Modeling pattern deposition subject to contact angle hysteresis and finite solubility

In this paper we propose a theoretical model for the pattern deposition of a non-volatile solute mass off an evaporating sessile drop of a dilute solution. The dynamics of the three phase contact line between the solution, vapor or air, and the solid is dictated by the temporal magnitude of the corresponding three phase contact angle. The contact line may undergo stick, slip, or stick-slip motions. We further consider the concurrent transport of soluble solute mass within the drop. Spatiotemporal variations of the concentration beyond the solubility limit of the solution support the deposition of solute mass on the solid.

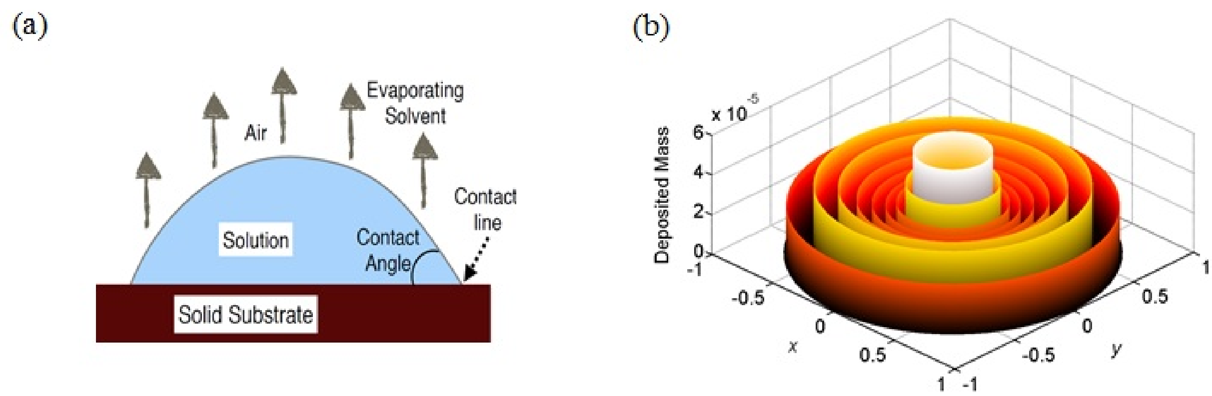

Fig. 1. (a) A sketch of a drop of solution on a solid substrate, undergoing evaporation, and (b) the mass of the deposit, scaled by the initial mass of the solution, (vertical axis) on the solid surface (mapped by the coordinates x and y) in the form of a series of concentric rings following the full evaporation of the liquid, where during evaporation the contact line underwent a stick-slip motion.

In particular, we consider a sessile drop of a dilute solution on a horizontal substrate, which is bounded by a contact line in the plane of the solid surface (Fig. 1a). We show that unless for a very small contact angle or a very rapid rate of evaporation the geometry of the drop is quasi-steady, satisfying the Young-Laplace equation to leading order. Further, the deposition of solute mass alters the chemistry and geometry of the solid surface, changing the characteristic value of the receding contact angle. We thus account for both the magnitude of the receding contact angle over the bare substrate and the deposited layer of solute mass. The contact line sticks to the surface as long as the contact angle is greater than the characteristic value of the receding contact angle, whether it is on the bare solid or on a deposit. The contact line slips to result in the dewetting of the solid once the contact angle is smaller than the characteristic value of the receding contact angle. Variations in the contact angle along with the evaporation of the solution may support a continuous stick-slip motion of the contact line.

The profile of the concentration in the liquid is assumed to satisfy an advection diffusion equation. The concentration in the vicinity of the contact line is further described using an integral condition, where we replace an exact geometric description of the vicinity of the contact line, which is usually unknown, with general insights about the concentration and its flux. Solute particles become insoluble and deposit on the solid as an independent phase whenever the concentration exceeds the solubility limit.

We study the geometry of the deposited pattern of solute mass following the full evaporation of the solvent. Different physical and initial conditions may render different distinct cases. The pinned contact line case supports the deposition of the majority of the solute mass in the vicinity of the contact line of the original drop of solution prior to evaporation, forming a ring-like deposit, which is known in the literature as the “coffee-ring” effect (Fig. 2a). The unpinned contact line case supports the deposition of the majority of the solute mass near the center of the original drop of solution, generating a “mountain-like deposit” (Fig. 2b). The stick-slip motion of the contact line supports repeating patterns of the deposit, giving a series of concentric rings of solute mass on the substrate (Fig. 1b).

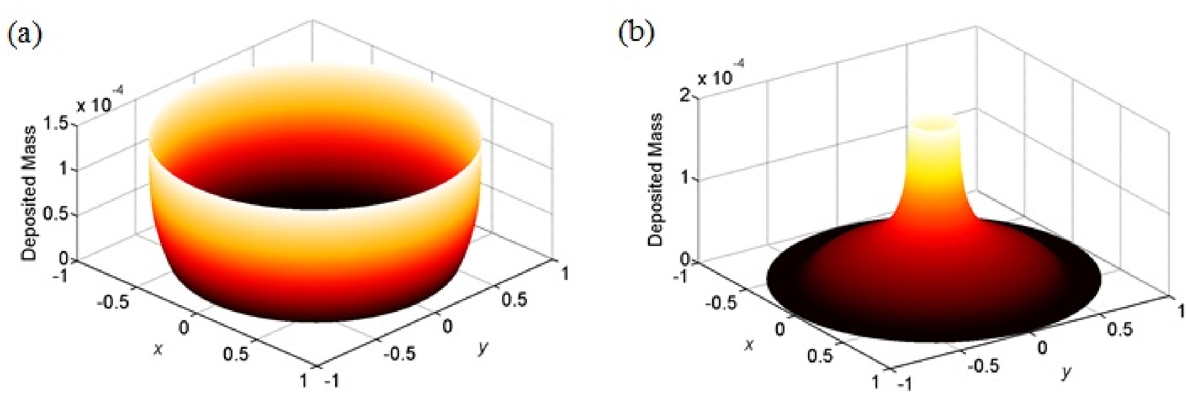

Fig. 2. The mass of the deposit, scaled by the initial mass of the solution, (vertical axes) in the form of (a) a ring and (b) a ‘mountain’ on the solid surface (mapped by the coordinates x and y) following the full evaporation of the liquid, where during evaporation the contact line was continuously stuck to the solid surface at its initial position or underwent a continuous slip motion, respectively.

We obtain a qualitative agreement between our theoretical analysis and previous studies in terms of the relation between the physical parameters of the pattern deposition system, i.e., the physical conditions associated with the evaporating drop of solution, and the geometry of the deposit. A parametric study further suggests the existence of various trends of the geometry of the deposit subject to the physical conditions of the pattern deposition system. Thus, our model should serve as a predicting tool for the geometry of the deposit in fabrication processes that employ pattern deposition.

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