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**CONTROLLABLE WETTING AND
EVAPORATION OF A SESSILE COLLOIDAL
DROPLET**

REN JUNHENG

**SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY**

2021

**CONTROLLABLE WETTING AND
EVAPORATION OF A SESSILE COLLOIDAL
DROPLET**

By

REN JUNHENG

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

School of Mechanical and Aerospace Engineering

2021

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarized materials, and has not been submitted for a higher degree to any other University or Institution.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

Jan-19-2021

Prof Fei Duan

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Authorship Attribution Statement

*(B) This thesis contains material from 5 papers published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as the first or second author.

Chapter 3, is published as

J. Ren, A. Crivoi, and F. Duan, Disk-Ring Deposition in Drying a Sessile Nanofluid Droplet with Enhanced Marangoni Effect and Particle Surface Adsorption. *Langmuir*, 2020, 36(49): 15064-15074. <https://doi.org/10.1021/acs.langmuir.0c02607>

The contributions of the co-authors are as follows:

- Prof F. Duan provided the initial project direction and edited the manuscript drafts.
- Dr. A. Crivoi gave the suggestions to develop the code.
- I prepared the manuscript drafts.
- I performed the simulation and laboratory work at the School of Mechanical and Aerospace Engineering. I also analyzed the data.

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Chapter 6, Section 6.1 is published as

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- Prof F. Duan provided the initial project direction and edited the manuscript drafts.
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Abstract

The wetting and evaporation of the sessile colloidal droplet are receiving increasing attention due to their potential in controlling droplet drying behavior and acquiring desired dried patterns. It is closely related to the wetting manner of the sessile droplet which is dominated by the interplay effect of the liquid type and surface wetting property. Motivated by this, this study aims to investigate the wetting and evaporation dynamics of colloid droplets with a solution or suspension and to explore potential applications with the surfaces. The first and second efforts are to model nanofluid droplet drying on flat surfaces, under the pinning and depinning wetting conditions. A three-dimensional (3D) diffusion-limited cluster-cluster aggregation model has been developed to simulate the pattern formation of pinned drying droplets, with accounting for the enhanced Marangoni effect, the strong particle aggregation possibility, and the particle adsorption at the liquid-vapor interface. The formation of a disk pattern inside an outer ring has been simulated. In the case of the dewetting droplet drying, branched structures are observed to form. A 3D kinetic Monte Carlo model has been developed, including the particle diffusion and contact line retreating effect. The numerical model reproduced the particle deposits agreeable to the experimental ones. The third effort of this study is to experimentally investigate the evaporative dynamics and deposition patterns of sessile saline droplets on various flat surfaces or with surfactant additives. On the silicon wafer and poly (methyl methacrylate) (PMMA) substrate, the pure saline droplets undergo a unique period of drying where the contact angle keeps increasing and the contact line keeps receding. On the soda lime glass, the droplets always evaporate in a pinned mode. The lower wettability and the weaker pinning effect of silicon wafer and PMMA substrate result in the morphology of crystalline cubes at the droplet center. While the

high wettability and strong pinning effect of soda lime glass lead to exterior cracked layers of salt and interior separated small cubes for low salt concentrations, whereas large crystalline chunks stay near the droplet rim for high salt concentrations. With the dilute surfactant additives in the saline solution, the droplet resting on the silicon wafer exhibits an initial autophobing effect with its wetting contact angle rising continuously in the later evaporation process. As the surfactant concentration increases, the initial autophobing effect is weakened and the droplet gets pinned gradually. Under a relatively high surfactant concentration, dendritic precipitation patterns are observed to form around the central crystals for high salt concentration and to cover the whole wetted area for the dilute salt concentration. The fourth section of the study is to explore the evaporation and wetting dynamics of sessile colloidal droplets on a micropyramid patterned surface. The droplet liquid property is controlled by adding potassium chloride or cetyltrimethylammonium bromide into the pure water. The saline droplet formed an initial octagonal wetting interface on the patterned surface and then experienced constant contact radius and constant contact angle evaporation mode before crystallization happened. The evolution of the wetting interface from octagonal to circular shape was found to be brought by the receding of the contact line. For the surfactant droplets, an “octagonal-to-square” wetting transition was found to exist during the evaporation process. The maintenance of droplet octagonal wetting shape could be attained at a dilute surfactant concentration and square shape at a high surfactant concentration. The above study on how a sessile droplet dries differently on smooth surfaces, patterned surfaces, and how it varies under different liquids has contributed to the further understanding of droplet wetting and drying behavior. Future recommendations call for experimental work of controllable particle depositions on the patterned surfaces and the related modeling on droplet wetting and drying dynamics.

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List of Symbols

Symbols

A	Interfacial surface area [m ²] / Scaling value
B	Size of the simulation domain
C_0	Initial surfactant concentration [mM]
C_t	Dynamic surfactant concentration [mM]
C_{O-S}	Surfactant concentration at the onset of “octagon-to-square” transition [mM]
C_{S-R}	Surfactant concentration at the onset of “square-to-rectangle” transition [mM]
C_{surf}	Surfactant concentration [mM]
C_{salt}	Salt concentration [%]
C_{KCl}	Potassium chloride concentration [%]
c_{ij}	Scaling coefficient
D	Droplet base diameter / Diffusivity of water vapor in air [m ² /s]
D_0	Initial droplet base diameter
$E_{\angle}$	Surface energy change along the line-of-sight “ $\angle$ ” [J]
$E_{\parallel}$	Surface energy change along the line-of-sight “ $\parallel$ ” [J]
$e_{\angle}$	Surface energy change for unit length along the line-of-sight “ $\angle$ ” [J/m]
$e_{\parallel}$	Surface energy change for unit length along the line-of-sight “ $\parallel$ ” [J/m]
$F_{\angle}$	Surface energy difference along the line-of-sight “ $\angle$ ” [J]
$F_{\parallel}$	Surface energy difference along the line-of-sight “ $\parallel$ ” [J]
F_c	Contact line force [N]

f	Fraction of the projected area of the solid surface area wet by the liquid / Force [N] / Marangoni function
g	Gravitational acceleration [m/s ²]
G	Gibbs free energy [J]
H_{ave}	Averaged height
H_v	Vapor latent heat of water
h	Pillar height / Droplet height [m]
h_s	Thickness of the silicon water [mm]
h_{surf}	Surface height [μ m]
J	Evaporation flux [kg/(m ² ·s)]
k	Boltzmann constant
k_θ	Increasing rate
k_L	Thermal conductivity of water [W/(m·K)]
k_S	Thermal conductivity of silicon wafer [W/(m·K)]
N_m	Diffusion mobility
p_{stick}	Particle sticking parameter
p_{acc}	Metropolis probability
p_{move}	Particle moving probability
R	Droplet base radius
r_f	Roughness ratio of the wet surface area
S	Supersaturation
t	Time [s]
t_{apex}	Time corresponding to contact angle apex
t_p	Precipitation time [s]

t_p	Predicted precipitation time [s]
t_f	Droplet life time [s]
T	Temperature [K]
T_e	Surface temperature at the sessile droplet edge
T_c	Surface temperature at the droplet apex
V	Droplet volume
V_0	Initial droplet volume
V_t	Droplet volume at time t

Greek symbols

ΔA	Interfacial surface area increment [m ²]
ΔE	Energy spend per unit area [J/m ²] / Surface energy change [J]
ΔG	Decrease of total Gibbs free surface energy [J]
γ	Surface tension [mN/m]
γ_{SL}	Solid-liquid surface tension [mN/m]
γ_{LV}	Liquid-vapor surface tension [mN/m]
γ_{SV}	Solid-vapor surface tension [mN/m]
θ	Contact angle [°]
$\Delta\theta$	Contact angle reduction [°]
θ_0	Initial contact angle [°]
θ_A	Advancing contact angle [°]
θ_{apex}	Contact angle apex
θ_R	Receding contact angle [°]
θ_E	Equilibrium contact angle [°]

θ^*	Apparent contact angle [°]
$\Delta\theta^*$	Apparent contact angle reduction [°]
τ	Side ratio
ϕ	Global particle concentration [%]
ϕ_s	Pillar density
l_i	i -th lattice cell occupied by liquid or not
n_i	i -th lattice cell occupied by particle or not
s_i	i -th lattice cell occupied by substrate or not
$\mathcal{E}_{ll}$	Liquid-liquid interaction energy
$\mathcal{E}_{nl}$	Particle-liquid interaction energy
$\mathcal{E}_{ls}$	Liquid-substrate interaction energy
$\mathcal{E}_{nn}$	Particle-particle interaction energy
$\mathcal{E}_{ns}$	Particle-substrate interaction energy
μ	Chemical potential / Dynamic viscosity of water [Kg/(m·s)]
β_0	Surface tension-temperature coefficient of water [N/(m·K)]
ρ	Density [Kg/m ³]

Abbreviations

CCA	Constant contact angle
CCR	Constant contact radius
CMC	Critical micelle concentration
CTAB	Cetyltrimethylammonium bromide
DLA	Diffusion limited aggregation
DLCA	Diffusion limited cluster-cluster aggregation
KCl	Potassium chloride

KMC	Kinetic Monte Carlo
MCS	Monte Carlo step
NaCl	Sodium chloride

Chapter 1. Introduction

1.1. Background

The evaporation of a sessile droplet with suspended colloidal particles and the corresponding deposition pattern have received many research interests in the past two decades [1]. It has many applications in the practical manufacturing fields like inkjet printing [2, 3], functional materials [4], integrated circuits [5], DNA and protein sequencing [6]. It is closely related to the wetting manner of the droplets on the specific surfaces, which is a combined effect of surface property and liquid composition. For smooth surfaces, the wettability of the droplets is mainly dependent on the chemical property of the surface material and the surface roughness. While for patterned substrates, the topographic or chemical heterogeneities dominate the wetting effect. The multi-components of the droplet solution also add to the complexity of the wetting phenomenon during the evaporation process, as the liquid property changes with the enriching of the solutes. Some external disturbances can be brought in by the enriching solutes, such as the crystallization process in saline droplets [7] or the adsorption of solute molecules on surfaces in surfactant droplets [8]. It is of vital importance in the engineering field to understand the wetting and evaporation dynamics of colloidal droplets on various substrates and to control contact line dynamics, solution wettability, and pinning-to-depinning transition. If there are suspended particles in the droplet solution, the particle self-assembly and dried patterns would be dominated by the different drying mechanisms, including the evaporation induced flow, external forces, particle adsorption, and aggregation behavior, etc. And it always remains a challenge

for simulation work in how to model the droplet evaporation with the particle movement accurately.

1.2. Motivation

The wetting and evaporation dynamics of a colloidal droplet have a significant impact on the particle aggregation and final deposition pattern. Usually, a pinned sessile evaporating droplet has a higher evaporation rate near the three-phase line which induces an outward flow to replenish the fast loss of liquid there [9]. This uniform distribution of the evaporation rate would also generate a temperature gradient along the interface, which establishes a surface tension gradient and thus induces the thermal Marangoni flow [10]. In addition to the particle transportation behavior under these two flows, other factors also account for the pattern formation, such as the particle adsorption and interaction behavior [11]. To explore the particle transportation behavior under this pinned drying condition, both numerical and experimental works need to be carried out. A three-dimensional (3D) diffusion-limited aggregation (DLA) model has been developed with the various transportation mechanisms considered. In the case of the unpinned sessile droplet, however, the demand for liquid replenishment at the droplet edge will be greatly inhibited, leading to a weak inner flow field. Besides, the particle motion will be restricted by the receding drying front. Under this drying condition, a 3D kinetic Monte Carlo (KMC) model has been developed to investigate the competition between contact line retreating and particle self-assembly.

It has been shown from both the experimental and numerical aspects that the evaporation and deposition characteristics of a colloidal droplet are closely related to its wetting conditions on the flat surface. For some materials, with their dissolved solutes enriches in the solution during the drying process, a precipitation process could be initiated.

Crystallization of this kind of material, like salts in the evaporating droplets, has been investigated from many aspects. The previously reported studies mainly focus on the supersaturation degree, the nucleation mechanisms, the crystalline motion, the precipitation profile, and so forth [12-14]. It is crucial to understand the interplay between droplet evaporation and salt precipitation, particularly to get to know how the surface wettability determines the evaporative dynamics and the associated precipitation, and how the nucleation and motion of crystalline affect the droplet wetting and drying behavior. Motivated by these, flat substrates with different wettabilities are used to investigate the evaporative and crystallization characteristics of the sessile droplets with various initial salt concentrations. In addition to this, the wettability of the sessile droplet is also closely related to the droplet liquid property. As the surfactant additives have been shown to be an effective way in altering the wettability and drying behavior of the sessile droplet [8], it remains an interesting topic that how the crystallization pattern changes under the surfactant adsorption behavior.

If colloidal droplets are deposited on the topographic or chemical heterogeneous surfaces, the wetting behavior at the solid-liquid interface can be controlled, generating wetting state transitions [15] or even self-propagated movement of the droplet [16]. On the other hand, droplet wettability can be simply controlled by altering the liquids. The droplet imbibition can be achieved using liquids with low surface tension and different wetting interfaces can be realized by varying the liquid compositions [17, 18]. What's more, droplet evaporation could also induce a change in wetting behavior. As for colloid droplets, part of their compositions enriches during the evaporation process, causing a variation in the liquid property. It is an interesting topic to explore the wetting behavior and evaporation dynamics of colloid droplets on patterned surfaces.

1.3. Objectives and scopes

This study aims to investigate the wetting and evaporation dynamics of colloid droplets with a solution or suspension and to explore potential applications with the surfaces. We mainly examine how a sessile droplet dries differently on smooth surfaces, patterned surfaces and how it varies under different liquids. The present work focuses on the global evaporation dynamics, revealed by the droplet evaporation modes; the precipitation pattern, revealed by the growth of crystals; the wetting interface evolution during the evaporation process and under different liquids; and the wetting behavior of contact line, including pinning, receding and advancing.

The other important aspect is the pattern formation of drying droplet suspensions, which is closely related to the evaporation induced flows and the wetting condition of the edge. Numerical methods are used to simulate the particle transportation behavior and how different dried patterns are formed.

1.4. Organization of thesis

Chapter 2 is a literature review on the sessile droplet wetting and droplet evaporation on patterned surfaces. Different wetting states and the corresponding wetting equations have been introduced, together with the different surface structures (both in nature and engineering area) and fabrication methods. The evaporation dynamics are shown with the different evaporation modes and the corresponding evaporation theories.

In Chapter 3, the pattern formation of an evaporating nanofluid droplet has been investigated under the pinning drying condition. The evaporation induced thermal Marangoni flow is included in the 3D DLA model, with the particle aggregation and adsorption behavior considered. A close link has been established between the simulated patterns and the experimental ones.

In Chapter 4, the pattern formation of an evaporating nanofluid droplet has been investigated under the dewetting drying conditions. A 3D KMC model has been developed to simulate the competition between the particle aggregation and contact line retreating during the drying process. Experiments of nanofluid droplet drying have also been performed with the 3D branched structures analyzed and compared with the simulated ones.

In Chapter 5, the wetting and drying dynamics of sessile saline droplets have been investigated on various smooth substrates or with surfactant additives. The evaporation modes, wetting morphology, and crystal growth are the main concerns.

In Chapter 6, the wetting behavior and evaporation dynamics of multicomponent droplets have been investigated on a patterned surface. This chapter mainly focuses on how the surface structure shapes the wetting interface under different solute concentrations.

Finally, Chapter 7 presents the main conclusions acquired from Chapters 3-6 with some future recommendations. The future recommendations focus on the modeling of droplet wetting on patterned substrates and the particle deposition patterns with controllable shapes.

Chapter 2. Literature Review

Droplet is the form of a small column of liquid that can be seen almost everywhere. A colloidal droplet is the droplet which liquid solution is suspended with colloidal particles. The dispersed particles usually have a diameter of approximately 1 nanometer to 1 micrometer[19]. When a droplet is placed on a substrate in a specific environment, it will interact with the surrounding objects. The manner that a droplet behaves when it touches a solid phase is called wetting. It is obvious that the wetting behavior of a droplet is related to a lot of factors. In this chapter, I will introduce the different wetting states, wetting processes, wetting theories, and wetting factors, aiming to provide a general understanding of wetting behavior and explain it under various conditions. Besides wetting, another important manner of droplet is evaporation. It refers to the process that happens in an unsaturated vapor environment where the droplet liquid changes to the vapor phase gradually. This is a quite complex procedure that needs to be explored from many aspects. If a droplet is formed by complex fluids or by liquid suspended with particles, dried patterns may be left after the droplet evaporates out. Here for the droplet evaporation part, we mainly focus on droplet evaporation modes, evaporation induced flows, and the dried patterns of colloid droplets.

2.1. Sessile droplet wetting

2.1.1. General surface wettability and surfaces in nature

Wetting phenomenon refers to how a liquid makes contact with a solid surface. In nature, this liquid refers to water, and the various solid surfaces are leaves, feathers, insect wings, etc. The wettability is closely related to the force balance established by the adhesive and cohesive forces, which is indicated by the contact angle formed by the liquid-vapor

interface and the solid-liquid interface. The wetting on different solids can be roughly categorized into two series, hydrophobic wetting and hydrophilic wetting, as shown in Figure 2.1.

The global hydrophobic or hydrophilic wetting behavior is associated with both the surface chemical/physical structure and the wettability property of the liquid. The wettability of a liquid is determined by the intrinsic wetting threshold (IWT) of the liquid, defined by the contact angle of a droplet resting on the ideal smooth substrate [20].

Figure 2.1. Different surface wettability [21]

In order to adapt to the surrounding environment, nature itself has developed a massive amount of functional surfaces with the wetting property ranging from superhydrophilic wetting to superhydrophobic wetting [22-24]. Many studies have been focusing on this area, to reveal the linkage between the actual wetting behavior and the corresponding chemical and physical surface structure. Achievements in these aspects have provided us with the most effective way to design and fabricate superwetable surfaces. Two design criteria have been established in making superhydrophilic and superhydrophobic surfaces: micro- and nanoscale hierarchical structures and hydrophobic/hydrophilic surface coating.

Many plants and insects have been reported to have water-repellent surfaces [25], of which the two most efficient hierarchical structures are: bumps with the 10 μm

characteristic length, and submicronic microfibers [26]. Figure 2.2 displays these two typical structures on the plant leaves [27]. Figure 2.2 (a) shows the nearly spherical water droplet on a lotus leaf. This hydrophobic phenomenon is also named as “lotus effect”, due to its super self-cleaning property and low contact angle hysteresis.

Figure 2.2. Two typical examples of hydrophobic surfaces. (a) Water droplets on a lotus leaf. (b-c) The surface structure of lotus leaves acquired by the scanning electron microscope (SEM) images under different magnifications. (d) Water droplets on the rear face of ramee leaf. (e-f) The surface structure of the rear face of ramee leaf acquiring by the SEM images under different magnifications [28].

Figure 2.2 (b-c) shows two SEM images of a lotus leaf marked with 50 μm and 1 μm bars. The lotus leaves are decorated with micro bumps covered by nanostructures. Besides this hierarchical structure, there are also water-repellent wax-like films covered on the surfaces, resulting in a superhydrophobic property. This micro-nanostructured surface is a typical example of the binary structure of the natural superhydrophobic plant leaves. Another type of superhydrophobic structure of plant leaves is shown in Figure 2.2 (d-f), which is called unitary structure, where the network of micro slick fibers can help to trap a lot of air and form a superhydrophobic surface.

Despite these hydrophobic surfaces introduced above, there are also many hydrophilic surfaces, like the fish scales. What's more, nature has developed many functional surfaces for special purposes. Such as water harvesting [29], with the surface structure hydrophilic spots on a superhydrophobic background; directional water collection [30], with the surface structure spindle-knots on the fibers. The various surface structures in nature have inspired researchers to build functional surfaces for engineering applications.

