Monte Carlo simulation of surfactant dynamics during evaporation of a colloidal drop

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1. Background/ Objectives and Goals

Evaporation of a colloidal droplet typically leaves ring-like deposit patterns on a substrate, now well-known as the coffee ring effect. The addition of surfactant alters the coffee ring effect by generating surface tension gradients, and hence Marangoni flows from low to high surface tensions. Understanding the complex interplay between droplet dynamics and surfactant dynamics during evaporation is crucial to control the terminal deposition patterns. However, to our knowledge, the details of surfactant dynamics coupled with the droplet dynamics have not been thoroughly investigated but only been inferred from the dynamics of colloidal particles. In particular, there is little work on the quantitative research on the coupled effects between the flow patterns and various characteristics of surfactants, and their effects on the dried colloidal particles. In the present work, therefore, we develop a Monte Carlo (MC) model based on the analytical solutions for the vortex flow by Hu and Larson and the Langmuir adsorption model to systematically investigate the effects of characteristics of surfactant on the droplet flow patterns, and the resulting deposition formation of colloidal particles.

2. Methods

We employ a Monte Carlo method to consider the configurations (υ) of two types of particles, surfactant (*SP*) and colloidal particles (*CP*), and their evolutions for the transport and deposition during drying. This method has been widely used to obtain equilibrium configurations of Ising-type lattice models, where a Hamiltonian is defined at each configuration. The present model uses a two-dimensional lattice for the cross section of a droplet to capture the movement of re-circulating particles. Since the configuration of surfactant also affects the flow field, the configuration of colloidal particles depends on the surfactant distribution on the droplet surface (M_j): $\upsilon_{CP}=\{n_{ij}|\boldsymbol{v},M_i\}$ and $\upsilon_{SP}=\{m_{ij},M_i|\boldsymbol{v}\}$, where the velocity field $\boldsymbol{v}=(v_r,v_z)$ is analytically given by Hu et al., n_{ij} is the number of colloidal particles at a cell (i,j), m_{ij} is that of surfactant particles, and M_j is that of particles on the surface. Note the surfactant particles can absorb to the surface while colloidal ones cannot.

The Hamiltonian for each particle type is defined as following: $H_{CP}=H_{conv}=\Sigma\ f_{ij}n_{ij}$; $H_{SP}=H_{conv}=\Sigma f_{ij}m_{ij}$, where $\partial f_{ij}/\partial r=-6\pi\eta_m R_C\sqrt{a_0}v_r(i,j,t)$, and $\partial f_{ij}/\partial z=-6\pi\eta_m R_C\sqrt{a_0}v_z(i,j,t)$, where η_m is the viscosity of a solvent, R_C is the radius of colloidal particles, and $a_0=L^2$ is the area of a

cell. The surface tension dependent on the surface concentration is computed using the Langmuir's surface state of equation: $\sigma = \sigma_0 + \Gamma_\infty RT \log(1-\Gamma/\Gamma_\infty)$.

Using the Monte Carlo method, we find the equilibrium configurations of two types of particles. A randomly chosen particle moves to a nearest neighbor into the randomly chosen direction with the acceptance rate of $p_{acc} = \exp(-\Delta H^x_v/k_BT)$, where $x=CP$ or SP. However, the movement into the cell of which the particle fraction is above the predefined maximum volume fraction of particles is never accepted to simulate the deposition phase. Particles located on the surface cell are not able to move upward, outside of the drop. Also, the number of cells in the z-direction reduces due to evaporation with time, so particles are redistributed accordingly.

3. Expected Results/ Conclusion/ Contribution

We have investigated deposit patterns after evaporation of a colloidal droplet containing small surfactant particles. During evaporation, surfactant particle dynamics alters droplet dynamics and thus the resulting patterns. Based on a coarse-grained lattice model simulated with Monte Carlo method, the role of surfactant in the transport and the deposition of colloidal particles have been examined by systematically including non-zero Marangoni stresses. The strength of the Marangoni stress can be increased by increasing temperature (RT) to reduce further the surface tension per concentration, by increasing initial concentration of surfactant, or by increasing the maximum concentration on the surface (Γ_∞).

We found that the Marangoni flow induced by surfactant not only competes with the outward capillary flow to delay particle transport to the pinned line but also induces fluctuation of particles near the droplet edge before finally producing a coffee ring. The resulting pattern is wider than that created with zero-Marangoni stress, as previously shown in experiments by Still et al. In general, the dynamics of colloidal particles follows similarly that of surfactant particles except on the surface. Interestingly, when there is a surge of surface concentration close to the final time, multiple-ring patterns are created. This occurs, for example, due to the self-concentration effect with the loss of solvent, the large initial concentration, or the limited maximum surface concentration for adsorption. Our results reveal the evolution process of pattern formation that is related to the surfactant dynamics with evaporation, which is, to our knowledge, the first quantitative studies.

Keywords: Surfactants, Coffee rings, Deposition patterns, Monte Carlo simulation.