\beta\phi_i^2\Delta T/\mu)$. In this equation, $\phi$ is the wetting angle of the drop, $\mu$ is dynamic viscosity, $\beta$ is the gradient of surface tension with respect to the temperature, and $\Delta T$ is the temperature difference between the edge and the top of the droplet.

![Figure 3: Three convective mechanisms compete to form the deposit. In (1) a ring forms due to radial flow caused by a maximum evaporation rate at the pinned wetting line; in (2) a uniform deposit forms due to an attractive DLVO force between the particles and the substrate; in (3) a central bump forms due to a Marangoni recirculation loop.](http://proceedings.spiedigitallibrary.org/ on 10/13/2014 Terms of Use: http://spiedl.org/terms)
convective flow patterns using a two-dimensional phase diagram. The horizontal axis expresses the ratio of the Marangoni recirculation over the radial flow, $V_{Ma}/V_{rad}$. The vertical axis expresses the ratio of the particle deposition driven by DLVO forces over the radial flow, $V_{DLVO}/V_{rad}$. In Figure 2, five deposit patterns (A-E) obtained experimentally are shown for the three domains of the phase diagram. For a system where Marangoni effect and DLVO forces are negligible with respect to the radial flow caused by a maximum evaporation rate at the wetting line, the pattern is a ring. This case falls on the origin of the map shown in Figure 2 (case C). In a system where the attractive DLVO forces between particles and substrate dominate over radially outward flow and over Marangoni convection, the pattern is a uniform deposit over the entire wetted area. The deposit is smooth if interparticle forces are negligible or is a uniform dispersion of flocculated particles if interparticle forces are important. For a system where Marangoni convection dominates over radially outward flow and over attractive DLVO forces, the deposition pattern will be a central bump. The phase diagram has therefore three domains, a bottom left corner where the deposit tends to be a ring, a top left zone where the deposit tends to be a uniform layer, and a bottom right zone where the deposit tends to be a central bump.

3. SELF-ASSEMBLY DURING CONVECTIVE DEPOSITION

3.1 Description of the process and physics

Drop evaporation is convenient, but does not allow the coverage of surfaces larger than the wetted diameter. Also a process might be sought to form mono-crystalline layers of colloidal crystals, using small amounts of solution. Convective deposition offers this possibility: it is a material processing technique where an evaporating meniscus of a colloidal suspension is dragged along a solid substrate to deposit layers of micro or nanoparticles. The process is a typical multiphysics process where fluid dynamics, mass and heat transfer come into play in a small deforming domain, as shown in Figure 4. Particles are transported to the receding contact line where evaporation is compensated by a liquid flux towards the contact line. Particles transported towards the receding contact line feed the growth of a colloidal crystal. The principle of mass transport is similar to that of “coffee ring effect”, described above, where particles accumulate at the periphery of an evaporating coffee drop, except that the contact line is moving along the substrate. Uniform coatings of particles have been deposited over multiple square centimeters on the time scale of minutes.  

Figure 4. a: Typical experimental setup for performing convective deposition; b: Example deposited monolayers and multilayers of colloidal crystal; c: parametric study for convective deposition. (b and c reproduced from 1)
Previous research on convective deposition has been focused on characterizing optically the quality and uniformity of the coating. Also, a significant amount of work has experimentally identified the appropriate conditions for uniform particle deposition through experiments. This value depends on several variables, such as the blade deposition, the evaporation rate, the liquid concentration in particles, the monodispersity of the particles, or the relative humidity. For instance, Figure 4 shows that the relative velocity between the blade and the substrate, called deposition speed, determines the transition between a sub-monolayer, a uniform monolayer and several superimposing layers. This transition has been explained by comparing the colloidal crystal growth velocity (which depends on the evaporation-driven particle flux towards the wetting line), with the blade velocity. However no theoretical or numerical work has been done to study the flow field within the fluid domain. Such numerical study is presented here, and allows the investigation of parameters such as the transient motion of the blade, the geometry of the blade, and the volume of the pulled meniscus.