2.1.2. Wetting theory of sessile droplet

2.1.2.1. Ideal wetting and Young equation

On an ideal surface that is rigid, smooth, and chemical homogeneous, the droplet deposited on it can be considered to form a spherical cap, as shown in Figure 2.3. Near the three phase line, an equilibrium condition is established among the three interfacial tensions: solid-liquid, γ_{SL} , liquid-vapor, γ_{LV} , and solid-vapor, γ_{SV} . θ is the equilibrium contact angle of the droplet. This equilibrium wetting state is quite similar to a force balance, which can be described by the Young equation[31]:

$$\gamma_{SL} + \gamma_{LV} \cos \theta = \gamma_{SV} \quad (2.1)$$

Figure 2.3. Wetting on an ideal surface [21]

It is known that systems in nature tend to reach their most stable state, where their total energy reaches the minimum value. The total energy of the system that a droplet deposit on a solid surface is the Gibbs free energy, G [32]:

$$G = \gamma_{SV} A_{SV} + \gamma_{SL} A_{SL} + \gamma_{LV} A_{LV} \quad (2.2)$$

where A is the interfacial surface area. The wetting process of a droplet usually stops when its Gibbs energy of the system reaches a minimum value [33]. As a result, energy analysis is often used in deriving the equation of equilibrium or apparent contact angle of droplets on various surfaces. Figure 2.4 shows the wetting of a single droplet on an ideal surface. This wetting process exists only if the total Gibbs free energy decreases. When the droplet spreads over a small displacement of wetting area ΔA , the decrease of total Gibbs free surface energy ΔG can be expressed as [34]:

$$\Delta G = \Delta A(\gamma_{SL} - \gamma_{SV}) + \Delta A\gamma_{LV} \cos(\theta - \Delta\theta) \quad (2.3)$$

where $\Delta\theta$ is the decrease of droplet contact angle due to the displacement of wetting area ΔA .

Figure 2.4. Droplet wetting on ideal surface [34]

When the wetting process stops, the total interfacial energy G reaches a minimum state. The first derivative of G is equal to zero, which derives the Young equation (2.1).

2.1.2.2. Contact angle hysteresis

For an ideal solid surface, the wetting contact angles of the droplet with the same liquid are thought to remain unchanged. While for real solid surfaces, the situation is different. Real solid surfaces in nature are rarely smooth and chemical homogeneous. Most of them have rough micro- or macrostructures. Even for molecularly flat surfaces resulting from solidifying a liquid film, the thermal roughness could be brought in. These defects could offer a pinning effect of the droplet contact line and act like local energy barriers

for droplet to overcome [35]. As a result, when a droplet spreads on a rough surface, its total Gibbs free surface energy does not decrease smoothly. Instead, it may quickly jump from one state to another, resulting in the stick-slip manner of the droplet three phase line [36]. The chemical heterogeneous of the solid material could also induce a similar effect like the surface roughness. As droplets are confined by the local surface structure variations, which then make their apparent contact angle θ^* varies in a range. This variation range is called contact angle hysteresis. Usually, a slight vibration could help θ^* to move closer to the minimum Gibbs free surface energy state, but rarely the minimum itself [37].

Contact angle hysteresis is usually valued by the deviation between the advancing contact angle θ_A and the receding contact angle θ_R , $\Delta\theta = \theta_A - \theta_R$. A common method to measure these two angles is shown in Figure 2.5, θ_A is the largest static contact angle measured when replenishing liquid into the droplet and θ_R is the opposite, the smallest contact angle measured when removing liquid from the droplet. According to the previous experimental studies, the apparent contact angle on rough surfaces seems to be close to the advancing contact angle [36, 38-40]. This phenomenon may be explained by the fact that in most cases the initial spreading process of a sessile droplet on surfaces is quite similar to the advancing process when measuring θ_A . An important thing to be noted here is that the apparent contact angle θ^* is an averaged effect of the random surface heterogeneous (both from roughness and chemical), which means the relative size of droplet and surface structure may have a great effect on θ^* and also the contact angle hysteresis.

Figure 2.5. Illustration of the advancing and receding contact angle [21]

2.1.2.3. Different wetting models on rough surfaces

Equation of the apparent contact angle θ^* on rough surfaces is first derived by Wenzel [41]:

$$r(\gamma_{SV} - \gamma_{SL}) = \gamma_{LV} \cos \theta^* \quad (2.4)$$

where r is the surface roughness factor and

$$r = \frac{\text{actual surface}}{\text{geometric surface}} \quad (2.5)$$

For ideal smooth surfaces, $r = 1$, Eq. (2.4) is equal to Eq. (2.1). For real surfaces, surface roughness always exists and r is larger than 1. An alternative form of the Wenzel equation is:

$$\cos \theta^* = r \cos \theta \quad (2.6)$$

where θ is the equilibrium contact angle of droplets on the ideal smooth surfaces with the same material. This equation reveals that if the intrinsic contact angle of a liquid on a smooth solid surface is below (above) 90° , roughing the surface would increase its hydrophilicity (hydrophobicity). This has been approved by the observation that natural superhydrophobic surfaces are a combination of porous microstructures and hydrophobic surface coating[42], just like roughing the hydrophobic surfaces. It should be noted here this Wenzel equation is corresponding to the Wenzel wetting state of a

droplet where the liquid completely invades the roughness grooves, as shown in Figure 2.6 (a). It is an averaged description that works better when the droplet size is much larger than the roughness scale. While in some cases when the surface roughness is high or surfactant exist in the solution [43], air may be trapped beneath the liquid, forming a Cassie-Baxter wetting state, as shown in Figure 2.6 (b).

Figure 2.6. Different wetting states of sessile droplets [44]

A common form of the Cassie–Baxter equation can be written as [35]:

$$\cos \theta^* = r_f f \cos \theta - (1 - f) \quad (2.7)$$

where r_f is the roughness ratio of the wet surface area and is defined as the ratio of the real surface in contact with liquid to its projection onto the horizontal plane, and f is the fraction of the projected area of the solid surface area wet by the liquid. This equation is particularly useful for wetting on hydrophobic rough surfaces where liquids fail to penetrate the surface structure. It is clear that the Cassie-Baxter equation equals to Wenzel equation when $f = 1$, $r_f = 1$. From the Young equation (2.1), for hydrophobic surfaces ($\theta > 90^\circ$), we can derive $\gamma_{SV} < \gamma_{SL}$. In order to minimize the surface energy, the solid-vapor interface is more preferred than the solid-liquid interface. As a result, it is common to see air bubbles trapped beneath the droplet on hydrophobic rough surfaces. Compared with the Wenzel wetting state, the presence of air bubbles decreases the adhesiveness of the surface and leads to a lower contact angle hysteresis.

Similarly, from the Young equation (2.1) for hydrophilic surfaces ($\theta < 90^\circ$), it can be derived that $\gamma_{sv} > \gamma_{sl}$. In order to minimize the total surface energy, the system prefers to have larger solid-liquid interface. Then it is easy to understand that for hydrophilic rough surfaces, the liquid may invade the solid microstructure and form a thin film beyond the contact line as this can help to increase the solid-liquid interface. This surface film wetting state is shown in Figure 2.6 (c).

A common form of the film penetration wetting state can be written as [35]:

$$\cos \theta^* = r_f f \cos \theta + (1 - f) \quad (2.8)$$

where r_f represents the roughness ratio of the solid-air interface, f represents the fraction of the projected area of the solid-air interface and $(1 - f)$ is the fraction of the eliminated liquid-air interface. The detailed derivation process of Eqs. (2.7) and (2.8) can be found in the Reference [45].

2.1.2.4. The full wetting regimes

The full relation between $\cos \theta^*$ and $\cos \theta$ over the complete interval $[-1, 1]$ of $\cos \theta$ is shown in Figure 2.7 and Table 2.1. There are two critical points $\cos \theta_{co}$ and $\cos \theta_{ci}$ which define three wetting models[46, 47]:

$$\cos \theta_{ci} = \frac{1 - f}{r - r_f f}, \cos \theta_{co} = \frac{1 - f}{r_f f - r} \quad (2.9)$$

When $\cos \theta_{co} < \cos \theta < \cos \theta_{ci}$, the wetting state can be described using the Wenzel model where the liquid of droplet penetrates the surface structures completely and leaves the rest of the solid dry. When $-1 < \cos \theta < \cos \theta_{ci}$, the wetting state can be described using the Cassie-Baxter model where there are air bubbles trapped beneath the droplet. When $\cos \theta_{ci} < \cos \theta < 1$, the wetting state can be described using the film penetration

model where the liquid of the droplet invades the surface structures and forms a thin film beyond the contact line.

Figure 2.7. Different wetting models on rough surfaces

Table 2.1. The wetting relations for rough surface

Region	Wetting model	Equation
$\cos \theta_{CO} < \cos \theta < \cos \theta_{CI}$	Wenzel wetting model	$\cos \theta^* = r \cos \theta$ (2.6)
$-1 < \cos \theta < \cos \theta_{CI}$	Cassie-Baxter wetting model	$\cos \theta^* = r_f f \cos \theta - (1-f)$ (2.7)
$\cos \theta_{CI} < \cos \theta < 1$	Film penetration wetting model	$\cos \theta^* = r_f f \cos \theta + (1-f)$ (2.8)

Near the two critical points $\cos \theta_{CO}$ and $\cos \theta_{CI}$, the wetting state of droplets may not follow Figure 2.7 exactly. For example, when $\cos \theta$ is larger than $\cos \theta_{CO}$, droplets may stay at a metastable Cassie-Baxter state though a Wenzel state holds a lower surface energy. It is due to the presence of local surface variations which act as energy barriers between the Wenzel and Cassie-Baxter state. As a result, the droplet may not be able to reach the global minimum surface energy state. Usually this metastable Cassie-Baxter state is fragile, it is easy to transfer to Wenzel state under perturbations like compression [48] or droplet evaporation [49]. This wetting transition has been reported to be irreversible as the surface energy decreases in this process [48].

2.1.2.5. Validation of the droplet wetting theory

The Wenzel and Cassie-Baxter wetting equations have become the fundamental knowledge of surface science and most researchers take them for granted. But as the measurement of the contact angle is a one-dimensional issue while the surface property may be considered as 2-D for chemical heterogeneous smooth surfaces and 3-D for rough surfaces, the droplet contact angle cannot always reflect the surface wetting property. The work done by Gao and McCarthy [50] has indicated that the contact angle behavior of a droplet is only determined by the local structure variations at the three-phase line and has nothing to do with the surface area within the droplet edge. Figure 2.8 gives a failure example, with an isolated circular hydrophobic defect, a droplet contact angle relies greatly on the position of its contact line. In this case, we cannot define a general surface fraction f for this surface and the previously introduced theories become invalid. Then there comes a need to clarify the requirement and limitations of the Wenzel and Cassie-Baxter models, and many studies have been focusing on this area [44, 50-52]. A common approach is to go back to the original Wenzel and Cassie-Baxter equations and find the implicit assumptions. Johnson and Dettre [53], and McHale [54] have reviewed the derivation process of Wenzel and Cassie-Baxter equations and summarized the assumptions embodied. It has been found that the derivation of these two equations requires the roughness and surface fraction parameters of the surface to be everywhere constant and to be independent of droplet position and droplet size. These requirements show that the Wenzel and Cassie-Baxter wetting equations are only applicable to specific surfaces. If those requirements cannot be satisfied, the failure of these two equations can be expected [55] or some additional assumptions need to be made [44].

Figure 2.8. Two different Young contact angles under the effect of an isolated circular hydrophobic defect. (a) top view of the substrate and (b) two different wetting statuses of the droplet with the minima in their local surface free energy under the same droplet volumes. θ_1 and θ_2 are the contact angle of the droplet, r is the radius of the circular hydrophobic defect [54].

2.1.3. Wetting on patterned surfaces

The main difference between a patterned surface and a general rough surface is that the structure of the patterned surface is highly ordered, which then makes the surface roughness describable. As a result, those parameters used in the wetting equations introduced in the previous sections can be calculated and then quantitative analysis can be made. Based on the achievements made on patterned surfaces, people can then apply different criteria to control the surface wettability for different application purposes. Some practical examples are superhydrophilic surfaces for anti-fog [56] and enhanced pool boiling [57], and superhydrophobic surfaces for self-cleaning [58] and fluidic drag reduction [59]. In addition, there are also some functional surfaces that combine the hydrophobic and hydrophilic wetting together for special purposes, like water harvesting [29] and transporting droplets [60].

2.1.3.1. Fabrication of patterned surfaces

Many surface modification methods have been developed to fabricate micro-/nano-structures on surfaces with particular wetting properties. Commonly used methods are the different lithographic techniques, such as UV lithography, Nanoimprint lithography, X-ray lithography, Deep reactive-ion etching, laser micromachining, etc [59, 61-64]. After the physical surface structure has been made, thin film coating may be carried out to modify the chemical property of the surface, making the surface exhibit superhydrophilic or superhydrophobic wetting behavior. Due to its highly ordered structures, the roughness of the surface is now describable. Detailed observation and analysis of its wetting property can be carried out, leading to a wide range of studies focusing on different wetting phenomena like hydrophobic/hydrophilic property [65], contact line topology [66, 67], contact line movement [18, 68-70], Cassie-Wenzel wetting transition [71], wetting shape control [18, 55], etc.

2.1.3.2. Wetting theory on patterned surfaces

In **Section 2.1.2**, we have shown the general forms of the wetting equations on the surface with randomly distributed roughness. In fact, these equations are first derived on those surfaces with highly ordered surface structures. There are many different kinds of surface structures, among which the two commonly used are patterned surfaces decorated with cylinder or square pillars, as shown in Figure 2.9. For cylinder pillars, each pillar has a height h and a diameter d . The arranged array of the pillars is controlled by the longitudinal and transverse pitches l_x and l_y respectively, and an angle α is used to adjust the skewness of each pillar array. For square pillars, each pillar has a height h and a width a . They are usually arranged in a square array with the longitudinal and transverse pitches both set as b . Besides these two common pillars, some other structures

are cylinder or square holes [40, 66, 68], stripes [40], hemispherical-top pillars [65], pyramid pillars, or cavities [36].

Figure 2.9. Two typical micropillars' structures on patterned surfaces

On patterned substrates decorated with pillars, the product $r_f f$ is often called the solid fraction or pillar density ϕ_s . If the pillars are cylindrical with a flat top and are arranged in a square array ($\alpha = 0^\circ$, $l_x = l_y$), $\phi_s = \pi d^2 / 4l^2$ [65], $r = 1 + \pi dh / l^2$, where d is the base diameter of cylinders, $r = 1 + 4ah / (a + b)^2$, where a is the width of the pillar and b is the spacing between pillars. If the liquid does not penetrate into the roughness, then we can assume $r_f = 1$ and $f = \phi_s$ [65]. Then the relation between $\cos \theta^*$ and $\cos \theta$ will be adjusted to the format shown in Table 2.2, and the two critical points are:

$$\cos \theta_{\text{CI}} = \frac{1 - \phi_s}{r - \phi_s}, \cos \theta_{\text{CO}} = \frac{1 - \phi_s}{\phi_s - r} \quad (2.10)$$

where θ_{CI} and θ_{CO} are the two critical points that separate different wetting states, as shown previously in Figure 2.7.

Table 2.2. The wetting relations for pillar surfaces

Region	Wetting model	Equation
$\cos\theta_{\text{CO}} < \cos\theta < \cos\theta_{\text{CI}}$	Wenzel wetting model	$\cos\theta^* = r \cos\theta$ (2.6)
$-1 < \cos\theta < \cos\theta_{\text{CI}}$	Cassie-Baxter wetting model	$\cos\theta^* = \phi_s \cos\theta - (1 - \phi_s)$ (2.11)
$\cos\theta_{\text{CI}} < \cos\theta < 1$	Film penetration wetting model	$\cos\theta^* = \phi_s \cos\theta + (1 - \phi_s)$ (2.12)

It has been shown that the Cassie-Baxter equation is only correct when the droplet stays on the flat top of the pillars without any penetration of the liquid [52]. The wetting property of a pillar surface is usually controlled by adjusting its pillar density or adding a surface coating. Based on these studies on pillar substrates, we have got a better understanding of how the microstructure and water-repellent films of lotus leaves lead to a superhydrophobic surface, both from theoretical [73] and experimental [65] aspects. As the droplet size is not large enough compared with the surface structure, droplet wetting behavior highly relies on the local structure shape. The wetting behavior of a droplet on a rough surface is usually investigated using the Wenzel equation or Cassie-Baxter equation, along with some appropriate energy analysis. These wetting theories have been verified in practical experiments and have been used in designing superhydrophobic substrates. Some derivative models have also been established to explain the dynamic wetting complexities [73, 74]. The easily manipulated structure and analyzable wetting behavior on pillar surfaces would make the wetting study on this kind of surface an interesting topic in future studies.

2.1.3.3. Wicking effects

For a droplet deposited on a patterned surface with the apparent contact angle $\theta^* < \pi/2$, there exist three different kinds of wetting types, as shown in Figure 2.10. If $\theta_{\text{CI}} < \theta^* < \pi/2$, the droplet would be in a Wenzel wetting state, the liquid penetrates into the surface structures beneath the droplet; If $0 < \theta^* < \theta_{\text{CI}}$, hemiwicking would exist where the liquid

is driven by capillarity to go beyond the droplet edge, forming a film penetration wetting state; If $\theta^* = 0$, complete wetting would be achieved and the droplet sinks into the surface structures entirely.

When $\theta^* < \theta_{CI}$, the liquid propagating within the forest of micropillars is shown in Figure 2.11. The film thickness matches the post height. The wetted area of the solid is proportional to $r - \phi_s$, while the area of the liquid-vapor interface is proportional to $1 - \phi_s$. For a propagating distance dx of the liquid film, the change of surface energy per unit length of the contact line could be expressed as $dE = (\gamma_{SL} - \gamma_{SV})(r - \phi_s)dx + \gamma_{LV}(1 - \phi_s)dx$. Then the force that drives the liquid hemiwicking can be expressed as $F = dE / dx = (\gamma_{SL} - \gamma_{SV})(r - \phi_s) + \gamma_{LV}(1 - \phi_s)$. Combine the above equation with $\cos \theta_{CI} = (1 - \phi_s) / (r - \phi_s)$ and $\cos \theta = (\gamma_{SV} - \gamma_{SL}) / \gamma_{LV}$ we have $F = \gamma_{LV}(r - \phi_s)(\cos \theta - \cos \theta_{CI})$. This force is related to the liquid wetting property and the surface structure.

Figure 2.10. Hydrophilic wetting states on patterned surfaces [46]

If the wetting is complete ($\theta^* = 0$), applying the film penetration wetting equation $\cos \theta^* = \phi_s \cos \theta + (1 - \phi_s)$, there must be $\theta = 0$. Then the force becomes $\gamma(r - 1)$, it only depends on the surface roughness r and vanishes on flat surface ($r = 1$). With the

presence of hemiwicking, the liquid could be guided to spread by the surface structure, which can be used in fabricating sensors [75] or enhancing pool boiling [57].

Figure 2.11. Liquid propagating within the forest of cylindrical pillars arranged in square arrays. The pillar height is h , the pillar diameter is d , and the pillar pitch is l [76].

2.1.3.4. Wetting shape control

If the size of a droplet is not sufficiently larger than the character length of the surface roughness, the droplet wetting shape would be greatly affected by the local surface structure variation. Some studies have been focusing on this wetting feature to achieve a well control of droplet wetting shape [17, 18, 55], which sheds light on liquid-based printing applications like integrated circuits [5], DNA, and protein sequencing [77]. Previous works on the wetting on patterned surfaces decorated with cylindrical pillars have shown that the shape of droplet wetting interface is affected by both the arranged array and density of pillars. As shown in Figure 2.12 (a), the droplet formed an octagonal wetting shape on a square array of cylindrical pillars. By increasing the pillar density, its wetting shape is changed to square. If the pitch of these cylindrical pillars is only changed in one direction, then the square droplet can be converted to a rectangle droplet. Besides the pattern surface microstructure, the liquid property has been found to have a large impact on the droplet wetting shape also. H Feng et al. [17] have reported the evolution of wetting shape from octagonal to square for water-ethanol binary droplets on a patterned substrate with the increase of ethanol concentration, as shown in Figure

2.12 (b). In addition to those wetting shape control via Wenzel wetting, partial imbibition is another strategy. Courbin et al. [18] have shown the possibility to generate desired square, octagon, or circular wetting shapes on cylindrical pillars decorated surfaces through partial imbibition, as shown in Figure 2.12 (c). The different wetting shapes can be obtained by varying the liquid or the arranged arrays of pillars. It should be noted here that the droplet wetting shape is usually achieved under Wenzel or film penetration wetting state where the droplet contact line can be easily shaped by the surface microstructure.

