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Historical perspective

A review on suppression and utilization of the coffee-ring effect

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ABSTRACT

Evaporation of sessile droplets containing non-volatile solutes dispersed in a volatile solvent leaves behind ring-like solid stains. As the volatile species evaporates, pinning of the contact line gives rise to capillary flows that transport non-volatile solutes to the contact line. This phenomenon, called the coffee-ring effect, compromises the overall performance of industrially relevant manufacturing processes involving evaporation such as printing, biochemical analysis, manufacturing of nano-structured materials through colloidal and macromolecular patterning. Various approaches have been developed to suppress this phenomenon, which is otherwise difficult to avoid. The coffee-ring effect has also been leveraged to prepare new materials through convection induced assembly. This review underlines not only the strategies developed to suppress the coffee-ring effect but also sheds light on approaches to arrive at novel processes and materials. Working principles and applicability of these strategies are discussed together with a critical comparison.

Contents

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1. Introduction

A phenomenon omnipresent in nature, the evaporation of sessile droplets containing non-volatile solutes received a great deal of attention due to the richness of fundamental phenomenon it entails and the number of applied aspects connected to it [1–3].

One ubiquitous phenomenon occurring in the evaporation of sessile droplets containing non-volatile solutes is the contact line pinning and the formation of ring-like residues, called the coffee-stains or coffee-rings [1–5]. Understanding and controlling the process of solute deposition in the presence of coffee-ring effect (CRE) is important in manufacturing processes involving evaporation on surfaces including printing [6–9] and fabrication of ordered structures [24], functional nanomaterials [25,26] and colloidal crystals [27,28]. CRE also hampers the performance of commercial applications including fluorescent microarrays [10,11], matrix assisted laser desorption ionization (MALDI) spectrometry [12–15], and surface enhanced Raman spectroscopy (SERS) [16,17]. CRE has also implications in plasmonics [18], diagnostics [19–21], solute separation [22] and electronics applications [23].

The solute deposition at the contact line is a complex process [1,2,4,29-31]. Contact line pinning and contact angle hysteresis (CAH) play a critical role in formation of coffee-ring effect [59]. The evaporation rate and hence the capillary flow diverges at the contact line due to the relatively larger proportion of the liquid-air interface there [5,30]. For evaporating droplets of colloidal suspension, the particle deposition at the contact line can be ordered (square and hexagonal packings) or disordered depending on the magnitude of capillary flow [32]. Marin et al. observed that the capillary flow diverges towards the end of the evaporation process and hence a transition from ordered to disordered packing is observed [32]. The solute deposition process is also influenced by a number of other aspects such as the presence of electric double layer at the liquid-substrate interface [33], the thermal Marangoni flows [34], the ratio of the thermal conductivities of the substrate and liquid [35], surface charge of the substrate and particle surfaces [36], and even the shape of the particles [37,38]. Deposition of large particles are also influenced by the inward capillary push due to the decreasing height of the liquid wedge near the contact line [39]. Similar forces due to geometrical constraints in a different configuration formed unique packings of colloidal particles at the interface of liquid emulsion droplets in the presence of slow evaporation [40,41].

Several theoretical models were developed to predict the morphology of the deposit, the resulting film thickness and the solvent flux. The first reported models by Parisse et al. could estimate the film thickness upon complete evaporation [29,30]. Later, the works of Deegan et al. [4,31] and others [1,2,5,42-44] gave more complete mechanistic understanding of CRE. Theoretical models incorporating the factors such as the receding of the contact line [45,46], center-enhanced flux [47], presence of polymers [48–51] and surfactants [52] have shown to alter the morphology of the residues. Frastia et al. included the stick-slip motion of the receding contact line and observed the formation of multi-ring deposition of the solutes [53,54]. The multiphase model of Kaplan et al. showed that relative strength of the capillary flow and the evaporative flux influences the deposition pattern [55] as also demonstrated by Shen et al. [56].

1.1. Outline of this review

The physical insights obtained through theoretical and experimental investigations of CRE have not only been utilized to develop CRE-free manufacturing processes but also they inspired novel strategies exploiting CRE as a method for convective assembly. We review this multi-faceted phenomenon in two sections: (i) the strategies to suppress CRE and (ii) the approaches leveraging CRE to arrive at novel processes and materials. Within each section we classify the methods based on their working principle.

2. Suppression of CRE

CRE can be suppressed through one of the three physical strategies (i) preventing the pinning of the contact line; (ii) disturbing the capillary flow towards the contact line and (iii) preventing the particles being transported to the droplet edge by the capillary flows. We will first briefly introduce these three strategies then discuss them in detail in different sections.

The contact line pinning of a sessile droplet is characterized by the CAH [57–59]. The pinning force per unit length and the contact angle hysteresis are related as $f_p = \gamma\ (\cos\theta_a - \cos\ \theta_r)$ where γ is the surface tension and θ_a and θ_r are the advancing and receding contact angles, respectively. Minimizing the hysteresis will facilitate smooth receding of the contact line upon evaporation hence preventing the formation of ring-like deposits as also suggested by the theoretical models [45,46,53]. Experimentally, it can be achieved by evaporating droplets on low CAH superhydrophobic surfaces [64-68,70] or through CAH suppression via electrowetting [77].

When the evaporation-driven outward capillary flow is disturbed the solute transport to the contact line can be minimized or even totally avoided. This can be achieved by inducing additional flow fields inside the droplet, for example, by surface tension gradients (Marangoni flows) [5,12], electrowetting [13,77], electroosmosis [80] and acoustic streaming [84].

The transport of solute particles to the contact line can be prevented by utilizing the particle-particle interactions and/or the interaction of particles with the solid-liquid (SL) interface and liquid-gas (LG) interface [60,118]. In this strategy, solute particles can aggregate at the SL interface or form arrested structures at the LG interface altering the capillary flows. Other methods to prevent the transport of particles are acoustics and phase transition of the liquid during evaporation [8,9].

2.1. Preventing the contact line pinning using hydrophobic surfaces

Increasing the hydrophobicity of surfaces is often accompanied by decreasing CAH [59]. Lower CAH in essence means reduced contact line pinning which leads to suppression of CRE. It can be achieved by patterning of controllable surface wettability as reviewed previously by Tial et al. [62]. These methods include chemical modification [61,62] and physical modification [62-68,70].

The hydrophobization by chemical modification involves covering the surface with hydrophobic molecules such as self-assembled monolayers [61,62]. The physical modification involves patterning the surface to create microscopic roughness on it, for example, an array of pillars, which in turn decreases the effective contact area of the solid-liquid interface. When hydrophobized, such rough surfaces act as superhydrophobic surfaces. Two different types of droplet configurations are possible on such surfaces: Cassie or Wenzel states (Fig. 1a). In the Cassie state, a droplet sits on the pillars and its evaporation can produce ball-like spherical [67] or disc-like [68] deposit (Fig. 1b, c). In the Wenzel state, the liquid fills in between the pillars. Cassie to Wenzel transition of the droplet was studied previously [68,69]. It depends upon the balance between the Laplace pressure $P_L = 2\gamma/R$ and the capillary pressure $P_c = -4\gamma cos\theta_Y[\phi/(w(1-\phi))]$, where R is the radius of the droplet, θ_Y is the equilibrium contact angle, ϕ is the surface solid fraction and w is the pillar width. The capillary pressure decreases with increasing pillar pitch. As the droplet evaporates, the Laplace pressure increases due to the decreasing droplet radius. Cassie to Wenzel transition occurs when the droplet becomes small enough such that the Laplace pressure exceeds the capillary pressure. It means that there