### 3.2 Modeling challenges and opportunities

Similarly to the drop evaporation process, convective deposition can be modeled by solving the incompressible Navier-Stokes equations, with convective and diffusive heat and mass transport. Details on the governing equations and the Final Element implementation are given in, with some key results discussed here. The fluid dynamics, heat transfer and mass transfer equations are solved in a deforming geometry using a moving mesh (Arbitrary Lagrangian-Euler, ALE) method. Weak form equations are derived in order to be easily implemented in COMSOL, and a special focus is placed on the representation of free surfaces.

The baseline geometry corresponds to a typical convective deposition setup as illustrated in Figure 4, a glass slide with thickness of 100 μm called the blade is placed at a distance h = 100 μm above a glass substrate, and the angle between the blade and substrate is α = 22.5°. A typical volume of 10 nL of particle solution is placed between the blade and the substrate, where 25mm stands for the width of glass slide. The blade is then moved while the substrate is kept stationary. The blades moves toward the direction of acute angle, i.e. towards the left in Figure 4, a direction that induces stronger evaporation and faster deposition rates than the opposite direction. The shape and radii of curvature of the two free surfaces are a function of the blade angle α, the height h between the blade and substrate, and the two wetting angles θ₁ and θ₂. θ₁ = 11°, θ₂ = 31° and R = 200 μm in this work.

### 3.3 Results and Interpretation

The streamlines in Figure 5 shows the general flow pattern during convective deposition. An outward liquid flux, appears at the bottom right, at the interface between the meniscus and the thin film where the colloidal crystal grows. This flux is driven by evaporation in the thin film. A recirculation loop is developing in the liquid domain. A flow bifurcation is seen developing in the middle of the right meniscus. Also, the diffusion and convection of particles is resolved. The concentration is indicated by the color of Figure 5, showing maximum concentration near the thin film, because of the stronger evaporation rate. This type of model allows the determination of evaporation rates as a function of geometry and ambient conditions. Another parameter influencing the deposition process is the radius of curvature. The radius of curvature is calculated from the distance between the upper and lower ends of the meniscus, assuming the free surface is a section of circle. In Figure 6, two cases are compared: the curvature for a meniscus experiencing evaporation and one experiencing no evaporation. The simulations show that the radius of curvature decreases with time for the evaporating cases. This is explained by the fact that the radius of curvature is determined by the geometrical parameters: h, α, θ₁, θ₂ and volume of liquid. For constant h, α, θ₁ and θ₂, a smaller amount of liquid corresponds to a smaller radius of curvature. This modification of the meniscus curvature influences the evaporation rate and can induce perturbation in the growth of the colloidal crystal.
4. CONCLUSION AND OUTLOOK

This paper has described the influence of DLVO forces on the shape of deposits left by drying drop containing colloidal particles. Experiments have been described where the pH is used to control DLVO forces between the colloidal particles. A phase diagram is put forth to explain that the ratio of three characteristic velocities determines the deposit to be either a peripheral ring, a central bump and a uniform deposit. Convective deposition has also been described a rapid and highly-efficient technique to assemble micro- and nano- particles with crystalline structures. The well ordered monolayer or multilayer particle coatings have interesting optical properties, since their structural length scale is on the same order as the wavelength of light. Applications are of interest for solar cells, photonic crystals, and the manufacturing of micro lenses to enhance the light extraction efficiency for LED. The well ordered structures can also find applications in surface-enhanced Raman spectroscopy (SERS). In addition to modifying the optical properties of a surface, the particle coatings can alter the roughness of a surface, forming a superhydrophobic surface. The particle array can also serve as a mask for a novel lithography called “nanosphere lithography.” Applications of micro- and nano- particles also cover other fields, such as biology, electronics and chemistry. The main challenge that prevent wide application of convective deposition techniques to manufacturing is the improvement of the quality of the coatings and the minimization of defects. While numerical simulation allow the investigation of several design parameters, novel colloidal formulations such as the use of suspensions containing micro and nano-particles with binary size distributions, have been shown to enhance the quality of the optical coatings.

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