Figure 2.12. Various wetting interfaces on different patterned substrates. (a) Different wetting shapes by varying the cylindrical pillar arrays [55]. (b) Different wetting shapes by varying the liquids on a patterned surface decorated with micro pyramid cavities [17]. (c) Different shapes formed by imbibition by varying the liquids on cylindrical pillars decorated surface [18].

2.1.3.5. Wetting transition

It can be seen from Figure 2.7 that the Wenzel wetting state can be either hydrophilic or hydrophobic, while the Cassie wetting state is only hydrophobic. For Wenzel wetting state, droplet liquid penetrates into the surface roughness completely, generating a

strong pinning effect and therefore large contact angle hysteresis [48]. As a result, the initially hydrophobic wetting may become hydrophilic during the droplet evaporation process [78], denoting an unstable hydrophobic property. For Cassie wetting state, air is trapped beneath the droplet, which reduces the adhesion lateral on the droplet and then generates small contact angle hysteresis. Thus, the Cassie wetting state is required to generate stable hydrophobic wetting property. However, as the Wenzel state is usually the less energetic one, when a Cassie wetting state is close to the critical point $\cos\theta_{co}$, any disruption may provoke a wetting transition to Wenzel state. Therefore, it is of vital importance to quantify the stability of a Cassie state and to investigate the mechanism in the wetting transition process.

Figure 2.13 shows the two wetting states and the transition states between them. During the transition process, the liquid penetrates into the surface structures gradually until the wetted Wenzel state is reached. Whyman and Bormashenko [79] have carried a detailed analysis on the total surface energy of both Wenzel wetting and Cassie wetting, an energy barrier was found to exist between these two wetting states. To evaluate this energy barrier, here we take the wetting on a patterned surface decorated with cylindrical pillars as an example, the pillars are arranged in square arrays. The pillar density is $\phi_s = \pi d^2 / 4l^2$, and the total roughness is $r = 1 + \pi dh / l^2$, where d is the base diameter of cylindrical pillars, h is the height of the pillar, and l is the center to center pillar pitch. Assuming the liquid-vapor interface does not change as the droplet sinks into the pillar arrays, the only change in surface energy is generated by the wetting of the pillars' side walls and the bottom ground surface. Then the energy spend per unit area is

$$\Delta E = (r - \phi_s)(\gamma_{SL} - \gamma_{SV}) = -\gamma(r - \phi_s)\cos\theta = -(1 + \frac{\pi dh}{l^2} - \frac{\pi d^2}{4l^2})\gamma_{LV}\cos\theta \quad (2.13)$$

Figure 2.13. Wetting states on rough hydrophobic and hydrophilic surfaces. The hydrophilic or hydrophobic substrate means the flat surface made by the same material has the Young contact angle less than or larger than 90° [79].

It should be noted here that this equation can only be used in a hydrophobic situation. As in a hydrophilic situation ($\cos \theta > 0$), this quantity is negative, meaning a spontaneous penetration without any energy barrier [79]. For a rough approximation, the bottom ground solid-vapor interface can be neglected and ΔE can be expressed as $\Delta E \approx -\pi d h \gamma_{LV} (\cos \theta) / l^2$ [76]. This equation offers us three straightforward ways to increase the hydrophobicity of the surface. The first one is to enlarge the pillar height h , the second one is to use hydrophobic materials or apply hydrophobic surface coatings (by increasing $\cos \theta$), and the third one is to have a dense pillar distribution (by decreasing l). For a hydrophilic situation, the energy barrier between Cassie and Wenzel state may result from the pinning of local discontinuities, leading to the formation of a new liquid-air interface, as shown in Figure 2.13 (c). This new interface could be assumed to be identical to the side walls of the pillars, then we can get $\Delta E \approx (r-1) \gamma_{LV} = \pi d h \gamma_{LV} / l^2$. This equation also shows the availability to enhance the

hydrophobicity of a patterned surface by increasing the pillar height h and having a denser pillar distribution.

In order to overcome the energy barrier between Cassie wetting state and Wenzel wetting state, the Cassie-to-Wenzel wetting transition needs an external energy input, which can be supplied by evaporation [71, 80], droplet impact [26, 81], vibration [82], electrowetting [83] or pressing [48]. As the wetting property of the patterned surface reaches the superhydrophobic region, the wetting under droplet impingement becomes a quite interesting topic, which could help to set guidelines for non-wetting surfaces [84]. By changing the impact velocity of the droplet, the different energy barriers of Cassie to Wenzel wetting transition could be examined. Then can find the design criteria of superhydrophobic surfaces under different circumstances, like the non-wetting surfaces under rainfall [85] or in aircraft and steam turbines [26].

2.2. Evaporation dynamics of sessile droplet

2.2.1. Evaporation modes

The evaporation dynamics of a droplet are determined by the wetting dynamics of the droplet, which is closely related to the wetting property of the solid surface and the wetting property of the droplet liquid. It is mainly studied from two aspects, droplet contact angle versus time and droplet contact radius versus time. For pure droplet evaporation on an ideal smooth chemical homogeneous solid surface, the droplet wets ideally with no contact angle hysteresis. With the evaporation going on, the droplet remains at a constant contact angle with a receding contact line. As shown in Figure 2.14 (a), this evaporating mode is called the constant contact angle (CCA) mode. While on patterned surfaces, there are always some chemical or physical heterogeneous which could make the contact angle hysteresis no longer zero. The CCA mode doesn't happen

initially. The droplet would first evaporate in another mode called constant contact radius (CCR) mode. As shown in Figure 2.14 (b), the evaporation happens with constant contact radius and decreasing contact angle. During this stage, the depinning force at the three-phase line increases until the droplet contact line starts to recede and then the evaporation enters the CCA mode. Usually at the late stage of evaporation, the droplet would evaporate in a mixed mode with its contact angle decreasing and contact line receding simultaneously. Figure 2.15 shows the typical evaporation process (CCR mode $\rightarrow$ CCA mode $\rightarrow$ Mixed mode) of a sessile droplet on the patterned surface. This evaporation diagram with three successive evaporation modes is usually reported to exist on superhydrophobic patterned surfaces [15, 86, 87], which have low contact angle

Figure 2.14. Two evaporation modes of a droplet on a surface [88]

Figure 2.15. Schematic diagram of the three successive evaporation modes. r_b refers to the droplet base diameter [89].

hysteresis. For those patterned surfaces with large contact angle hysteresis, the droplet may evaporate in CCR mode for the majority of its lifetime followed by a mixed mode at the very late stage [90, 91]. Usually, CCA and CCR are the two dominating modes in droplet evaporation. A larger contact angle hysteresis would lead to a longer CCR mode.

2.2.2. Flow induced by droplet evaporation

For the evaporation of pure droplet, two kinds of flows usually exist. They are capillary outflow and Marangoni flow. Capillary flow traditionally refers to the flow driven by surface tension, like through capillary tubes. However, it is also used in describing the replenishing liquid from droplet bulk to contact line[92-94], which is induced by the uneven evaporation of droplet along the liquid-vapor interface. As indicated in Figure 2.16 (c), usually droplet evaporates faster near droplet periphery. If there were no flows, the droplet would retreat its contact line gradually, as sketched in Figure 2.16 (a). However, if the droplet contact line was not allowed to move, liquid must flow outward to replenish the evaporation loss near the edge, as shown in Figure 2.16 (b). Deegan et al. [9] have established the theoretical basis in describing the uneven evaporation rate and the diverging velocity in the evaporating droplet with the contact line keeps pinned. This nonuniform distribution of the evaporation rate is due to the varying liquid thickness from droplet's edge to its center, which results in different heat conduction capacities from the substrate to the surface of the droplet [95].

The Marangoni flow arises from the surface tension gradients along the liquid-vapor interface of a droplet. For a pure droplet, this surface tension gradient is driven by the temperature gradients, resulting from the uneven evaporation rate along the droplet free surface. Hu and Larson [96] have obtained an analytical solution of the flow field inside an evaporating sessile droplet, the effect of thermal stress has been included. The Marangoni flow is a recirculation convection whose direction was found to be related

with the temperature profile along the droplet surface. As sketched in Figure 2.17, the temperature profile is controlled by the ratio k_R between the surface thermal

Figure 2.16 Mechanisms of capillary outflow. (a) The result of evaporation without flow: the droplet shrinks, (b) The replenishing flow under a pinned contact line, (c) Schematics of how the flow is initiated. J refers to the evaporation flux [9].

Figure 2.17 Schematics of the Marangoni flows and temperature gradients under different thermal relative conductivities $k_R = k_s / k_L$. Arrows outside the droplet indicate the direction that temperature increases, arrows inside the droplet mark the directions of the Marangoni flow [97].

conductivity k_s and the liquid thermal conductivity k_L , resulting in Marangoni flows with different directions. If the droplet liquid is not pure but multicomponent, the Marangoni flow can be driven by the concentration gradient, as it would induce a surface tension gradient.

2.2.3. Aggregation pattern of droplet suspensions

If the droplet solution is suspended with particles, different deposition patterns would be formed after the droplet dries out. A commonly seen pattern is the “coffee-ring”, which is named after the ring-like deposit left by a spill of coffee. The dominating mechanism here is the capillary outflow. Initially, in a colloid droplet, the suspended particles disperse over the entire liquid domain. Droplet edge is pinned on the substrate and a capillary outflow exist which carries the suspended particles to the droplet edge as the evaporation goes on. After the droplet dries out, most particles concentrate at the droplet edge, forming a “coffee-ring” deposit, as shown in Figure 2.18 (A). However, in many application fields, like coating and ink-jet printing, uniform depositions are preferred. With the presence of strong Marangoni flow, the coffee-ring effect could be suppressed, and uniform deposition could be formed, as shown in Figure 2.18 (B).

Figure 2.18. (A) Motion of particles in a pinned droplet under the capillary outflow, leading to the coffee-ring pattern. (B) Motions of particles in a pinned droplet under the recirculation Marangoni flow, overcoming coffee-ring formation and leading to a uniform deposition [98].

Besides the particle transportation behavior under the capillary and Marangoni flow, other factors also account for the pattern formation, such as the pinning and depinning wetting behavior of the contact line. In case of the depinning drying droplet, the demand of liquid replenishment at the droplet edge is greatly inhibited, leading to a weak capillary flow. In addition, the particle motion is restricted by the receding drying front. Subsequently, the “coffee-ring” effect would be suppressed. For repetitive stick-slip receding of the contact line, the nanoparticles aggregated into multi- or stick-slip ring structures[99, 100], as shown in Figure 2.19 (a) and (b). If the pinning effect was weak enough, the contact line could recede continuously and pull all the particles inwards to aggregate into a dot like pattern[101], as shown in Figure 2.19 (c). While under a local pinning effect, the structures like radial spokes[100], fingers[102], and branches[103] were formed due to the instability of the receding line (see Figure 2.19 (d-f)).

Figure 2.19. The various deposition patterns formed under the depinning drying condition. (a) Stick-slip pattern[99]; (b) Multi-ring pattern[100]; (c) Dot pattern (the blue dashed line marks the initial wetting position)[101]; (d) Radial spoke pattern[100]; (e) Finger pattern[102]; (f) Branched pattern[103].

As the liquid-air interface descends continuously during the drying process, it may collect those particles with a slower descending speed. Some recent progresses have

been made in this area to reveal this particle adsorption behavior at the droplet interface. In the case of a fast-drying droplet, the particle adsorption would be greatly enhanced by the fast descending interface, which could trap the particles into a uniform pattern[93], or in the study done by Yunker et al.[11], the ellipsoidal particles were shown to have a stronger interaction than the spherical ones, the loosely packed structure of particles was produced at the water-air interface with formation of a uniform deposition pattern. For the pendant drying droplet, the particle adsorption behavior could also help to form the central dome deposition pattern[104]. The pattern formation of a drying colloidal droplet is quite a complex phenomenon which always requires researchers to investigate the multiple transportation mechanisms and their interplay effect, especially to distinguish the dominating factor.

2.2.4. Precipitation pattern of droplets with dissolved solutes

For evaporating colloidal droplets with dissolved solutes, the drying of the solution could lead to the precipitation and crystallization of salts. This produces various deposition patterns that closely rely on surface wettability and the pathway of salt growth [7, 105]. Compared with the active domain of colloidal sessile droplets with suspended particles, far lesser studies are stressed in this area. With a higher evaporation rate near the contact line, the induced outward flows could result in a non-uniform distribution of ions and the associated higher supersaturation degree. As a result, it is common to observe that the crystals first occur near the contact line [105-107]. If the crystals stick on the substrate, ring stains would be formed. As shown in Figure 2.20 (a) and (b), the CaSO_4 crystal grows into ring stains on the hydrophilic glass and silicon surface under the strong pinning effect brought by its needle cluster structure, while a thick NaCl salt ring formed on a rough hydrophobic surface (see Figure 2.20 (c)). They all hold the same feature that the crystallization helps to pin the contact line. However,

as the crystal grows bigger, the deformed liquid-air interface would exert the capillary force on the crystal that may push it to the center. If there exists a lubricant treatment to reduce the friction of the solid surface, then the ring-like pattern could be greatly suppressed, as shown in Figure 2.20 (d). And if the cubic NaCl crystal is allowed to grow on a relatively smooth surface, it would be pushed to the center of the droplet, as shown in Figure 2.20 (e). What's more, the crystal morphologies could also be modulated by the droplet solution composition. As shown in Figure 2.20 (f), by adding a polyelectrolyte into the salt solution, concentric rings are formed. These complex profiles of sessile colloidal droplet drying require more studies on the interaction between droplet drying dynamics and the salt precipitation process, especially to understand the role of salt in varying droplet evaporation dynamics.

Figure 2.20. Various crystallization patterns. (a) CaSO_4 ring stain on a glass slide [105]; (b) CaSO_4 ring stain on a silicon surface [7]; (c) NaCl ring stain on a rough hydrophobic surface [107]; (d) Suppressed CaSO_4 ring stain lubricant treated surface [7]; (e) NaCl cubic crystal on a glass slide [105]; (f) Concentric ring stains left by droplets of solutions of a polyelectrolyte and salt [14].

2.3. Modelling evaporative self-assembly

The modeling and simulation of particle self-assembly in evaporating droplets require well numerical descriptions of the different transporting mechanisms. It mainly lies in two aspects, one is the evaporating dynamics of the droplet liquid phase, the other is the various interactions acting on the particles. In this section, we would introduce the theoretical and numerical studies of the droplet evaporation process with the various strategies applied in describing particle transportation behavior.

2.3.1. Particle transportation mechanisms

2.3.1.1. Evaporation induced inner flows

The transportation of particles suspended in the droplet solution would be inevitably affected by the flow field of the liquid phase. In fact, the evaporation induced flows act as the main particle transportation mechanism in almost all modeling works. The role of this kind of flow in particle deposition was first qualitatively analyzed by Deegan et al. [9] to be the cause of ring stains. A series of work has been done since then, aiming to obtain an accurate analytical solution of droplet evaporation flux and the capillary outflow induced [95, 108, 109]. Hu and Larson [96, 108, 110, 111] have carried a systematic analysis in this area by combining the finite element modeling result with the semianalytical solution derived under a lubrication theory. Assumptions of quasi-steady state (slow evaporation) and small droplet (negligible gravity) are made to simplify the governing equations as follows:

Vapor concentration distribution:

$$\Delta c = 0 \tag{2.14}$$

Continuity equation:

$$\frac{1}{r} \frac{\partial ru_r}{\partial r} + \frac{\partial u_z}{\partial z} = 0 \quad (2.15)$$

Momentum equation:

$$\mu \left(\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (ru_r) \right) + \frac{\partial^2 u_r}{\partial z^2} \right) = \frac{\partial P}{\partial z} \quad (2.16)$$

$$\mu \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial u_z}{\partial r} \right) + \frac{\partial^2 u_r}{\partial z^2} \right) = \frac{\partial P}{\partial z} \quad (2.17)$$

Energy equation:

$$\Delta T = 0 \quad (2.18)$$

By solving the above governing equations with finite element method, the streamline plots under different considerations of Marangoni stress are shown in Figure 2.21. Continuous capillary outflow can be simulated in the absence of Marangoni stress while recirculation flow is obtained when thermal Marangoni effect is included. The semianalytical form of evaporation flux and flow field are then derived from Eqs. (2.14) to (2.18) by using the lubrication theory, which accuracy is confirmed by the FEM result for small contact angle (up to 40°). Due to the convenience of this analytical solution in describing the droplet evaporation and the flow field induced, it has been widely applied in many modeling works to describe the particle transportation behavior and to simulate the deposition patterns [111-114].

There also exists another analytical approach of the flow field without the lubrication approximation [115]. Given the weak flow inside a slow evaporation droplet, the inertial terms has been neglected in Eqs. (2.16) and (2.17), making them in the form of stokes equation. If the shear stress along the liquid-gas interface can be neglected, the stokes flow inside the evaporating droplet can be derived by the stream function formulation (vorticity equation) under the bipolar coordinate system [116]:

$$\nabla^4 \psi = 0 \quad (2.19)$$

where ψ is the stream function which can be converted to the analytical solution of the flow. This Stokes flow can be applied to evaporating droplets of any contact angle with negligible Marangoni effect, provided the evaporation flux is known. It has been applied in Kang et al.'s [117] theoretical model for “coffee-ring” pattern simulation.

Figure 2.21. Streamline plots of the flow field. (a) With no Marangoni stress boundary condition ($Ma = 0$); (b) With Marangoni stress boundary condition ($Ma = 841$).

It should be noted here that droplet evaporation itself is a quite complex problem. Accurate modeling of droplet evaporation needs to include many aspects like the evaporative cooling effect, different heating and humidity conditions, substrate property, gravity, etc. In the modeling work of nanofluid droplet drying, assumptions are usually made on those factors with little effect on droplet evaporation and particle transportation. Then the study focus can be put on the several dominating mechanisms.

2.3.1.2. Forces acting on suspended particles

Inside a drying colloidal droplet, the suspended particles are under the effect of various forces [118]. There is no doubt that the van der Waals force always exists between particles and between particles and substrates. Due to the existence of evaporation induced flow, the drag force would be exerted on the particles. As particles are immersed

in the liquid, it is common that they are electrically charged or surrounded by an electrical layer, which would lead to the electrostatic force between particles and between particles and substrates. For particles captured by the descending interface, surface tension force would be exerted on the particles, which may lead to the capillary attraction between particles [119]. During the evaporation process, particles may touch the substrate under the flow transportation or gravitational sedimentation, then the friction force exists to hinder any further particle motion. This would also induce a self-pinning effect when there is a preferred accumulation of particles near the edge [120].

In addition, the body forces also exist which act on the particles in a predefined direction. The most common one is the gravitational force, leading to particle sedimentation. It has been observed to bring an evident change to the final dried pattern under an inclined orientation of the drying droplet [121]. Another body force that has been applied to tune particle deposition pattern is the magnetic body force with controllable orientation and field strength [122].

The above analysis has shown that the forces acting on the suspended particles are quite complex. However, in the real modeling work, we do not need to consider all the existing forces, as their ability in driving particle motion may differ greatly. The strategy is planned to adopt several dominating forces based on the specific situation, which is similar to the one applied in the previous section of simulating droplet evaporation.

