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Regular Article

The deposition of colloidal particles from a sessile drop of a volatile suspension subject to particle adsorption and coagulation

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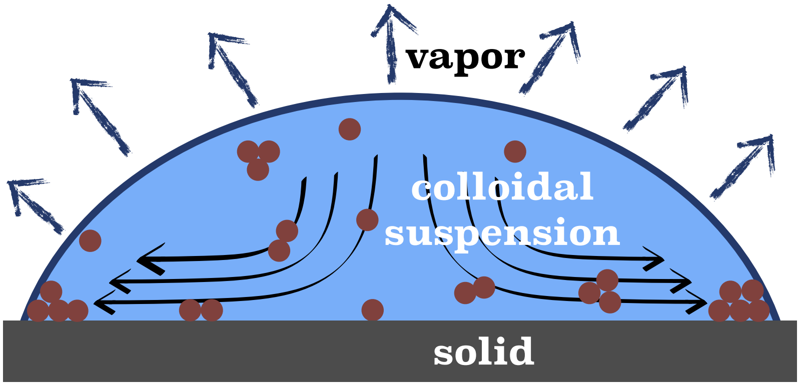
GRAPHICAL ABSTRACT



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ABSTRACT

Electrical double layer and van der Waals (DLVO) forces are known to determine the morphology of the deposit of colloidal particles following the evaporation of the carrier liquid. It is assumed that the adsorption of particles to the solid substrate and their coagulation in the liquid are the mechanisms connecting DLVO forces to the morphology of the deposit. We use theory to test this assertion. We model the deposition of particles from a volatile drop while accounting for the contribution of adhesion and coagulation. The rate of both mechanisms is connected to DLVO forces via the interaction–force boundary layer and the Smoluchowski theorems, respectively. We present analytical solutions for the morphology of the deposit, accounting for particle adsorption and pair–limited coagulation, and a corresponding numerical analysis for the case where particle adhesion and coagulation are concurrent. We conclude that larger aggregates of particles are found near the edge of the drop at the expense of the smaller ones in the absence of adhesion. The adhesion of particles to the substrate smears the deposit, rendering large aggregates to appear near the center of the drop. The analysis is in agreement with a previous experiment when accounting for the corresponding DLVO forces.

1. Introduction

The drying of a sessile drop containing a colloidal suspension will leave a pattern of deposited particles on the substrate [1–4]. The most common patterns are shaped like a ring [3], a bump [5], a uniform deposit [6–8], multiple concentric rings [9], a networks of polygons [10], and hexagonal arrays [11]. The main mechanism supporting the formation of patterned deposits is the flow of liquid generated by the evaporation of the drop. The flow convects particles to the pinned contact line, increasing the concentration of particles in its vicinity [3,4]. Other mechanisms responsible for the

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pattern of the deposit are known to be the flow generated by capillary and Marangoni mechanisms, motion of the three phase contact line between the liquid, vapor and the solid substrate (stick, slip, stick-slip motions), hard interactions between particles due to their geometry, steric effects due to the size of the particles and geometry of the liquid near the three phase contact line, colloidal forces, etc. [8,12,13]. In this paper we model the contribution of coagulation and adhesion to the morphology of the deposit, following the evaporation of a drop of a colloidal suspension. In particular, we connect between colloidal forces and the rate of the coagulation of particles in the volatile liquid and the adhesion of particles to the solid substrate. Overall, the analysis links colloidal forces to the morphology of the deposit.

By altering the pH of drops of volatile colloidal suspensions, Bhardwaj et al. [8] showed that the morphology of the deposit correlates with the magnitudes of the electrical double layer (EDL) and van der Waals (VdW) forces (DLVO forces) between the particles and between the particles and the solid substrate in the liquid. They suggested that the coagulation of particles and the adhesion of the particles to the solid substrate are the mechanisms that connect between DLVO forces and the deposit. They further showed an agreement between their experimental results and a mathematical model when the coagulation of particles in the liquid was negligible. Their model accounted for the influence of the DLVO forces between the particles and the substrate on the flow in a volatile drop.

Further investigating the influence of pH on pattern deposition, Dugyala and Basavaraj [12] studied volatile sessile drops, containing submicron colloidal ellipsoids. They confirmed the results obtained by Bhardwaj and coworkers. The adsorption of particles to the liquid-air interface rather than to the solid substrate supported a ring-shaped deposit. The ring-shaped deposit was converted to a uniform deposit when the colloidal forces between the particles and the substrate were attractive.