2.3.2. Strategies in describing particle motion

2.3.2.1. Particle concentration function

Particles suspended in a drying droplet can be directly treated as solutes and described using a concentration function. Assumptions are usually made that particles have no effect on droplet shape, inner flows, and the evaporation of droplet liquid. Then the

particle self-assembly behavior can be simulated by solving the continuum advection and diffusion equation of particle concentration [123]:

$$\frac{\partial c}{\partial t} + \nabla \cdot (c \mathbf{v}) = D \nabla^2 c \quad (2.20)$$

where $\mathbf{v}$ is the advective velocity of particles, c is the particle concentration function, and D is the diffusion coefficient of particles in the droplet liquid. Bhardwaj et al. [124] have applied the finite element method to solve Eq. (2.20) together with the governing equations of droplet evaporation, the simulated particle concentration distribution is shown in Figure 2.22. A ring structure is found to form gradually near the wetting line with the droplet dries out.

Figure 2.22. Particle concentration contours near droplet edge [124].

If the advective velocity $\mathbf{v}$ in Eq. (2.20) is expressed as $\mathbf{v} = \mathbf{v}_{\text{fluid}} + \mathbf{v}_{\text{DLVO}}$, where $\mathbf{v}_{\text{fluid}}$ represents the hydrodynamic velocity of the fluid, $\mathbf{v}_{\text{DLVO}}$ represents the velocity estimated by balancing Derjaguin-Landau-Verwey-Overbeek (DLVO) force with drag force, then the effect of DLVO forces on particle motion can be estimated. The DLVO forces include the electrostatic and van der Waals forces between a particle and the substrate or the liquid-air interface. By including this DLVO force effect, Bhardwaj et al. [125] have simulated the pattern formation under different PH values, which agrees well with the experimental results.

In some studies, the above equation has been simplified by neglecting the diffusion transfer of particles [95, 126], transferring Eq. (2.20) into the form:

$$\frac{\partial c}{\partial t} + \nabla \cdot (c \mathbf{v}) = 0 \quad (2.21)$$

Then some qualitative features of particle deposition at contact line can be analyzed [126], or even to derive an analytical result [112, 117, 126, 127]. It is clear that this model doesn't include the collisions between individual particles, making it unsuitable for cases where particle interaction has a big effect.

2.3.2.2. Kinetic Monte Carlo model

The particles can also be treated separately using the kinetic Monte Carlo (KMC) model, which is first introduced by Rabani et al. [128] to simulate the self-assembly patterns of evaporating thin-film nanofluids. In the two-dimensional lattice gas domain established (as shown in Figure 2.23), each cell of a square lattice may represent either liquid, vapor or nanoparticle, which state can be denoted as cell-liquid ($l_i = 1, n_i = 0$), cell-vapor ($l_i = 0, n_i = 0$) and cell-nanoparticle ($l_i = 0, n_i = 1$). Based on the state of cells around the domain, it can be classified as closed domain (with liquid around) or open domain (opposed to the drying front) [129]. The equilibrium of the system is controlled by the Hamiltonian energy equation:

$$H = -\frac{\varepsilon_{nn}}{2} \sum_{\langle ij \rangle} n_i n_j - \frac{\varepsilon_{nl}}{2} \sum_{\langle ij \rangle} n_i l_j - \frac{\varepsilon_{ll}}{2} \sum_{\langle ij \rangle} l_i l_j - \mu \sum_i l_i \quad (2.22)$$

where ε_{nn} , ε_{nl} , and ε_{ll} are the interaction energies for adjacent cells (nanoparticle, nanoparticle), (nanoparticle, liquid) and (liquid, liquid) respectively, and μ is the chemical potential which controls the evaporation and condensation of the liquid. In each simulation step, there exist two processes:

1. Evaporation (condensation) of one liquid (vapor) cell;
2. Diffusion of nanoparticles in liquid cells.

The energy change ΔH is calculated in each step and the Metropolis probability $p_{acc} = \min[1, \exp(-\Delta H / kT)]$ is used to determine if the process is accepted or not. Here k is Boltzmann's constant and T is temperature.

Figure 2.23. Schematic picture of the two-dimensional lattice gas model [130]. The size of a liquid or gas cell is 1×1 . The size of a nanoparticle is 3×3 , which can also be varied to other sizes like 1×1 , 2×2 , 4×4 , etc.

The above model is then extended to three dimensions [131-133] and a sigmoidal function [134] is usually used to couple the chemical function μ with the solvent coverage. The particle-substrate and liquid-substrate interactions can also be added [132, 135], so as to address the effects of substrate like roughness and patterning [136]. Stannard et al. [130] have carried a thorough parameter space exploration which provides a clear view of how the various deposition patterns are related with the different parameters like particle concentration, temperature, and chemical potential. Some of the patterns simulated can be found in Figure 2.24, which shows that this kinetic Monte Carlo model could provide strong visual correspondence between experimental results and numerical results. If the KMC model is applied to a circular domain, it can then be

used to simulate the branched aggregations left by the evaporation of sessile droplet [137], as shown in Figure 2.25.

Figure 2.24. Various self-assembly patterns simulated by the kinetic Monte Carlo model [131]. Simulated results: (a1), (b1) and (c1). Experimental results: (a2), (b2), and (c2). (a1, a2): Dual-scale cellular networks; (b1, b2): Nanoparticle rings; (c1, c2): Nanoparticle fingering.

Figure 2.25. Branched aggregations left by dried sessile droplet [137]. (a) Experimental results of a dried copper nanofluid droplet. (b) Simulated results of KMC model.

However, for sessile droplet drying, the convective transfer of nanoparticles may play a key role. The study done by Deegan et al. [95] has shown that an outward flow could be induced by the evaporation of droplet with a pinned boundary, leading to the deposits at contact line. As a result, the original KMC model has been modified to incorporate the convection of nanoparticles [113, 138]. Jung et al. [139] have proposed another form of Hamiltonian equation:

$$H = \sum_i f_i N_i - \sum_i g_{ij} N_i N_j \quad (2.23)$$

where f_i is the convective potential field, N_i is the number of particles, g_{ij} is the interaction energy between different particles. Now the energy equation deals with the particle transportation only and the evaporation of liquid is controlled by a linear decrease of droplet contact angle. This model has been applied to simulate the formation of coffee-ring pattern and the wave-like pattern, as shown in Figure 2.26.

Figure 2.26. Patterns formed by modified KMC model [139]. (a) Ring like pattern; (b) Wave-like pattern.

2.3.2.3. Diffusion limited aggregation model

The diffusion limited aggregation (DLA) model is another approach in describing the particle motion in the bulk solution. It is first developed by Witten Jr and Sander to simulate the growth of fractals [140]. This model describes the repeated process where a single particle is randomly added into the bulk solution which performs random walks and adheres to the existing stationary particles when encountered [141]. It is applicable to simulate the aggregation event in any systems where diffusion dominates the particle moving behavior. If a sticking probability is introduced into the process to check if the aggregation happens or not, the simulated DLA clusters would be changed. As shown in Figure 2.27, clusters are more closely packed under low sticking probability.

Figure 2.27. DLA clusters simulated under different sticking probabilities [142]. S is the sticking probability.

As the DLA model can simulate the aggregation event of particles, it shows the potential to simulate the particle transportation in a drying droplet. However, under the effect of evaporation induced flows or external forces, particle should perform biased random walk instead. At the same time, the aggregation events can be extended to three types: particle-particle, particle-cluster and cluster-cluster. In this case, the model is also named for diffusion limited cluster-cluster aggregation (DLCA) model [143]. Crivoi and Duan [144-147] have applied the DLCA model to describe the particle transportation and aggregation in the drying sessile nanofluid droplets, by combining particle motion with other model describing the evaporation of the liquid phase. In their model developed, a spherical domain had been established with a cubical lattice structure, mimicking a pinned droplet. The evaporation of the droplet is controlled by a linear decrease of droplet apex height with dimensionless time, during which all particles perform a biased random walk (BRW) inside the domain. The biased move of particles is controlled by a possibility distribution, which is calculated from the analytic solution of evaporation induced flow [96, 110]. As shown in Figure 2.28, the experimental coffee-ring and uniform patterns are in good agreement with the results simulated by the DLCA model,. The adding of surfactant into the droplet solution could inhibit the aggregation of particles, which is similar to the effect of a low sticking probability in the simulation, leading to the formation of the coffee-ring pattern. While uniform

patterns are preferred without surfactant in the droplet solution or at a high sticking probability.

Figure 2.28. Comparison between simulated results (a1, b1) and the experimental ones (a2, b2) [146]. (a1) $c_{\text{part}} = 0.2\%$, $c_{\text{surf}} = 0.01\%$; (a2) $\phi = 0.5\%$, $p_{\text{stick}} = 1$; (b1) $c_{\text{part}} = 0.2\%$, $c_{\text{surf}} = 0\%$; (b2) $\phi = 0.5\%$, $p_{\text{stick}} = 25$. c_{part} and c_{surf} are the mass concentration of nanoparticles and surfactant in the droplet solution respectively. ϕ is the volume concentration of particles in calculation domain. p_{stick} is the sticking probability of particles. The color bar indicates the height of the particle layer.

2.4. Summary

In this chapter, the wetting and evaporation characteristics of colloidal droplets, and the modelling work on evaporative particle self-assembly are reviewed. The different wetting behaviors of sessile droplets are introduced. By applying these wetting theories to the patterned surfaces, we can get to know the key factors on wetting and also the theories to describe the droplet wetting process. Then the evaporation dynamics of the droplet is introduced, including the evaporation modulated particle aggregation and

solute precipitation. Besides, theoretical and numerical studies of droplet evaporation and particle self-assembly are also introduced. The drying process of a colloidal droplet is closely related to its wetting conditions, like the pinning or dewetting contact line. Under the transportation effect of the evaporation induced flows, the spatial distribution of the suspended particles and dissolved solutes would be greatly changed. The resultant non-uniform deposits would in turn change the droplet wetting and drying behaviors. As a result, the complex interplay mechanisms between droplet wetting, evaporation, and deposition call for more systematic investigations.

In the following studies, the particle self-assembly under different pinning conditions of the drying droplet, and the complex wetting and drying behaviors of different colloid droplets on various surfaces will be investigated in detail.

Chapter 3. Disk-ring pattern formation during the evaporation of pinning droplets¹

3.1. Introduction

The pattern formation left by a drying nanofluid droplet is closely related to the evaporation modulated particle self-assembly. In this chapter, the pattern formation of an evaporating nanofluid droplet has been investigated on a flat substrate under the pinning drying condition, from both experimental and numerical approaches. A three-dimensional (3D) diffusion-limited cluster-cluster aggregation (DLCA) model has been developed to combine the evaporation induced flow field with the particle movement, where “coffee-ring” and disk-ring pattern have been simulated under different Marangoni effects.

3.2. Experimental setup

A simple setup has been designed to enhance the Marangoni effect for the sessile nanofluid droplet drying. As shown in Figure 3.1 (a), the system only includes a vacuum chamber, a vacuum pump, and a pressure gauge to monitor the vacuum conditions. To isolate the vibration of the pump, the pressure gauge is fastened to a solid base and flexible silicon tubes were used to connect the pressure gauge to the pump and the chamber respectively. By conducting the experiments in a reduced pressure condition, the evaporation flux of the droplet could be enhanced, the evaporation cooling can lead to a larger temperature gradient along the droplet liquid-vapor interface [10] and

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accordingly enhance the Marangoni effect. The nanoparticles used in the experiments was aluminum oxide (Al_2O_3) nanopowder (gamma phase) having a highly porous structure and high surface area. Their small size (5 nm) allows them to suspend in the water solution for a long time and to follow the fluid flows easily. The nanofluid solution is prepared by dispersing the nanopowder into the deionized (DI) water with the resistance at $18.2 \text{ M}\Omega\cdot\text{cm}$. The solution was firstly stirred by a magnetic bar for two hours and then ultrasonicated for 30 min, then the droplet would be made right away on the substrate for drying in the designed setup. The silicon wafer (Latech Scientific Supply Pte Ltd) was used for the solid substrate. The ambient temperature was controlled at $22\pm 1 \text{ }^\circ\text{C}$ and the relative humidity was at $55\pm 5\%$. The droplet size was controlled by a Micropipette at $0.94\pm 0.03 \text{ }\mu\text{L}$, it formed an initial contact angle around 30° on the silicon substrate. A summary of the experimental conditions is listed in Table 3.1.

Table 3.1. A summary of the experimental conditions

Solution type	Concentration (g/L)	Volume (μL)	Substrate	Environmental condition	Pressure condition (mmHg)
Aluminum oxide (5 nm) nanofluid	0.5, 1.0, 1.5, 2.0, 3.0	0.94 ± 0.03	Silicon wafer	Temperature: $22 \pm 1 \text{ }^\circ\text{C}$ Humidity: $55 \pm 5 \%$	0, -200, -400

As the height of the droplet is at around 0.35 mm, which is much smaller than the capillary length $\sqrt{\gamma/\rho g}$ (2.7 mm) of the water droplet, the gravitational effect is assumed to be negligible and the droplet is assumed to hold a spherical cap shape. After the droplet was placed onto the silicon wafer inside the vacuum chamber, the pressure of the chamber was quickly reduced to a predicted value (within 10 seconds) by the vacuum pump and maintained until the droplet was dried. As the vacuum condition was

established very fast, we neglected the effect of the initial pressure reducing process on the droplet evaporation rate. With the presence of nanoparticles inside the liquid, the droplet contact line kept pinned all the time. After the evaporation process ended, the final deposition patterns were captured using Nikon Eclipse LV100ND microscope from top view, one sample of the dried sessile nanofluid droplet is shown in Figure 3.1 (b). A 3D profiler microscope (Leica DCM8) was used to measure the local height of the final dried particle aggregation patterns.

Figure 3.1. (a) Experimental setup for the vacuum chamber. (b) Disk-ring deposition pattern of a nanofluid droplet on the silicon wafer. The solution of the droplet is 1.0 g/L Al_2O_3 (5 nm). The scale bar indicates 0.5 mm.

3.3. Mathematical model

3.3.1. Simulation domain

The center inset in Figure 3.2 (a) illustrates the simulation domain, which is a spherical cap mimicking a small sessile droplet and filled by the cubic lattice cells with the size $1 \times 1 \times 1$. Those red-color lattices represent the solid particles, which are set to be uniformly distributed initially, while the blue ones represent the liquid phase. In the simulation, the base diameter, B of the simulation domain, is set to 1000 cells. The initial contact angle of the sessile droplet is denoted by θ_0 , the initial height of droplet

apex is denoted by h_0 , and the initial particle volumetric concentration is denoted by ϕ .

During the simulation, the droplet evaporates in the constant contact radius mode and the droplet apex height is assumed to decrease linearly with time:

$$h(0, \tilde{t}) = h_0(1 - \tilde{t}) \quad (3.1)$$

where $\tilde{t} = t / t_f$, and t_f is the lifetime of the droplet. Previous studies have shown that this assumption provides a very good approximation of droplet drying under small initial contact angle ($\theta_0 < 40^\circ$) [95, 108].

3.3.2. Transport mechanisms of particles

In view of the complex transport phenomenon inside a drying nanofluid droplet in this study, we assume three mechanisms of particles movement to be considered: (1) Particle transport by the evaporation induced capillary outflow and Marangoni flow; (2) particle adsorption at the descending liquid-air interface; and (3) particle-particle aggregation. The particles are mainly transported by the evaporation induced capillary outflow and Marangoni flow, as shown in Figure 3.2 (a). As the liquid-air interface descends during the evaporation process, it could collect particles with slower downward moving speeds or those transported by the Marangoni reverse flow to approach the interface. In this study, the parameter studies were carried out under both weak and strong Marangoni effects, adsorption and non-adsorption functions, and weak and strong particle aggregation possibilities, so as to find the mechanisms responsible for the formation of the disk-ring patterns which were observed in the experiments. During the simulation process, the particles are treated separately and are not allowed to overlap with each other. The aggregation event follows the DLCA model, it assumes particles aggregate into fractal structures during which process particles diffuse through the surrounding medium and bond together upon collisions [148]. When two particles meet with each

other, they may aggregate into one cluster, which process is controlled by a sticking parameter, p_{stick} . In addition, the particle-cluster interaction and cluster-cluster interaction are also considered by checking the embedded particle-particle interaction. This model, though not reflecting the real physics of particles interaction, has been proved to be an effective way in simulating the network structures observed in the experiment [141].

Figure 3.2. Schematics of the simulation domain and mechanisms of particle motion. (a) The mechanisms of particle motion. (center) schematics of the calculation domain; (left top) no adsorption of particles under weak Marangoni effect; (right top) no adsorption of particles under strong Marangoni effect; (left bottom) adsorption of particles by surface layer under weak Marangoni effect; (right bottom) adsorption of particles by surface layer under strong Marangoni effect; (b) Schematics of particle moving directions at the xy horizontal plane.

3.3.3. Particle motion used for the simulation

For each particle lattice, it has six moving directions and one additional choice to stay at its original position. During each Monte Carlo step (MCS), every particle performs a

biased random movement into a nearby vacant cell. A biased probability distribution with seven components is calculated to control this movement,

$$p_{move} = \{p_{x_+}, p_{x_-}, p_{y_+}, p_{y_-}, p_{z_+}, p_{z_-}, p_w\} \quad (3.2)$$

where the subscripts x , y , and z represent the three Cartesian axes, “+” and “-” indicate the positive and negative directions of each axis, and p_w is expressed as the possibility that a particle stays. Once p_{move} is calculated, the direction of the current move can be determined. The seven components of p_{move} are defined as,

$$\left\{ \begin{array}{l} p_{x_-} = \frac{1}{6} - \frac{\tilde{v}_x}{6A\tilde{v}_{max}}, \quad p_{x_+} = \frac{1}{6} + \frac{\tilde{v}_x}{6A\tilde{v}_{max}}, \\ p_{y_-} = \frac{1}{6} - \frac{\tilde{v}_y}{6A\tilde{v}_{max}}, \quad p_{y_+} = \frac{1}{6} + \frac{\tilde{v}_y}{6A\tilde{v}_{max}}, \\ p_{z_-} = \frac{1}{6} - \frac{\tilde{v}_z}{6A\tilde{v}_{max}}, \quad p_{z_+} = \frac{1}{6} + \frac{\tilde{v}_z}{6A\tilde{v}_{max}}, \\ p_{wait} = 1 - p_{x_+} - p_{x_-} - p_{y_+} - p_{y_-} - p_{z_+} - p_{z_-}. \end{array} \right\} \quad (3.3)$$

where $\tilde{v}_x$, $\tilde{v}_y$, and $\tilde{v}_z$ are the dimensionless velocity components along the three axes; $\tilde{v}_{max}$ is the maximum value of $\tilde{v}_x$, $\tilde{v}_y$, and $\tilde{v}_z$, at a given MCS; and A is a value associated with the moving ways of the particles.

A particular treatment was made for the movement of particles on the horizontal xy plane, as demonstrated in Figure 3.2 (b). Since the simulation domain is constructed by the cubic lattices, the number of steps needed for a particle to move from the droplet center to the edge is different along the different angular directions, which would then lead to non-uniform transportation of particles. In order to eliminate the asymmetry effect, a new coordinate system ($x'y'z$) has been applied, which is generated by rotating the original coordinate system (xyz) 45° anticlockwise around the positive z axis. Four new horizontal moving directions are then added with the vertical moving direction

remaining the same. During the simulation process, every particle would perform the biased random walk in these two coordinate systems alternatively, as shown by Steps 1 and 2 in Figure 3.2 (b). In Step 1, one step move represents one cell distance, A is set to 1; while in Step 2, one step move represents $\sqrt{2}$ cell distance, A is set to be $\sqrt{2}$.

3.3.4. Analytical solution of the flow field

The dimensionless velocities, $\tilde{v}_x$, $\tilde{v}_y$, and $\tilde{v}_z$, are computed from the analytical solutions of the droplet inner flow [96, 110, 111],

$$\left\{ \begin{array}{l} \tilde{u}_r = \frac{3}{8} \frac{1}{1-\tilde{t}} \frac{1}{\tilde{r}} [(1-\tilde{r}^2) - (1-\tilde{r}^2)^{-\lambda(\theta)}] \left(\frac{\tilde{z}^2}{\tilde{h}^2} - 2 \frac{\tilde{z}}{\tilde{h}} \right) - \frac{g(\tilde{r}, \tilde{t}) \tilde{h}_0 \tilde{h}}{2} \left(\frac{\tilde{z}}{\tilde{h}} - \frac{3}{2} \frac{\tilde{z}^2}{\tilde{h}^2} \right) \\ \tilde{u}_z = \frac{3}{4} \frac{1}{1-\tilde{t}} [1 + \lambda(\theta)(1-\tilde{r}^2)^{-\lambda(\theta)-1}] \left(\frac{\tilde{z}^3}{3\tilde{h}^2} - \frac{\tilde{z}^2}{\tilde{h}} \right) - \\ \frac{3}{4} \frac{1}{1-\tilde{t}} [(1-\tilde{r}^2) - (1-\tilde{r}^2)^{-\lambda(\theta)}] \left(\frac{\tilde{z}^2}{2\tilde{h}^2} - \frac{\tilde{z}^3}{3\tilde{h}^3} \right) \frac{\partial \tilde{h}}{\tilde{r} \partial \tilde{r}} + \\ \frac{g(\tilde{r}, \tilde{t}) \tilde{h}_0}{4\tilde{r}R} \left(\tilde{z}^2 - \frac{\tilde{z}^3}{\tilde{h}} \right) + \frac{g'(\tilde{r}, \tilde{t}) \tilde{h}_0}{4} \left(\tilde{z}^2 - \frac{\tilde{z}^3}{\tilde{h}} \right) + \frac{g(\tilde{r}, \tilde{t}) \tilde{h}_0 \tilde{h}}{4} \left(\frac{\tilde{z}^3}{\tilde{h}^2} \right) \frac{\partial \tilde{h}}{\partial \tilde{r}} \\ g(\tilde{r}, \tilde{t}) = -2\tilde{h}_0 \tilde{r} [\tilde{J} \lambda(\theta)(1-\tilde{r}^2)^{-\lambda(\theta)-1} + 1] - f(Ma, \tilde{T}, \tilde{r}) \end{array} \right\} \quad (3.4)$$

where the dimensionless instantaneous variables are defined as: radial velocity, $\tilde{u}_r = u_r t_f / R$; vertical velocity, $\tilde{u}_z = u_z t_f / R$; horizontal x velocity, $\tilde{u}_x = \tilde{u}_r x / r$; horizontal y velocity, $\tilde{u}_y = \tilde{u}_r y / r$; time, $\tilde{t} = t / t_f$; radial coordinate, $\tilde{r} = r / R$; vertical coordinate, $\tilde{z} = z / h_0$; local height of droplet surface, $\tilde{h} = h / h_0$; droplet apex height, $\tilde{h}_0 = h_0 / R$; R is the droplet base radius; $\lambda(\theta) = 1/2 - \theta / \pi$; g' is the first-order partial derivative of the function of $g(\tilde{r}, \tilde{t})$ with $\tilde{r}$; $f(Ma, \tilde{T}, \tilde{r})$ is a Marangoni effect function; $\tilde{J}(\theta)$ is the dimensionless evaporative flux at the droplet apex.

The evaporation flux at droplet apex, $J(\theta)$, can be written as [111],

$$J(\theta) = \frac{D(c_s - c_\infty)}{R} (0.27\theta^2 + 1.30) \left(0.6381 - 0.2239 \left(\theta - \frac{\pi}{4} \right)^2 \right) \quad (3.5)$$

where $0 < \theta < \pi/2$, c_s and c_∞ are the vapor concentrations at the droplet surface and in the ambient environment, respectively, and D is the diffusivity of the vapor. The dimensionless form of $J(\theta)$ is expressed as,

$$\tilde{J}(\theta) = \frac{J(\theta)t_f}{\rho h_0} \quad (3.6)$$

where ρ is the density of droplet liquid.

The Marangoni function, $f(Ma, \tilde{T}, \tilde{r})$, is defined as,

$$f(Ma, \tilde{T}, \tilde{r}) = Ma \frac{d\tilde{T}}{d\tilde{r}} \quad (3.7)$$

where Ma is the Marangoni number, and $\tilde{T}$ is the dimensionless temperature distribution along the droplet surface. The strength of Marangoni effect in the drying droplet is controlled by the Marangoni function, f . In the previous numerical studies [146, 147], the Marangoni function, f , was set to be a constant and small value. While in this study, we are able to estimate its value according to the temperature gradient along the liquid-air interface. However, as the Marangoni flow is rather weak in the water droplets under the normal conditions, the Marangoni function might not be as strong as the theoretical predictions, suggested by Hu and Larson [111]. We follow it in the present simulation. By varying the value of the surface tension-temperature coefficient, β , we can control the Marangoni number, Ma . The Marangoni number, Ma , is defined as,

$$Ma = - \frac{\beta(T_e - T_c)t_f}{\mu R} \quad (3.8)$$

where μ is the viscosity of the liquid, T_e is the surface temperature at the sessile droplet edge, and T_c is the surface temperature at the droplet apex. Ma represents the ratio of the Marangoni force to viscous force. This non-traditional form of Ma is defined when deriving the analytical solutions of the flow field (Eq. 3.4) with a Marangoni stress boundary condition. The detailed process can be found in Reference [110]. Previous experiment and simulation studies have demonstrated that the particle adsorption at the liquid-air interface lowers the surface tension [149-152]. It is then reasonable to assume that disturbed by the adsorbed particles, the temperature gradient cannot be transferred to the surface tension gradient effectively. Here we consider this effect in a simple way by lowering the surface tension-temperature coefficient, β , during the simulation process with the following model,

$$\beta = \beta_0 \cdot (1 - \chi) \quad (3.9)$$

where β_0 is the initial value of the surface tension-temperature coefficient, and χ is the fraction of the surface area occupied by the particles captured at the local liquid-air interface region. In addition, the droplet lifetime can be estimated by [39]:

$$t_f = \frac{\rho V}{-\dot{m}} = \frac{\pi \rho h_0 (3R^2 + h_0^2)}{27RD(c_s - c_\infty)} \quad (3.10)$$

To obtain the temperature gradient, $d\tilde{T}/d\tilde{r}$, the heat transfer equation needs to be solved. Here we consider a pinned small sessile droplet resting on a flat substrate. For simplicity, we only assume the heat transfer in the vertical direction and treat it as a one-dimensional problem [111, 153]. The temperature distribution along the droplet liquid-vapor interface can be written as,

$$T(r) = T_0 - \frac{H_v R}{k_L} J(r) \left(1 - \left(\frac{r}{R} \right)^2 \sin^2 \theta \right)^{-\frac{1}{2}} \left(\left(\frac{1}{\sin^2 \theta} - \left(\frac{r}{R} \right)^2 \right)^{\frac{1}{2}} - \frac{1}{\tan \theta} + \frac{h_s k_L}{R k_s} \right) \quad (3.11)$$

where h_s is the thickness of the substrate, and k_L & k_s are the thermal conductivities of the droplet liquid and the substrate respectively. The dimensionless form of $T(r)$ is,

$$\tilde{T}(r) = \frac{T(r) - T_c}{T_e - T_c} \quad (3.12)$$

The Marangoni function f can then be estimated by combining Eqs. (3.7), (3.8), (3.11) and (3.12) together. Based on the full analytical solution of the flow driven by the evaporation induced temperature gradient, we can calculate the possibility distribution listed in Equation (3.3).

3.3.5. DLCA simulation process

The flow chart of the DLCA simulation process is shown in Figure 3.3. Initially, the particles are randomly distributed in a spherical cap domain. During each Monte Carlo Step (MCS), the possibility distribution, p_{move} , is firstly calculated to determine the possible moving direction of each particle or cluster. Afterward, some attempts of particle motion are rejected, as the particles are required to stay in the simulation domain, and not allowed to overlap with each other. The other constraints are also applied that the particles adsorbed by the liquid-air interface are restricted to move within the interface layer and the particles inside the same cluster are required to move as a whole. After updating the position of those moving particles, the particle aggregation events are checked. Afterward, the simulation domain is updated to mimic the drying of the droplet and the evaporation time is updated by adding the time consumption, $\Delta \tilde{t}$, of the current MCS. The MCSs are repeated until the non-dimensional evaporation time, $\tilde{t}$,

reaches 1. The $\Delta\tilde{t}$ during each Monte Carlo step is calculated as $1/(3B\tilde{v}_{max})$, in which B is the base diameter of the simulation domain, which is 1000 in this study. The aggregation event of two neighbouring particles is considered both in the bulk of the droplet and at the liquid-air interface, which possibility is expressed as $p_{stick}\Delta\tilde{t}$.

Figure 3.3. Flow chart of the simulation process.

3.3.6. Value of parameters

The values of parameters used in the simulation are all listed in Table 3.2. The typical property of the working liquid is set to be the same as water at 20 °C and the property of the solid substrate is set to be the same as the silicon wafer (Latech) used in the experiments.

Table 3.2. Value of parameters used in the simulation

Parameter	Definition	Typical value
H_v	Vapor latent heat of water	2453.6e3 J/Kg
k_L	Thermal conductivity of water	0.598 W/(m·K)
k_s	Thermal conductivity of silicon wafer	150 W/(m·K)
μ	Dynamic viscosity of water	0.001 Kg/(m·s)
β_0	Surface tension-temperature coefficient of water	-0.1514e-3 N/(m·K)
D	Diffusivity of water vapor in air	0.242e-4 m ² /s
ρ	Density of water	1000 Kg/m ³
R	Base radius of the droplet	1 mm
h_s	Thickness of the silicon wafer	0.5 mm

3.4. Results and discussions

3.4.1. Dominating mechanisms of disk-ring pattern formation

The disk-ring deposition pattern in the experiment under a normal pressure condition is shown in Figure 3.1 (b), from which we could observe a disk-ring aggregation region locating inside an outer ring, with a clear gap between the two. This preference of particle aggregation at the central region reveals the existence of the Marangoni reverse flow. With the numerical model established, we are trying to obtain a similar deposition configuration in the simulation and therefore trying to find the underlying particle transporting mechanisms.

The simulation begins without considering the particle adsorption function at the liquid-air interface under both weak and strong Marangoni effects. The drying processes are shown in Figure 3.4. The initial contact angle θ_0 of the droplet in simulation is set to be 30°, which is the same with that in the experiment. The sticking parameter p_{stick} is set at 0.05, which means the particles has a low possibility to aggregate when they meet

each other. The images from a1 to a10 of Figure 3.4 display the drying processes of a single droplet under a weak Marangoni effect, where particles are continuously carried to move outwards and aggregate near the edge, forming a coffee-ring pattern. While for the images from b1 to b10, due to the existence of strong Marangoni flow, the particles

Figure 3.4. Drying processes of a single droplet under the weak and strong Marangoni effects.

(a1-a10) $Ma \approx 10$ and $\beta_0 = -1.19 \times 10^{-7} \text{ N/(m} \cdot \text{K)}$; (b1-b10) $Ma \approx 240$ and $\beta_0 = -2.85 \times 10^{-6} \text{ N/(m} \cdot \text{K)}$.

(a1, b1) $\tilde{t} = 0$; (a2, b2) $\tilde{t} = 0.1$; (a3, b3) $\tilde{t} = 0.2$; (a4, b4) $\tilde{t} = 0.3$; (a5, b5) $\tilde{t} = 0.4$; (a6, b6)

$\tilde{t} = 0.6$; (a7, b7) $\tilde{t} = 0.7$; (a8, b8) $\tilde{t} = 0.8$; (a9, b9) $\tilde{t} = 0.9$; and (a10, b10) $\tilde{t} = 1.0$. $\theta_0 = 30^\circ$,

$\phi = 1\%$, and $p_{\text{stick}} = 0.05$. The base diameter of the simulation domain is set to 1000 cells.

are found to move inwards and concentrate at the inner region of the droplet. The very center area is observed to have fewer particle accumulation than its surrounding area, mainly due to the local weak inward flow as the surface temperature gradient decreases to zero when approaching droplet apex. At the later drying period, the accumulative particles close to the droplet centerline are pushed backwards to the rim by the capillary outflow, which also leads to a coffee-ring deposition. The concentrating behavior of the particles indicates that the presence of strong Marangoni flow should be one mechanism accounting for the inner deposition inside the domain. However, in order to form a disk-ring pattern, there must exist other mechanisms to counter the final capillary outflow and to trap the particles in the inner region.

For a drying droplet, as its liquid-air interface keeps descending, particles with a lower descending speed could be adsorbed on the interface. The previous studies have shown that upon decreasing particle size, the adsorption capacity of nanoparticles increases significantly [154]. As a result, the small sized nanoparticles used in the experiment should have very good adsorption property and be collected by the droplet interface easily. In the following simulation, the particle adsorption function is incorporated into the DLCA model. The validity of this adsorption function can also be verified by the particle moving behavior in the experiments. If we focus on the region near droplet edge, we can observe two types of flows. One is the capillary outflow which transports the particles outward to the droplet rim, the other is the Marangoni flow which transports the particles inward to the inner region. With the liquid-air interface descending, many inward moving particles would be adsorbed by the vapor-liquid interface, leading to the formation of a floating surface layer.

Figure 3.5 (a1-a10) shows the simulated drying processes of a single droplet with the particle adsorption function and under strong Marangoni effect. At this time, as the

reverse Marangoni flow carries the particles to move inward, those reaching the droplet surface will be captured. With the continuous particle accumulation and aggregation at the interface, we could observe the formation of a floating surface layer. With the evaporation goes on, the Marangoni flow would decay, and the capillary outflow

Figure 3.5. Drying processes of a single droplet under the strong Marangoni effect ($Ma \approx 240$) and with the particle adsorption function. (a1, b1) $\tilde{t} = 0$; (a2, b2) $\tilde{t} = 0.1$; (a3, b3) $\tilde{t} = 0.2$; (a4, b4) $\tilde{t} = 0.3$; (a5, b5) $\tilde{t} = 0.4$; (a6, b6) $\tilde{t} = 0.6$; (a7, b7) $\tilde{t} = 0.7$; (a8, b8) $\tilde{t} = 0.8$; (a9, b9) $\tilde{t} = 0.9$; and (a10, b10) $\tilde{t} = 1.0$. (a1-a10) $p_{\text{stick}} = 0.05$; (b1-b10) $p_{\text{stick}} = 10$. $\theta_0 = 30^\circ$, $\phi = 1\%$, and $\beta_0 = -2.85 \times 10^{-6} \text{ N/(m} \cdot \text{K)}$. The base diameter of the simulation domain is set to 1000 cells.

becomes dominant gradually. With this evolution of the flow field, particles adsorbed by the liquid-air interface then disperse apart and transport along the liquid-air interface to the rim, forming a coffee-ring pattern eventually. Deegan et al. [95] have experimentally reported similar particle self-assembly behavior in a drying droplet suspended with polystyrene microspheres, where a surface excess layer was observed to form and at the late drying stage was found to break up and particles inside transported to the contact line, also forming a coffee-ring pattern. However, in our experiment, the excess surface layer is found to maintain and deposit down to form the final disk-ring region. Considering the small size (5nm) of Al_2O_3 particles used in this study, particles form aggregations easily, mainly due to the small interaction energy barrier and the preference to lower the free energy of the system (small particles have large surface energy) [155]. This strong aggregation possibility may be the reason which holds the form of the surface layer. To validate it, the sticking parameter p_{stick} of particles is increased from 0.05 to 10, the simulated drying processes are shown in Figure 3.5 (b1-b10). The particles prefer to aggregate into the clusters, which are not as densely packed as the ones shown in Figure 3.5 (a1-a10).

The floating surface layer forms a sparse structure which covers more liquid-air interface area. The branched structure of the adsorbed clusters restricts their possible movement along the liquid-air interface and thus help to maintain the floating surface layer till the end of drying. Finally, we are able to simulate a disk-ring pattern quite similar with the one shown in Figure 3.1 (b). We have also checked the dried patterns under different p_{stick} that are shown in Figure 3.6. As the sticking parameter increases, a central deposit of particles emerges and expands, with the outer ring becoming thinner. When p_{stick} reaches a relatively high value, 10, the final residual becomes very close to

the disk-ring pattern observed in the experiment. When p_{stick} reaches as high as 40, the final residual becomes very close to a uniform coverage. From the above simulation runs, we could conclude that the strong Marangoni effect, particle adsorption, and aggregation behavior at the liquid-air interface are the main mechanisms responsible for the formation of a disk-ring deposition pattern.

Figure 3.6. Simulated dried patterns under different sticking parameters p_{stick} ($Ma \approx 240$). (a) $p_{\text{stick}} = 0.05$; (b) $p_{\text{stick}} = 1$; (c) $p_{\text{stick}} = 5$; (d) $p_{\text{stick}} = 10$; (e) $p_{\text{stick}} = 20$; (f) $p_{\text{stick}} = 40$; $\theta_0 = 30^\circ$, $\phi = 1\%$, and $\beta_0 = -2.85 \times 10^{-6} \text{ N}/(\text{m} \cdot \text{K})$.

3.4.2. Comparison of simulation and experimental results

We have simulated the final dried patterns under various Marangoni effects and compare them with the ones obtained in the experiments under different evaporating pressures. The experimental results are shown in Figure 3.7 (a1-a3), the evaporation time under different vacuum conditions are at around 13.2 min (0 mmHg), 8.8 min (−200 mmHg), and 4.5 min (−400 mmHg), respectively. With the enhanced vacuum condition, we can see that the outer coffee ring becomes thinner, and the inner central disk becomes smaller. This indicates the existence of a stronger Marangoni flow, which carries more particles to move further inward. A similar trend could be observed in the numerical

results. Figure 3.7 (b1-b3) indicates that an increase of Marangoni number resulting in more particles being found to aggregate at the inner region of the droplet and produce a smaller and more concentrated inner disk region. We measured the local particle deposition from the light intensity of the final experimental residuals and the simulated ones along the base diameter line. As shown in Figure 3.7 (c1-c3), the experimental and numerical results hold a similar particle distribution, which is closer to the “dual-ring” pattern [156, 157]. With the more intense particle inward transportation, the inner ring becomes more extensive than the outer ring.

Figure 3.7. Experimental and simulated dried patterns under different Marangoni effects. (a1-a3) Experimental deposition pattern of 1.0 g/L Al_2O_3 (5 nm) droplet under normal pressure(a1), -200 mmHg gauge pressure(a2), and -400 mmHg gauge pressure(a3). (b1-b3) Simulated deposition patterns under $Ma \approx 240$ and $\beta_0 = -2.85 \times 10^{-6} \text{ N}/(\text{m} \cdot \text{K})$ (b1), $Ma \approx 360$ and $\beta_0 = -4.27 \times 10^{-6} \text{ N}/(\text{m} \cdot \text{K})$ (b2), and $Ma \approx 480$ and $\beta_0 = -5.70 \times 10^{-6} \text{ N}/(\text{m} \cdot \text{K})$ (b3). (c1-c3) Comparison of particle distribution along the diameter line between experimental results and numerical results. The solid lines are the normalized light intensity profiles of the experimental residuals, the dash-dotted lines are the normalized particle distribution profiles of the numerical residuals. In the simulation, $\theta_0 = 30^\circ$, $\phi = 1\%$, and $p_{\text{stick}} = 10$. The red scale bar indicates 0.5 mm.

To reveal the real distribution of the final residuals in the experiment, we have measured the height of the deposited particles with a 3D profiler microscope, the results are shown in Figure 3.8. Here we focus on a small region near the contact line, which covers the

structure of the outer and inner ring. A distinguishable coffee-ring effect can be observed from the 3D view of the final depositions, where a high “wall” stands at the rim of the droplet. A clear gap exists between the outer ring and the inner disk region, where little particles are found to deposit there. As the central aggregation is mainly formed by the deposition of the floating surface layer, its thickness is quite thin with only dozens of nanometers and much lower than the outer ring (see Figure 3.8 (d)). The height profile bumps up a little bit at the boundary of the disk-ring region, revealing the existence of

Figure 3.8. Experimental dried patterns of nanofluid droplet under vacuum conditions. The red dashed rectangles mark the region where the local height profiles are measured. (a-c) Deposition patterns of 1.0 g/L Al_2O_3 (5 nm) droplet under 0 mmHg gauge pressure(a), -200 mmHg gauge pressure(b), and -400 mmHg gauge pressure(c). (d) Height profile averaged from the red dashed rectangular area. The red dashed rectangles mark the region where the local height profiles are measured. The red scale bar indicates 0.5 mm.

an inner ring. With the enhanced vacuum condition, the outer ring is found to become thinner and lower and the inner aggregations move inward to the droplet center. This indicates the existence of an enhanced Marangoni flow, which could transport more particles to move reversely from droplet edge to its center, as compared with the outward motion of particles under the capillary outflow. More particles would then adsorb on the droplet surface, forming a more concentrated floating surface layer and depositing into a smaller inner disk region. Meanwhile, the coffee-ring effect is found to become weaker as now lesser particles can reach the edge.