Studying the effect of surfactants on the pattern deposition of colloidal particles from a volatile drop, Anyfantakis et al. [14] revealed three pattern regions of interest according to the concentration of the surfactant. For low and high concentrations the deposit took the shape of a ring. For intermediate surfactant concentrations the deposit was uniform. Anyfantakis and coworkers suggested that the adsorption of the surfactants on the particles altered the electrical potential of the particles. Thus, the extent of substrate coverage of the particle by the surfactants influenced the EDL force between the particles and the substrate and between the particles and the liquid-air interface. Morales et al. [15], further concluded that the presence of surfactants affects the attachment strength of deposits to the solid and thus the colloid-substrate friction. This effect takes place alongside with the influence of the surfactant on the surface tension of the volatile drop. Both of which alter the dynamics of the contact line. Further, the effect of surfactants on the formation of particle aggregates in volatile drops was studied theoretically and experimentally by Crivoi and Duan [16]. In their theory they employed a diffusion limited cluster-cluster aggregation approach, coupled with a biased random walk of particles on a two-dimensional (2D) lattice in a circular domain. Aggregates of particles were allowed to stick to each other with the same sticking probability to form larger aggregates. Low sticking probability was found to support the formation a ring-like deposit. High sticking probability was found to support a uniform deposit. In experiment they obtained that the surfactants supported the deposition of ring-like patterns – claimed to be equivalent to the low sticking probability in their simulations. Furthermore, Crivoi et al. [17] have generalized the previous 2D approach to a three-dimensional stochastic model. Using Monte Carlo simulation, they showed that by altering the intensity of particle-particle attraction they were able to switch the morphology of the deposit from a ring geometry to a uniform geometry.

Adding an electrolyte to the colloidal solution, Nguyen et al. [18] examined the stick/slip motion of the three-phase contact line, observing the formation of an inner coffee-ring deposit. The morphology of the deposit was shown to depend on the concentration of the colloidal particles and the electrolyte. The influence of the later on the morphology of the deposit was connected to the strength of particle-substrate interactions. Similarly, Kuncicky and Velev [19] observed that the addition of electrolyte to volatile drops of colloidal suspensions altered the morphology of the deposit. They studied the influence of the contact angle and the initial particle concentration. The addition of electrolyte to the suspension led to the suppression of the EDL force, which was assumed to support the coagulation of particles and their adhesion to the substrate. Yan et al. [20] further concluded that EDL and hydrophobic interactions between suspended particles and the substrates play an important role in the ordering process of the deposit.

Moraila-Martínez et al. [2] studied the contribution of particle-particle and substrate-particle interactions to the morphology of the deposit. They, monitored the contact line dynamics of shrinking drops of suspensions in order to identify stick-slip events. The morphology of the deposit was found to depend on the strength of the particle-particle EDL repulsion, the substrate-particle wettability contrast, and the receding contact angle of the substrate. They concluded that particle-particle repulsion had greater influence on the morphology of the deposit than the attraction between the substrate and the suspended particles in their experiments. Similar conclusion was given by Marín et al. [21], who studied the effect of the electric charge on the particles in convection-driven self-assembly. Employing substrates of different wetting properties, Marín and coworkers concluded that the contribution of EDL substrate-particle interaction, either repulsive or attractive, to the morphology of the deposit is smaller than the contribution of the EDL particle-particle interaction and the convective and diffusive fluxes of particles.

Here, we study the morphology of the deposit of colloidal particles from a volatile carrier liquid, taking into account the adsorption of the colloidal particles to the substrate, the coagulation of particles in the liquid, and both mechanisms concurrently. We present the general equations for our theory in Section 2 and analytical solutions for the morphology of the deposit in Section 3, where we consider the spatiotemporal variations in the concentration of particles in the drop in the absence of adhesion or coagulation in Section 3.1, the added contribution of adhesion in Section 3.2 and the added contribution of pair-coagulation in Section 3.3. A simulation for the case of both coagulation and adsorption is given in Section 4. We discuss the insights of our findings in Section 5.1, show the implications to a previous experimental study in Section 5.2, and conclude in Section 6.

2. Model

We derive a theoretical model for the deposition of particles from a volatile sessile drop, containing a colloidal suspension, shown in Fig. 1. In the model, we account for the irreversible adsorption of particles to the solid substrate and the irreversible coagulation of particles in the liquid. We are able to directly connect between colloidal forces and the morphology of the deposit by using the interaction-force boundary layer theorem for adsorption and the Smoluchowski theorem for coagulation. For simplicity, we assume that the three phase contact line is pinned and that the three phase contact angle is small (in practice this means that the contact angle is smaller than 30°). In addition, we simplify our problem by assuming that the density and viscosity of the suspension, and the surface tension at the free surface of the drop are