Besides the effect of Marangoni strength, we also explore the variation of the final patterns under different initial particle concentrations. The evaporation time under different particle concentrations are all at around 13.2 min. Figure 3.9 (a1-a5) gives the top view recording of the experimental residuals and Figure 3.9 (b1-b5) demonstrates that of the numerical ones. In both cases, with an increase of the initial particle concentration, an enlargement of the disk-ring region could be observed and the final residuals are found to evolve into uniform coverage gradually. The observable particle distributions are shown in Figure 3.9 (c1-c5), where the solid lines are the normalized light intensity measured along the diameter line of the experimental residuals and the dash-dotted lines are the normalized height profiles measured along the diameter line of the numerical residuals. Similar particle distribution and evolution trend could be observed from the experimental and numerical results. The profiles have high ridges at the contact line and bump up at the central area, which correspond to the outer ring and the inner disk structure, respectively. With the initial particle concentration increasing, the gap between the inner disk and outer ring diminishes and the central bumping up region rises up to approach the outer ridge gradually, evolving to more uniform coverage.

Figure 3.9. Experimental and numerical deposition patterns under different initial particle concentrations. Experimental results: (a1) 0.5 g/L; (a2) 1.0 g/L; (a3) 1.5 g/L; (a4) 2.0 g/L; (a5) 3.0 g/L. Numerical results: (b1) 0.5%; (b2) 1.0%; (b3) 1.5%; (b4) 2.0%; and (b5) 3.0%. (c1-c5) Comparison of particle distribution between experimental results and numerical results along the diameter line. The solid lines are the normalized light intensity profiles of the experimental residuals, the dash-dotted lines are the normalized height profiles of the numerical residuals. In the simulation, $\theta_0 = 30^\circ$, $p_{\text{stick}} = 10$, $Ma \approx 240$, and $\beta_0 = -2.85 \times 10^{-6} \text{ N}/(\text{m} \cdot \text{K})$. The red scale bar indicates 0.5 mm.

We further focus on a small region to measure the real height profiles of the experimental residuals. Figure 3.10 (a) illustrates the “dual-ring” structure of the disk-ring pattern at a dilute particle concentration of 0.5 g/L. With an increase of the particle

Figure 3.10. Local height profile of the experimental dried patterns under different initial particle concentrations. The red dashed rectangles mark the region where the local height profiles are measured. (a) 0.5 g/L; (b) 1.0 g/L; (c) 1.5 g/L; (d) 2.0 g/L; and (e) 3.0 g/L. (f) Comparison of the local height profiles under different initial particle concentrations. The 2D height profiles are averaged from the 3D ones. (a-e) The red scale bar indicates 0.5 mm.

concentration, the outer ring is found to become wider and taller. With the liquid-air interface descending down at a higher particle concentration, the floating surface layer would be established more easily, which restricts the inward motion of the adsorbed particles, resulting in the enlargement of the disk-ring deposition region.

3.5. Summary

Numerical simulations have been carried in this chapter to explore pattern formation under the pinning drying condition. By developing a 3D DLCA model and comparing the numerical residuals with the experimental ones, it is concluded that strong Marangoni effect, particle adsorption and aggregation behavior at the liquid-air interface are the main mechanisms responsible for the formation of the disk-ring deposition pattern. Under a stronger Marangoni effect, the disk-ring region of the simulated pattern was smaller and more concentrated. With an increase of the initial particle concentration, the disk-ring pattern was found to evolve into uniform coverage, with the enlargement of the disk-ring region and the outer ring becoming taller and wider. The simulation results were demonstrated by the designed experiments of nanofluid droplet drying in vacuum conditions. The qualitative agreement was found in the comparison of local deposition distribution between the related experiments and simulations. In the following chapter, the study would focus on the pattern formation of a drying droplet with a continuous retreating wetting front, from both numerical and experimental approaches also.

Chapter 4. Dendritic pattern formation during the evaporation of dewetting droplets¹

4.1. Introduction

In the previous chapter, the disk-ring pattern formation has been observed to form under the pinning drying condition, where the evaporation induced capillary outflow and Marangoni flow play a key role. However, in the case of an evaporating colloidal droplet with a dewetting drying front, the demand of liquid replenishment at the droplet edge will be greatly inhibited, which then leads to weak inner flows. The pattern formation will then be dominated by the competition between contact line retreating and particle aggregation. With the presence of local pinning effects, particles may be left after the receding front, depositing into the structures like spider webs, spokes, or fingers [158, 159]. To simulate this kind of drying process, we present a 3D Monte Carlo model and perform simulations exhibiting the detailed process of the dendritic particle deposition. The simulated distribution of particles has been analysed and compared with the experimental results. Constant chemical potential has been applied and the substrate effect has been explored.

4.2. Methods

4.2.1. 3D KMC Monte Carlo model

In the simulation, the 3D mathematical model is derived from the works of Sztrum et al. [135] and Rabani et al. [128] and uses the binary variables l_i , n_i and s_i which indicate

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¹ Published paper: J. Ren, A. Crivoi, and F. Duan, *Dendritic nanoparticle self-assembly from drying a sessile nanofluid droplet*. Physical Chemistry Chemical Physics, 2021, in press.

the presence of liquid, particle or substrate in the i -th cell of the cubical lattice. The simulation domain mimics the shape of a spherical cap with a given initial contact angle value, θ . The lattice cells inside this domain are initially filled with liquid or randomly dispersed particles (see Figure 4.1 (a)). The diameter of domain base is D , and the lowest layer is occupied by substrate throughout the whole simulation run. The lattice cell, i , is in the status of either liquid ($l_i = 1, n_i = 0, s_i = 0$), vapor ($l_i = 0, n_i = 0, s_i = 0$), nanoparticle ($l_i = 0, n_i = 1, s_i = 0$), or substrate ($l_i = 0, n_i = 0, s_i = 1$). The volumetric concentration of particles is denoted by ϕ , and each particle occupies one lattice cell. The total system energy is given by Hamiltonian:

$$H = - \frac{\sum_{\{ij\}} (\varepsilon_{nn} c_{ij} n_i n_j + \varepsilon_{nl} c_{ij} n_i l_j + \varepsilon_{ll} c_{ij} l_i l_j + \varepsilon_{ls} c_{ij} l_i s_j + \varepsilon_{ns} c_{ij} n_i s_j)}{1 + \sqrt{2}} - \mu \sum_i l_i \quad (4.1)$$

where μ is the chemical potential, ε_{ll} represents the energy of interaction between liquid cells, ε_{nl} and ε_{nn} represent the energy of interaction between the adjacent liquid-particle and particle-particle cells respectively, ε_{ls} and ε_{ns} stand for the energy of interaction between liquid-substrate and particle-substrate cells; $\Sigma_{\{ij\}}$ indicates that the sums are calculated from the nearest and next-nearest interactions; c_{ij} is a dimensionless coefficient to scale the interaction ε -values based on the distance between the two interaction cells, which is 1 for nearest interaction and $1/\sqrt{2}$ for next-nearest interaction. The distribution of the nearest and next-nearest neighbours are shown in Figure 4.1 (b). This implementation allows reducing the anisotropy in the solvent evaporation process, which was discussed by Sztrum et al. [135] but also acknowledges the inevitable anisotropy in the particle motion, discussed by Kletenik- Edelman et al. [160], arising from a limited number of possible particles moving in only six directions. Further implementation of diagonal (or more complicated) particle moves in the future

work could probably make sense for the calculation of the next-nearest or next-next-nearest interactions as well. The interaction terms are also scaled by the weight factor $1+\sqrt{2}$ in the calculations, to ensure the even contribution of the energy terms. As there are no changes in the substrate-substrate interactions, they are excluded from calculations.

Figure 4.1. Schematics of the 3D KMC model in a spherical cap domain. (a) Isometric view of the initial configuration; (b) Illustration of the cell interactions.

In this 3D model, the chemical potential μ lies in the range of $\mu < -3$, where the equilibrium state of the system is vapour. The mechanics of the Monte Carlo simulation is based on the Metropolis algorithm [130, 137]. Each step of the simulation consists of two attempts to make possible moves in the system:

1. Evaporation (condensation) of each liquid (vapor) cell.
2. Random walk of nanoparticles within the liquid.

During each Monte Carlo step, each particle tries several attempts to make a random move in the randomly chosen direction, which is defined by the N_m parameter. The resulting system energy change ΔE , caused by each possible move is calculated using the Hamiltonian expression from Eq. (4.1), and afterward the Metropolis probability value is derived:

$$p_{acc} = \min[1, \exp(-\frac{\Delta E}{kT})] \quad (4.2)$$

where T is the temperature, k is the Boltzmann constant and p_{acc} is the probability that considered move is accepted in the simulation. If the move is rejected, the system state does not change, and the next possible move is considered.

The main advancement over the previously used 2D model [23] is that the droplet shape is naturally presented in a 3D domain as a spherical cap, so we do not need to modify the chemical potentials for the various local droplet thickness as in a 2D model. A constant value of chemical potential is adopted to be more representative for the actual solvent evaporation in the sessile nanofluid droplet. In addition, the substrate effect on pattern formation can be explored, while the 2D model cannot. In all the numerical results reported in this study, $\theta = \pi / 6$, $\varepsilon_{nl} = 1.5$, $\varepsilon_{ll} = 1.0$, $kT = 0.2$.

4.2.2. Experiments

In experiments, the nanofluid solutions were prepared by dispersing 40 nm aluminum oxide nanoparticles (Al_2O_3 , SkySpring Nanomaterials, 99.0%) into the deionized water. The mixed nanofluids were first stirred for two hours and then put in an ultrasonic bath for half an hour before use. The silicon wafer (Bonda Technology Pte Ltd) was used as the substrate for the nanofluid sessile droplet drying. The volume of the droplet was set to be $4 \mu\text{L}$. As the height of the droplet is at around 0.6 mm, which is much smaller than

the capillary length (2.7 mm) of the water droplet, the gravitational effect is assumed to be negligible and the droplet is assumed to hold a spherical cap shape. The droplet drying was performed in an open controlled at $22 \pm 1^\circ\text{C}$ and the relative humidity was at $55 \pm 5\%$. A summary of the experimental conditions is listed in Table 4.1.

Table 4.1. A summary of the experimental conditions

Solution type	Concentration (g/L)	Volume (μL)	Substrate	Environmental condition	Pressure condition (mmHg)
Aluminum oxide (40 nm) nanofluid	2.0, 3.0, 4.0, 5.0	4	Silicon wafer	Temperature: $22 \pm 1^\circ\text{C}$ Humidity: $55 \pm 5\%$	0

The dried patterns were captured with the optical microscope (Leica Nikon Eclipse LV100ND) and scanned by the 3D profiler confocal microscope (DCM8, Leica Microsystems). The processes are shown in Figure 4.2. The measured patterns were further processed with MATLAB code for statistical calculations.

Figure 4.2. Schematics of the experimental process.

4.3. Results and discussion

Compared with the 5 nm nanoparticles used in **Chapter 3**, the nanoparticles here have a much larger size (40 nm). At the same particle concentration, the total number of nanoparticles is much smaller than that of 5 nm nanoparticles, then lesser nanoparticles could reach the contact line, which provides a much weak self-pinning effect. The nanofluid droplet was observed to evaporate with a receding contact line and the dendritic structures were formed in the nanofluid droplet drying. Figure 4.3 (a1-a6), as one example, gives the snapshots of the drying nanofluid droplet with the particle concentration at 5.0 g/L. The evaporation begins with slowly receding stage, followed by the continuous dewetting drying with branches forming. As shown in Figure 4.3 (a3), small branches are found to form after the retreating line. As the evaporation goes on, more particles are collected by the dewetting front, accordingly, the local pinning effect would be strengthened. The retraction of the contact line slows down, making it unable to counteract the liquid loss there (see Figure 4.3 (a5)). An outward capillary flow is then induced, and transports particles to aggregate near the sessile droplet edge. Therefore, the pinning effect of the contact line is further enhanced, leading to the formation of a central void core eventually. The detailed drying process of the nanofluid droplet, shown in Figure 4.3 (a1-a6). In addition, a close view observation of the 2.0 g/L droplet is provided in Figure 4.3 (b1-b3)), focusing on the growing of branches and the collection of particles near the contact line. With the retreating of the edge, particles are found to be collected by the wetting front and merge into branches. The inset image in Figure 4.3 (b3) demonstrates a local accumulation of particles under the collective effect.

Figure 4.3. Experimental drying process of the nanofluid droplet with the particle concentration is 5.0 g/L. The normalized evaporation time are (a) 0%, (b) 30%, (c) 54%, (d) 73%, (e) 92%, (f) 100%. The red scale bar indicates 1 mm. (b1-b3) The growth of branches and collection of particles near the wetting front with the particle concentration at 2.0 g/L. The yellow scale bar indicates 0.4 mm.

The formation of the dendritic structures from a drying nanofluid sessile droplet in the 3D KMC simulation and experiment is of interest in the present study. Figure 4.4 shows a detailed investigation of the whole formation process. The simulation starts from a configuration mimicking a droplet with a spherical cap (see Figure 4.4 (a)). Different from the numerical model in **Chapter 3**, this spherical cap domain of the drying droplet is not confined to hold a pinned edge. There are no circular conditions for the three-phase contact line, where the drying behaviour obeys the same energy equation (see Eq. (4.1)). The particle motion is assumed to be random and uniform in all directions and there are no significant capillary outflow and recirculating Marangoni flow in the unpinned case. The approximation is acknowledged to low evaporation case of the

sessile nanofluid droplet on the substrate under the open conditions. As the evaporation progresses, the droplet starts to shrink, and the retracting contact line leaves some particles behind to deposit into the shape of separated islands or branches (see Figure 4.4 (b-c)). The contact line movement starts to slow down subsequently, and the shape becomes increasingly ramified (see Figure 4.4 (d-e)). In the later stages, the fingers continue to extend slowly towards the domain center, and their thickness increases as well along the way, as illustrated in Figure 4.4 (f-g). Finally, the evaporation process halts completely, and a ramified patch is formed from the particles around the geometrical center of the domain (see Figure 4.4 (h-i)). The final shape of the dendritic structure in Figure 4.4 (i) very well resembles the experimentally observed dried branched structure formed from an evaporated unpinned sessile nanofluid droplet [137].

Figure 4.4. Progression chart of a single simulation run. Images of isometric view are captured every 350 MCS from (a) 0 MCS till (i) 2800 MCS. Parameter values: $\phi = 0.6\%$, $N_m = 5$, $\varepsilon_{nn} = 2.0$, $\varepsilon_{ns} = 1.5$, $\varepsilon_{ls} = 1$, $\mu = -3.3$, $kT = 0.2$, $D = 500$. (j) The top view of the simulated pattern at 2800 MCS. (k) The branched pattern left by a dewetting drying droplet, recalculated using the 2D model from Crivoi et al. [137]. The dashed circle line marks the initial boundary of the droplet.

Here we also provide a comparison between the 3D simulated pattern with the previously reported 2D case. Figure 4.4 (j) is the top view of the final dried pattern at 3000 MCS. A large gap exists between the initial boundary of the droplet and the branched deposits, which indicates an obvious effect of particle collection by the retreating contact line. These collected particles are found to accumulate into a solid core at the center. For the corresponding 2D approach as shown in Figure 4.4 (k), the effect of particle collection is weaker. Particles are only allowed to move within a one-layer domain and are also confined by the presence of nearby particles, as they cannot overlap with each other. As the wetting front retreats, particles may deposit behind into branched structures or be collected within the inner liquid phase. With high calculation steps, the branches grow from the initial boundary to the very central region without forming the solid core. While in a 3D approach, the particles distribute and move in a 3D spherical cap domain. With the evaporation of the droplet, particles not only accumulate with the receding of the contact line but also with the descending of the liquid-vapor interface. As a result, in a 3D case, particles can deposit into a thick core under a relatively low concentration (0.6%) as compared with the thin core in the 2D case with a high concentration (20%). The 3D model can more practically reflect the nanofluid droplet drying with the receding of the contact line.

We have carried parameter studies to investigate the influence of different parameters on the final particle deposition patterns. As shown in Figure 4.5, the effect of particle concentration and particle mobility has been investigated. The blue arrows mark the increasing variation trend of the corresponding parameter. The finishing point has been chosen at 3000 MCS since either all the solvent fully dries or the evaporation process halts significantly by that time. It is assumed that the particle structures at this moment resemble the structures left after the visible drying of the sessile nanofluid droplet. All

the patterns in Figure 4.5 express some degree of branching but the extent strongly depends on the parameters. With an increase in the particle concentration, ϕ , the highly branched fingers become wider and thicker, along with the formation of a solid central core. Upon increasing the mobility of particles, N_m , particles are found to aggregate into more compact structures with fewer branches, as shown by the variation of patterns from Figure 4.5 (a1-a4) to (b1-b4) and (c1-c4). An enlargement of the solid central core can also be observed. This could be explained by the assumption that as the particles become more mobile, they are more easily to travel long distance and to be pulled inward by the retreating contact line.

Figure 4.5. Morphology of final particle deposition patterns under different particle concentration, ϕ , and particle mobility, N_m , after 3000 MCSs. The blue arrow marks the increasing trend of the corresponding parameter. The varying parameter values are: (a1-c1) $\phi = 0.2\%$, (a2-c2) $\phi = 0.4\%$, (a3-c3) $\phi = 0.6\%$, (a4-c4) $\phi = 0.8\%$; (a1-a4) $N_m = 2$, (b1-b4) $N_m = 5$, (c1-c4) $N_m = 10$. The other parameters are: $\mu = -3.3$, $\varepsilon_m = 2.0$, $\varepsilon_{nl} = 1.5$, $\varepsilon_{ns} = 1.5$, $\varepsilon_{ls} = 1.0$.

The second series of parameter study includes the effect of chemical potential, μ , and particle-particle interaction, ε_{nn} , as shown in Figure 4.6. The dependence of branching on μ is found to be in agreement with the behaviour observed in 2D KMC models [130, 134, 137]. It is known that a higher absolute value of μ in the KMC model leads to a faster solvent drying, making it more easily for particles to be left over from the retreating drying front and deposit into more branches behind [130], as shown in Figure 4.6 (a1-a4). Figure 4.6 (a1-c1) indicates that an increase in the particle-particle interaction ε_{nn} brings a similar variation trend of deposits with more and thinner branches. This is because when ε_{nn} is high, it would be easy for particles to aggregate together, which makes the particles less mobile and also easy to be stuck by other

Figure 4.6. Morphology of final particle deposition patterns under different chemical potential, μ , and particle-particle interaction, ε_{nn} , after 3000 MCSs. The blue arrow marks the increasing trend of the corresponding parameter. The varying parameter values are: (a1-c1) $\mu = -3.2$, (a2-c2) $\mu = -3.3$, (a3-c3) $\mu = -3.4$, (a4-c4) $\mu = -3.5$; (a1-a4) $\varepsilon_{nn} = 1.8$, (b1-b4) $\varepsilon_{nn} = 1.9$, (c1-c4) $\varepsilon_{nn} = 2.0$. The other parameters are: $\phi = 0.6\%$, $N_m = 5$, $\varepsilon_{nl} = 1.5$, $\varepsilon_{ns} = 1.5$, $\varepsilon_{ls} = 1.0$.

particle aggregates. Overall, the parameter study results show that the 3D model of the branching structures agrees well with the trends observed in the 2D results, and thus can be considered a natural extension of the previously developed versions [129, 134, 137].

With the present 3D model, we now can explore the substrate effect on the final particle deposition patterns. The results are shown in Figure 4.7, where 3D height profiles of the patterns have been provided. The blue arrows mark the increasing variation trend of the corresponding parameter. A small second layer particle deposition is found to exist in Figure 4.7 (e2, f2), with a low particle-substrate interaction $\varepsilon_{ns} = 1.5$ and high particle concentration $\phi = 1.0\%$. Upon increasing ε_{ns} , the second layer disappears and more branches are formed, as shown in Figure 4.7 (g2, h2). This is because particles now become easily sticking onto the substrate, which restricts the collection of particles by the dewetting front. More branches would then form with particles not enough to aggregate into a second layer. It is reported that substrate tends to remain wet for large values of ε_{ls} [135], which leads to a slow dewetting contact line. Particles would then have enough time to move within the liquid phase and deposit into central core and fewer branches, as shown by the comparison from Figure 4.7 (a1-a2, b1-b2) to (e1-e2, f1-f2).

Here we provide a qualitatively comparison between the experimental patterns and the numerical ones in Figure 4.8. Both the top view 2D images and the corresponding 3D patterns are listed in Figure 4.8. For the experimental results listed in Figure 4.8 (a1-a4) and (b1-b4), small branches are found to form near the contact line. While going inside the deposition region, small branches merge into large ones. Upon increasing the particle concentration, branches are found to become thicker and a central core is found to form at high particle concentration. Similar trend could also be observed in the numerical

patterns, as shown in Figure 4.8 (c1-c4) and (d1-d4). Branches become thicker upon either approaching the center region or increasing the particle concentration. At high particle concentration, both experimental and simulated patterns consist of a ramified “core” and multiple thinner branches extending to the periphery.

Figure 4.7. Substrate effect on particle deposition patterns. The black arrows show how the liquid-substrate interaction ε_{ls} or particle-substrate interaction ε_{ns} change between different groups. (a1-a2), (c1-c2), (e1-e2), and (g1-g2) are the isometric view of the particle structure. (b1-b2), (d1-d2), (f1-f2), and (h1-h2) are the corresponding 3D scaled height profile H_{ave}/R , where R is the radius of the droplet contact line. (a1-a2, b1-b2) $\varepsilon_{ls} = 0.8$, $\varepsilon_{ns} = 1.5$; (c1-c2, d1-d2) $\varepsilon_{ls} = 0.8$, $\varepsilon_{ns} = 10$; (e1-e2, f1-f2) $\varepsilon_{ls} = 1.0$, $\varepsilon_{ns} = 1.5$; (g1-g2, h1-h2) $\varepsilon_{ls} = 1.0$, $\varepsilon_{ns} = 10$. (a1-h1) $\phi = 0.4\%$, (a2-h2) $\phi = 1.0\%$. $N_m = 10$, $\varepsilon_{nm} = 2.0$, $\varepsilon_{nl} = 1.5$, $\mu = -3.3$.

Figure 4.8. Comparison between the experimental and numerical patterns under different particle concentrations. (a1-a4) are the experimental results from top view and (b1-b4) are the corresponding 3D height profile from isometric view. The red bar indicates a length of 0.5 mm. The particle concentrations are: (a1, b1) 2.0 g/L; (a2, b2) 3.0 g/L; (a3, b3) 4.0 g/L; (a4, b4) 5.0 g/L. (c1-c4) are the numerical results from top view and (d1-d4) are the corresponding 3D height profile from isometric view. The particle concentrations are: (c1, d1) 0.2%; (c2, d2) 0.4%; (c3, d3) 0.6%; (c4, d4) 0.8%. $N_m = 5$, $\varepsilon_{nn} = 2.0$, $\varepsilon_{nl} = 1.5$, $\varepsilon_{ns} = 1.5$, $\varepsilon_{ls} = 1.0$, $\mu = -3.3$.

We have measured the height profiles of the experimental and numerical results at the 80% radius position ($0.8R$), as shown in Figure 4.9. An overall tendency could be observed that as the particle concentration increases, the branches rise both in number and in width.

Figure 4.9. Experimental and numerical height profiles (H/R) measured from 80% radius ($0.8R$). R is the radius of the droplet contact line. (a) Experimental results at 2.0 g/L, 3.0 g/L, 4.0 g/L, 5.0 g/L; (b) Simulation results at 0.2%, 0.4%, 0.6%, 0.8%.

Based on the height profiles, we have counted the number of branched structures at various radius positions (from $r = 0.05$ to $r = 0.85$), as shown in Figure 4.10 (a-d). The similar rising and agreeable trend of the branch numbers are observed in the experimental results and the simulated ones. With the particle concentration increasing, the number of branches goes higher near the edge, indicating that more branches are formed there, and the number of lines become flattened near the center, indicating the emergence of a core structure. The branch numbers as a function of particle concentration are plotted in Figure 4.10 (e). It is obtained from 3 repeated dried patterns and counted based on the pattern profile at 85% radius position ($r = 0.85$), as indicated in the inset of Figure 4.10 (e). The small error bars show good repeatability of the formed branches in the same concentration work fluids under the carefully prepared experiments. In addition, it should be noted here that there exist void areas at the central core region of experimental patterns, which can be seen from the 3D profiles in Figure 4.10 (b3-b4). This is because when the particle concentration is high, as more particles

are collected by the dewetting front, the pinning effect strengthens gradually. Then the retracting of contact line slows down, and could not counteract the loss of liquid there, which induces a capillary outflow. As a result, particles are carried to aggregate at the wetting line, forming a central void core.

Figure 4.10. Comparison of branch numbers (N) and repeatability of the experimental results. (a-d) The branch numbers at different radius positions. The particle concentrations in the experiment and simulation are: (a) 2.0 g/L, 0.2%; (b) 3.0 g/L, 0.4%; (c) 4.0 g/L, 0.6%; (d) 5.0 g/L, 0.8%. (e) The variation of branch number under a certain particle concentration in the experiment. The branch number is counted based on the pattern profile at 85% radius position, which is marked by the red circle as shown in the inset.

We have to notice the main limitation of present model on the scaling effect: while the original 3D KMC has been introduced to study the drying thin films [132, 135] with an assumed nanoscale thickness, the vertical dimension of a small sessile droplet with 1.0 mm base diameter is in a microscale. Therefore, more accurate representation of a sessile droplet with a realistic number of particles in the system would require a much larger domain than the 500-base one used in the present work. However, recalling the fact that the branched patterns have a fractal-like structure and thus exhibit statistical self-similarity [129, 137] and the domain size and model parameters are non-dimensional, allows assuming that small-scale simulations produce the variety of results qualitatively

similar to the virtual large-scale simulations which are out of reach with a given computational power. This hypothesis has also been analysed in the 2D parameter study with a varied domain size [137]. Another assumptions are that the particles are evenly distributed without agglomeration in clusters inside the liquid [144, 145], and the assumed lack of contact line pinning does not produce the strong outward flow inside the droplet [161]. However, considering the void areas existing in the experimental patterns, an improvement on the model would be needed in the future to reveal this phenomenon.

4.4. Summary

The study of this chapter was stressed on the dewetting collected particle aggregation. The experimental results demonstrate the formation of dendritic particle deposition after the liquid phase of unpinned sessile nanofluid droplets is fully evaporated. A 3D KMC approach has been applied to investigate the drying mechanisms. It is found that the dendritic structures are formed by particle merging in the receding front. The dried-in particle assemblies exhibit the dendritic patterns connecting the sprawling branches with a central core structure. The model owned a clear advantage over the reported 2D approaches, it provided a fully realistic view of the dendritic nanoparticle self-assembling process. A detailed analysis was also done to investigate the dependence of deposition patterns on the particle concentration, the particle-particle interaction, the diffusive mobility, and the chemical potential. With the 3D model, the effects of substrate on the pattern formation were studied. The numerical model reproduced the patterns agreeable to the experimental ones, and a similar variation trend was observed upon increasing the particle concentration. If the droplet solution contains dissolved materials instead of suspended particles, precipitation could occur with the solutes

enriching during the drying process. In the following chapter, the interaction between droplet wetting, evaporation, and precipitation would be investigated.

Chapter 5. Wetting and drying characteristics of saline droplet on flat surfaces

5.1. Introduction

The evaporation and deposition characteristics of a colloidal droplet are closely related to its wetting morphologies on the surface. For some materials, with their dissolved solutes enriches in the solution during the drying process, a precipitation process could be initiated. Crystallization of this kind of material, like salts in supersaturated solutions, has applications in various fields like the purification of seawater, surface coating, biochip manufacturing, deicing, inkjet printing, and so on. Understanding the role of droplet evaporation in modulating precipitation and the opposite effect of precipitation in varying evaporation could provide deep insights into the crystallization process. In this chapter, experiments have been conducted to investigate the dynamics of evaporation and precipitation of sessile saline droplets on various substrates or with surfactant additives.

5.2. Effect of different surface properties¹

5.2.1. Experiment setup

The various saline solutions were prepared by dissolving sodium chloride (NaCl, Sigma-Aldrich, > 99%) in the deionized water (18.2 MΩ-cm), with the initial concentrations, C_{salt} , at 0%, 2.5%, 5%, 10%, 20% and 25%. The saturated concentration of NaCl is at roughly $C_{\text{sat}} = 26.4\%$ [162]. The droplet was placed on the substrate using a

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micropipette with the volume controlled at 2 μL . The experiment was carried out in an open condition with the ambient temperature and relative humidity controlled at 22 ± 1 $^{\circ}\text{C}$ and $55 \pm 5\%$. Three kinds of evaporation substrates were used in this study: brand new silicon wafers (Latech), soda lime glass (Latech), and PMMA (POLY-A, cast acrylic sheet). A summary of the experimental conditions is listed in Table 5.1.

Table 5.1. A summary of the experimental conditions

Solution type	Concentration (%)	Volume (μL)	Substrate	Environmental condition	Pressure condition (mmHg)
Sodium chloride solution	0, 2.5, 5, 10, 20, 25	2	Silicon wafer Soda lime glass PMMA	Temperature: 22 ± 1 $^{\circ}\text{C}$ Humidity: 55 ± 5 %	0

The substrates were thoroughly cleaned using ultrasonication and plenty of deionized water before using. To reflect the wettability of these three surfaces, the surface roughness and the contact angle of the water droplet are measured and listed in Table 5.2. On these three surfaces, as the height of the droplets are all smaller than 0.8 mm, which is much smaller than the capillary length (2.7 mm) of the water droplet and the capillary length (2.6 mm) of the NaCl droplet (20%), the gravitational effect is assumed to be negligible and the droplet is assumed to hold a spherical cap shape.

Table 5.2. The wettability of the substrates shown by the averaged surface roughness and the contact angle of water droplet.

	Silicon wafer	PMMA	Soda lime glass
Roughness (μm)	0.1	0.05	0.2
Contact angle ($^{\circ}$)	39.6	67.0	20.1

As shown in Figure 5.1, the drying process of the saline droplet was recorded from both its top and side view simultaneously. The Nikon Eclipse LV100ND microscope was

used to give a top view recording while the HiSpec 2 high-speed camera was used to capture the droplet's side profile. After the experiment was done, an open-source software ImageJ was used to extract the contact angle and base diameter of the droplet[163]. As the droplet evaporated, the salt solutes kept enriching in the solution with the loss of water. A crystallization could be initiated after the droplet reached a supersaturation state. During the evaporation process, the instant salt concentration is denoted by $C_{\text{salt}}(t)$, the supersaturation degree at the onset of crystallization is estimated by $S = C_{\text{salt}}(t) / C_{\text{sat}}$. The moment when the crystallization started was called the “precipitation time” and is denoted by t_p . The moment when the salt concentration $C_{\text{salt}}(t)$ reaches C_{sat} was called the “predicted precipitation time” and is denoted by $t_{p'}$. Both of these two times are normalized to the lifetime of the droplet. As the crystals grew, the liquid-vapor interface could be deformed, making the spherical cap shape of the droplet no longer valid. However, to provide a full spectrum of the evaporation process, the contact angle and base diameter are measured and plotted both before and after the crystallization point. The error bars plotted in some figures were calculated from the standard deviations of the repeated cases under the same experimental condition.

Figure 5.1. Schematics of the experimental setup. The recording is performed from both the top view and side view simultaneously.

5.2.2. Results and discussion

The evaporation characteristics and the precipitation patterns of the saline droplets are investigated on the various substrates with different properties of surface wettability and roughness. The typical drying processes of the saline droplets at $C_{\text{salt}} = 10\%$ on the three substrates are shown in Figure 5.2, with the snapshots captured from both side view and top view. From the smallest thickness and largest base diameter of the droplet on the soda lime glass (see Figure 5.2 (c)), it can be concluded that this glass surface has a higher wettability than the other two. In addition, the droplet evaporates in different regimes on the different substrates. On the soda lime glass, the droplet dries in a pinned regime for most of its lifetime, whereas an obvious depinning regime exists in the drying process of the droplet on the PMMA substrate and the silicon wafer. The evaporation time of the saline droplet with C_{salt} at 10% are at around 60.7 min on the PMMA, 32.1

Figure 5.2. Drying sequences of the saline droplets with C_{salt} at 10% on the (a) silicon wafer, (b) PMMA substrate, and (c) soda lime glass. The red scale bar indicates 1 mm.

min on the silicon wafer, and 14.9 min on the soda lime glass. The droplets would evaporate more rapidly with a longer pinning stage and a larger wetting area.

After the evaporation process is completed, various crystallization patterns would form. Three series of deposits are listed in Figure 5.3 on the three substrates with C_{salt} ranging from 2.5% to 25%. As shown in Figure 5.3 (a, b), the crystallization patterns are quite similar on the PMMA surface and the silicon wafer, with either one or more cubic crystals formed with jagged edges, regardless of the various C_{salt} . The main difference is that the crystals are larger at a higher salt concentration. However, on the soda lime glass, the droplets deposit into a circular pattern which covers almost the entire initial wetting area of the droplet. It is composed of isolated cubic crystals and a thin layer of cracked crystallines. The above general view shows that the salt stains are similar on the silicon wafer and the PMMA substrate but are different from those on the soda lime glass. In the following two subsections, the study would be stressed on the detailed drying characteristics of the saline droplets on the PMMA and silicon wafer, and on the soda lime glass respectively. In the last subsection, a comparison has been carried out to investigate the motion and morphologies of crystalline on various substrates.

Figure 5.3. Crystalline patterns left by droplets with different C_{salt} on the (a) silicon wafer, (b) PMMA substrate, and (c) soda lime glass. The red scale bar indicates 1 mm.

5.2.2.1. Saline droplet evaporation on silicon wafer and PMMA plate

Figure 5.4 (a1, a2) plots the evolutions of the droplet contact angle and base diameter on the silicon wafer. Regardless of the various C_{salt} , the saline droplets first evaporate with the contact line pinned, demonstrated by the constant base diameter. Then the droplets go into a depinning drying stage. For C_{salt} from 2.5% to 20%, this depinning stage starts with a relatively long period of rising contact angle, followed by a redeclining period of contact angle till the end of drying. A continuous decrease of the base diameter can be observed during the depinning stage, which reducing slope becomes flattened at a higher salt concentration (see Figure 5.4 (a2)). Once the contact

Figure 5.4. Evolution of (a1) Contact angle and (a2) base diameter with time for droplets at various C_{salt} on silicon wafer. Evolution of (b1) Contact angle and (b2) base diameter with time for droplets at various C_{salt} on PMMA plate.

angle enters the redeclining stage, the droplet base diameter decreases more rapidly, corresponding to the final fast drying phase. For C_{salt} at 25%, the droplet undergoes a long period of pinned drying, which covers approximately 70% of its lifetime. The contact angle is observed to decrease all the time which slope becomes flattened with time. The evaporation dynamics of the droplets on the PMMA substrate is shown in Figure 5.4 (b1,b2), which show fairly similar evaporation characteristics but with a longer period of drying. The enlargement of the contact angle can be observed at different C_{salt} , together with the steep declining trend of the base diameter.

As the salt enriches in the droplet solution during the evaporation process, an enlargement of the contact angle has been observed in the middle of drying, which reflects the role of salt in changing the evaporative dynamics. A quantitative analysis on the contact angle increment is shown in Figure 5.5, where the increment $\Delta\theta$ and the corresponding increasing rate are plotted with C_{salt} on the PMMA substrate and the silicon wafer. The inset of Figure 5.5 (a) illustrates how $\Delta\theta$ and k_θ are obtained from

Figure 5.5. (a) Contact angle increment $\Delta\theta$ and (b) increasing rate of dynamic contact angle k_θ at various C_{salt} on silicon wafer and PMMA plates. The inset of (a) illustrates how $\Delta\theta$ and k_θ are calculated from the contact angle curve of the droplet with C_{salt} at 2.5% on silicon wafer.

the data, where $\Delta\theta$ is the largest increment of the contact angle and k_θ is the slope of the best-fitting linear line. In Figure 5.5 (a), a monotonous decreasing trend of $\Delta\theta$ and k_θ can be observed with the increase of C_{salt} , which indicates that a droplet with a higher initial C_{salt} is closer to its equilibrium state.

The retreating of the droplet contact line during the evaporation process can be explained by the contact line force F_c , which is generated by the deviation between the instant dynamic contact angle θ and the corresponding equilibrium contact angle $\theta_E(t)$. Based on the Young equation (see Eq. 2.1), F_c can be expressed as

$$F_c = \gamma_{\text{LV}}(\cos \theta - \cos \theta_E(t)) \quad (5.1)$$

where $\theta_E(t)$ is the equilibrium contact angle of the droplet under the ideal wetting condition. It is closely related to the instant salt concentration $C_{\text{salt}}(t)$ and can be normally reflected by the initial contact angle of the droplet under the same value of $C_{\text{salt}}(t)$ in the actual cases. The values of the initial contact angle θ_0 at different C_{salt} are listed in Table 5.3, which shows a larger θ_0 at a higher C_{salt} . Then a rising equilibrium contact angle $\theta_E(t)$ can be expected during the evaporation process with the concentrating of salt in the solution. What's more, as Figure 5.4 (a1, b1) shows that the dynamic contact angle keeps reducing during the initial pinned drying period. Then it can be concluded that $(\cos \theta - \cos \theta_E(t))$ increases with time. As the liquid-vapor surface tension γ_{LV} is larger at a higher C_{salt} , the contact force is further enhanced, which could pull the contact line inward, initiating the depinning drying stage and the resultant contact angle increment.

Table 5.3. Initial contact angle θ_0 at various C_{salt} of droplets on silicon wafer (S) and PMMA (P).

C_{salt} %	θ_0 (S)	θ_0 (P)
0	39.6	67.0
2.5	40.8	67.9
5	40.6	74.0
10	44.3	74.1
20	43.8	74.7
25	48.2	76.4

As the droplet evaporates, the saline solution reaches the supersaturation state gradually, which may initiate the crystallization process. Once the crystal occurs in the solution, the rising of salt concentration and the increment of θ would be both terminated. It could be concluded from Figure 5.5 that the intensified enlargement of the contact angle at a low C_{salt} is resulting from the large gap that exists from the initial wetting state to the moment of salt precipitation. In order to confirm this, a quantitative analysis has been performed on the normalized time t_{apex} when θ reaches its apex and the normalized time t_p when the precipitation starts, as shown in Figure 5.6. There also plots the normalized predicted precipitation time, t_p' , corresponding to the moment when the droplet solution reaches its supersaturation concentration C_{sat} . All times are normalized to the droplet lifetime. As the Bond number in this study is smaller than 1, the droplets are assumed to hold a spherical cap shape. As a result, the instantaneous volume V_t of the droplets during evaporation can be calculated by [108]

$$V_t = \frac{\pi r^3}{3} \left(\frac{2 - 3 \cos \theta + \cos^3 \theta}{\sin^3 \theta} \right) \quad (5.2)$$

where r is the instantaneous radius of the droplet and θ is the dynamic contact angle.

With the above equation, the volume of the droplet when $C_{\text{salt}}(t)$ reaches C_{sat} can be obtained, corresponding to the predicted precipitation time, t_p .

Figure 5.6. Normalized precipitation time t_p , normalized predicted precipitation time $t_{p'}$, and normalized time at contact angle apex t_{apex} of the droplet at various C_{salt} on the (a) silicon wafer and (b) PMMA plate. The supersaturation degrees S of the droplets are plotted with C_{salt} in the two insets on the (a) silicon wafer and (b) PMMA plate, respectively.

It can be observed from Figure 5.6 that the time t_{apex} when the contact angle reaches its apex is quite close to the moment t_p when the precipitation occurs for both surfaces. Compared with t_p , the smaller value of the predicted precipitation time, $t_{p'}$, indicates that the droplet solution is in a supersaturation state before the precipitation process. The supersaturation degree S for droplets under different initial C_{salt} has been plotted in the insets of Figure 5.6 (a) and (b) for the silicon wafer and PMMA substrate, respectively. A general upward trend of S with the increase of C_{salt} can be observed, indicating with more salts in the solution, the drying droplet needs to reach a higher supersaturation state so as to initiate the precipitation process. This delay of precipitation at a high initial

C_{salt} could be explained by the nonuniformly distributed salt ions within the droplet region.

To reveal the mechanisms that lead to the non-uniform distribution of ions, Peclet number Pe is introduced here which estimates the importance of advection versus diffusion in the ions transportation. Pe is expressed by $Pe = Ur / D_i$, where U is the velocity of the typical flow inside the droplet and D_i is the diffusion coefficient of Na^+ .

U is calculated by

$$U = \frac{J}{A(t)} \quad (5.3)$$

where J is the evaporation flux and $A(t)$ is the area of the spherical cap. The evaporation flux J is expressed as

$$J = \frac{-dV}{dt} \quad (5.4)$$

D_i for Na^+ can be estimated by [105]

$$D_{\text{Na}^+} = -0.1097 \times 10^{-9} m(t) + 1.324 \times 10^{-9} \quad (5.5)$$

where $m(t)$ is the instant concentration of salt ions. During the evaporation process before crystals occur, the concentration $m(t)$ may increase up to 10 M [105], leading to a variation of the solution viscosity and the diffusion coefficient. As shown in Figure 5.7, Pe is smaller than 1 on both the PMMA substrate and the silicon wafer, indicating that diffusion dominates over convection in transporting salt ions, which results in a relatively homogeneous distribution of ions in the droplet solution. The insets in Figure 5.7 (a, b) plot Pe at different evaporation time of the droplet with various initial C_{salt} .

The increase of Pe with time reveals that the convection effect on ions transportation becomes stronger during the evaporation process.

Figure 5.7. Peclet number Pe of the droplets at different C_{salt} on (a) silicon wafer and (b) PMMA plates. The insets show the value of Pe at 0, 420, and 780 s with different C_{salt} .

Based on the fact that the precipitation is always observed to occur near the edge of the droplet, the local salt concentration there should be higher than anywhere else. This indicates that though Pe is smaller than 1 for most of the droplet lifetime at various C_{salt} , a non-uniform distribution of ions is also generated and Pe can be used to value the heterogeneity of ions distribution. The smallest value of Pe at 25% of C_{salt} then suggests the weakest accumulation of ions at the droplet periphery compared with the other salt concentrations. Due to the enhanced viscosity of the solution at a higher C_{salt} , both the diffusion and advection transportation effect would be attenuated. As a result, the distribution of ions in the droplet should be more uniform at a higher C_{salt} , partially accounting for the delayed precipitation process. Another possible reason may be the relatively stable wetting state of the droplet at a higher C_{salt} . For C_{salt} at 25%, the droplet undergoes a longer pinning drying stage on both surfaces. In contrast, the droplets with other C_{salt} (see Figure 5.4 (a2, b2)) evaporate in the intense and lasting depinning stage, which could act as a stimulus that breaks the stability of the droplet solution and hence initiate the crystallization process. Under a pinning state, however, the external stimulus

is quite limited as the diffusion effect dominates the ions transportation, helping the droplet to reach a higher supersaturation state.

5.2.2.2. Saline droplet evaporation on soda lime glass

The evaporation dynamics of the saline droplets on the soda lime glass are very different from what have been shown on the silicon wafer and the PMMA substrate. The evolutions of the droplet contact angle and base diameter are also plotted with time, as shown in Figure 5.8. An attenuated wettability of the droplet can be observed at a higher salt concentration C_{salt} with a higher contact angle and a smaller wetting area. The droplet is found to evaporate in a pinned mode for nearly its entire lifetime. The contact angle keeps decreasing during the drying period while the base diameter remains constant until the ultimate plunging happens.

Figure 5.8. Evolution of (a) Contact angle and (b) base diameter with time for droplets at various C_{salt} on soda lime glass.

As there are no depinning stages for the evaporating droplets on the soda lime glass, the time t_{apex} when the contact angle reaches the apex is equal to 0 s. Then the comparison is only carried out between the precipitation time t_p and the predicted one $t_{p'}$. As shown in Figure 5.9, the precipitation process takes place under a supersaturation state for all

C_{salt} . As demonstrated in the inset of Figure 5.9, the supersaturation degree S varies little with C_{salt} and stays in a range between 1.3 to 1.6, which indicates a relatively similar supersaturation degree when the precipitation occurs. As the contact line dynamics is greatly suppressed under the pinned drying condition, the disturbance from the droplet edge is quite weak. The precipitation process should be dominated by the diffusion or advection effect. To clarify the phenomenon, Pe is plotted with time for various C_{salt} in Figure 5.9 (b). As Pe varies within the small range between 0.2 and 0.3, the competence between diffusion and advection are about the same at different C_{salt} . As a result, the distribution of the salt ions inside the droplet solution should remain alike for various C_{salt} , resulting in a similar degree of supersaturation when precipitation occurs.

Figure 5.9. (a) Normalized precipitation time t_p and normalized predicted precipitation time t_p' of the droplet at various C_{salt} on soda lime glass. The inset shows the supersaturation degree S on soda lime glass, silicon wafer, and PMMA substrate. (b) Peclet number Pe of the droplets with various C_{salt} on soda lime glass. The inset shows the value of Pe at 0, 180, and 420 s.

The supersaturation degree on the soda lime glass is found to be evidently higher than that on the PMMA substrate and the silicon wafer, as shown in the inset of Figure 5.9 (a). The strong pinning effect of the droplet on the soda lime glass brings strong

advection flows, which leads to the preferred accumulation of salt solutes near the edge. The lifelong pinning wetting state of the drying droplet makes its evaporation process barely disturbed by the stimulus from the contact line. The lower supersaturation degree on the PMMA substrate and the silicon wafer indicates that the contact line dynamics play a key role in initiating the precipitation process.

5.2.2.3. Motion and morphologies of crystalline on various substrates

The various crystallization patterns as shown in Figure 5.3 indicate a strong dependence of the crystalline morphologies on the surface properties. The motion and morphologies of precipitation are found to be determined by two crucial factors: the surface wettability and the pinning effect. The typical growth features of crystals on the silicon wafer or the PMMA substrate are shown in Figure 5.10. Regardless of the various values of C_{salt} , the crystal first occurs near the contact line which then grows bigger to occupy the confined liquid meniscus near the droplet periphery [105]. Once the enlarging crystal deforms the liquid-vapor interface, a capillary force would be exerted on the crystal cube and push it inward. The lower wettability and the accompanying receding phase ensure a large thickness of the droplet which makes enough space for the growth of crystals. Under this inward motion of the crystals, the liquid-vapor interface is less likely to be greatly deformed, as shown by the snapshots captured from the side view of the droplet in Figure 5.11 (a), where there exists an inward moving cube inside the droplet region. The almost unobservable deformation of the liquid-vapor interface indicates that the capillary force exerted on the crystalline cube is quite weak. The reason for this minor interface deformation can also be explained by the smaller Pe (see Figure 5.7) as compared with that on the soda lime glass, which indicates a moderate accumulation of salt ions at the periphery. Therefore, the crystal growth near the droplet periphery on the silicon wafer and the PMMA substrate will be much slower than that on the soda lime

glass. And with the inward motion of the crystalline cube, it wouldn't deform the liquid-vapor interface greatly like the case shown in Figure 5.11 (b) on the soda lime glass.

Figure 5.10. Emerging of crystal cube and the inward motion near the contact line of droplet with C_{salt} at 10% on (a) silicon wafer and (b) PMMA plate. The scale bar indicates 0.5 mm.

Figure 5.11. Deformation of the liquid-vapor interface recorded from side view of droplets with C_{salt} at 25% on (a) silicon wafer and (b) soda lime glass. The scale bar indicates 1 mm.

The crystal growth on the soda lime glass is quite different from that on the previous two surfaces. On this substrate with a high C_{salt} , the large crystals are observed to occur and stay near the edge. Led by the high wettability of the soda lime glass, the precipitation develops fast within the thin liquid meniscus of the droplet, resulting in the greatly deformed liquid-vapor interface near the edge (see Figure 5.11 (b)). Under the strong pinning effect of the glass surface, the growing crystalline fails to be pushed inward. Therefore, the crystalline no longer restricts to grow within the bulk solution. It

can be concluded that droplet wettability is crucial for the crystalline growth and the possible motion.

As the droplets on the soda lime glass hold similar lifelong pinning and a similar degree of supersaturation, the one with a high C_{salt} would have a larger droplet thickness at the moment of precipitation, as shown in Figure 5.12 (a) by the corresponding larger contact angle. The typical growth features of crystalline are shown in Figure 5.12 (b, c), with the precipitation process presented at 2.5% and 25% of C_{salt} . For C_{salt} at 2.5%, the droplet is quite thin at the onset of precipitation (see Figure 5.12 (a)). A branchlike crystalline occurs initially with a simultaneous shrinkage of the droplet solution toward the central wetted area. Several separated cubes are observed to form near the edge of the irregular solution while cracked salt stains cover almost the whole wetted area. For C_{salt} at 25%, once the crystallization begins, the relatively larger thickness of the droplet provides a larger space for crystals to grow (see Figure 5.13 (a)). A crystalline cube is observed to emerge and grow bigger near the edge, followed by the formation of thin layers of salt at the very late stage. Once the crystallization starts, the salt concentration of the adjacent region is reduced abruptly, which would establish a local concentration gradient of the salt ions and thus induce an advective flow to replenish the consumption of salt solutes. As the liquid thickness of the local meniscus dominates the liquid supply from the nearby region to the site of crystallization. The thicker the droplet thickness, the faster the ions supply. Therefore, the crystals can grow quite large for C_{salt} at 25%. While the branchlike growth of crystalline is observed for C_{salt} at 2.5%, mainly due to the limited solutes supply under a small droplet thickness. The above analysis shows that on the soda lime glass the droplet thickness is a critical factor not only affects the emerging site of precipitation but also determines the growth path of crystalline.

Figure 5.12. (a) Contact angle θ_p of the droplet at the precipitation time t_p with different C_{salt} . Formation of crystalline pattern from the droplet with C_{salt} at (b) 2.5% and (c) 25% on soda lime glass. The scale bar indicates 1 mm.

5.3. Effect of surfactant additive

5.3.1. Experiment setup

The various surfactant saline solutions were prepared by dissolving sodium chloride (NaCl; Sigma-Aldrich, $\geq 99\%$) salt and Cetyltrimethylammonium Bromide (CTAB; Sigma-Aldrich, $\geq 99\%$) powder into deionized water with resistivity at $18.2 \text{ M}\Omega \text{ cm}$. Two series of samples used in this study, as listed in Table 5.4.

Table 5.4. Concentration of the surfactant saline solution

Serie 1					
NaCl	10%				
CTAB	0 mM	0.01 mM	0.04 mM	0.2 mM	0.8 mM
Serie 2					
NaCl	0%	1%	5%	10%	15%
CTAB	0.8 mM				

The concentration of NaCl, C_{salt} , is expressed in mass concentration but the concentration for CTAB, C_{surf} , is expressed in molar concentration. The droplet was placed on a new silicon wafer with a micropipette. Droplet volume was controlled at $0.16 \pm 0.02 \mu\text{L}$. As the height of the droplet is smaller than 0.3 mm, which is much smaller than the capillary length (2.7 mm) of the water droplet and the capillary length (around 1.8 mm) of the surfactant saline droplet (15% NaCl 0.8 mM CTAB), the gravitational effect is assumed to be negligible and the droplet is assumed to hold a spherical cap shape. The recording setup was the same as the one in Section 5.2. Three repeated experiments were carried out for each sample to ensure the results were consistent. After the experiment was done, an open-source software ImageJ was used to measure the contact angle and diameter of the droplet. The experiment was carried in an open condition with the ambient temperature and relative humidity controlled at $22 \pm 1^\circ\text{C}$ and $45 \pm 5\%$. A summary of the experimental conditions is listed in Table 5.5.

Table 5.5. A summary of the experimental conditions

Solution type	Volume (μL)	Substrate	Environmental condition	Pressure condition (mmHg)
Surfactant saline solution	0.16 ± 0.02	Silicon wafer Soda lime glass PMMA	Temperature: $22 \pm 1^\circ\text{C}$ Humidity: $45 \pm 5\%$	0

5.3.2. Results and discussion

The evaporation dynamics and crystallization patterns of surfactant saline droplets are investigated under different CTAB and salt concentrations. As shown in Figure 5.13, snapshots have been taken from the top and side view of the drying droplet to provide a general view of the drying sequences. Based on the drying and crystallization dynamics, the sequences are divided into three stages: pinning, depinning, and crystallization. It can be seen that the droplets form a spherical cap shape on the flat silicon wafer. An initial pinning drying stage can be observed in all cases. For pure saline droplet as shown

Figure 5.13. Drying sequences of the various surfactant saline droplets. (a) 10% NaCl 0 mM CTAB, (b) 10% NaCl 0.04 mM, (c) 10% NaCl 0.8 mM, (d) 1% NaCl 0.8 mM. The red scale bar indicates 0.4 mm.

in Figure 5.13 (a), the droplet experiences a depinning stage until the crystal occurs. While under dilute surfactant concentration as shown in Figure 5.13 (b), the droplet is found to repin for a short period before the final crystallization stage. For saline droplets with high surfactant concentration, as shown in Figure 5.13 (c) and (d), droplets keep pinned all the time.

Various crystalline morphologies form after the evaporation ends. Two series of deposits are listed in Figure 5.14 with the variation of NaCl and CTAB concentration separately. As shown in Figure 5.14 (a1), a single large crystal is left by the pure saline droplet. With the presence of dilute surfactant, several small crystals prefer to form instead of one (see Figure 5.14 (a2) and (a3)). Further increase of C_{surf} to 0.2 and 0.8 mM would pin the droplet completely, leading to the emergence of dendrites structure throughout the wetted area, except for the nearby region of the central large crystals (see Figure 5.14 (a4) and (b3)). Similar patterns can also be observed in Figure 5.14 (b2) and (b4) for other C_{salt} at 5% and 15%. However, if the salt concentration is low enough, the central crystal vanishes with the wetted region fully covered by the dendritic structure. A close view of the dendritic precipitations can be found in Figure 5.15. As shown in Figure 5.15 (a), the coarse dendritic structure gets finer when it approaches the center zone and disappears at the adjacent region of the central crystal. An increase in salt concentration could inhibit the formation of the dendritic pattern (see Figure 5.15 (b1-b4)). It can be seen that the drying and deposition morphologies are closely related to the surfactant additive and salt concentration. In the following sections, the detailed evaporation dynamics will be stressed, followed by the morphologies of crystallization process.

Figure 5.14. Crystalline patterns of surfactant saline droplets at (a) different CTAB concentrations with 10% NaCl; (b) different NaCl concentrations with 0.8 mM CTAB. The red scale bar indicates 0.4 mm.

Figure 5.15. The enlarged view of the final crystalline pattern. (a) 10% NaCl 0.2 mM, (b1) 1% NaCl 0.8 mM, (b2) 5% NaCl 0.8 mM, (b3) 10% NaCl 0.8 mM, (b4) 15% NaCl 0.8 mM. The red scale bar indicates 20 μm . The yellow scale bar indicates 150 μm .

5.3.2.1. Evaporation dynamics of saline surfactant droplet

In Figure 5.16, the evolution of contact angle and dimensionless base diameter are plotted for evaporating saline surfactant droplets before the crystallization happens. As shown in Figure 5.16 (a1) and (a2), the water droplet (0% NaCl 0 mM) first evaporates

with its contact line pinned, followed by a constant contact angle depinning stage. For saline droplet (10% NaCl 0 mM), after an initial short period of pinned drying, the contact angle begins to increase continuously in the depinning stage until the crystal occurs. This increment of contact angle in the middle of drying is resulted from the salt concentrating during evaporation. If a trace amount of surfactant (0.01 mM) is added into the salt solution, the droplet would depin from the very beginning with its contact angle continuously rising to be higher than the pure saline droplet. This vanish of the initial pinned drying period reflects the autophobing-induced dewetting behavior brought by the surfactant molecules [8]. Once the surfactant saline droplet is deposited

Figure 5.16. (a1) Contact angle and (a2) dimensionless base diameter for 10% NaCl droplets with C_{surf} at 0 mM, 0.01 mM, 0.04 mM, 0.2 mM, 0.8 mM. (b1) Contact angle and (b2) dimensionless base diameter for 0.8 mM CTAB droplets with C_{salt} at 1%, 5%, 10%, 20%.

on the silicon wafer, the surfactant molecules would adsorb on this negatively charged surface with some assembling external to the contact line, leading to the enhancement of surface hydrophobicity and retracting of contact line.

Further increase of C_{surf} to 0.04 mM also brings an evident autophobing behavior initially. However, as the surfactant concentrates during the evaporation process, the droplet becomes pinned when the droplet approaches the crystallization point. A significant increase (≥ 0.2 mM) of C_{surf} would pin the droplet completely. As shown in Figure 5.16 (b1) and (b2), all droplets evaporate in the pinned mode under a high C_{surf} at 0.8 mM. Upon increasing the salt concentration, a slowing down evaporation rate can be observed and the deviation from linear trend becomes larger.

Figure 5.17 depicts the dependence of initial contact angle, θ_0 , with C_{salt} and C_{surf} . As shown in Figure 5.17 (a), compared with the pure water droplet (0% NaCl 0 mM), θ_0 increases with either the presence of salt or surfactant in the droplet solution. The increment of θ_0 for saline droplet (10% NaCl 0 mM) can be explained by its higher surface tension. While for the surfactant droplet (0% NaCl 0.8 mM), though the surfactant lowers the liquid-vapor surface tension, γ_{LV} , it also builds up a hydrophobic barrier at the solid-vapor interface, which inhibits the droplet spreading and leads to a higher θ_0 . A decrease of θ_0 can be observed when salt is adding into the surfactant droplet. This is because salt reduces the electrostatic repulsion between the ionized headgroups of surfactant molecules, leading to a closer packing at the liquid-interface and therefore a lower liquid-vapor surface tension [164]. However, we don't observe a clear trend of θ_0 with C_{salt} under the surfactant concentration at 0.8 mM. Figure 5.17

(b) demonstrates a larger θ_0 at a higher C_{surf} , as increasing C_{surf} facilitates the establishment of the hydrophobic barrier [165, 166].

Figure 5.17. Initial contact angle of droplets with the variation of (a) salt concentration and (b) surfactant concentration.

5.3.2.2. Motion and morphologies of crystalline

The various crystalline patterns as shown in Figure 5.14 indicate a strong dependence of crystalline morphologies on the presence of surfactant. The typical growth features of crystals are summarized in Figure 5.18. Regardless of the various values of C_{surf} and C_{salt} , the crystals first occur near the contact line. For a pure saline droplet (see Figure 5.18 (a)), once the precipitation is initiated, we could observe a burst growth of crystal in a short period, forming a single large crystal eventually. With a trace amount of surfactant in the solution (see Figure 5.18 (b)), crystals may grow in a branched morphology, which penetrate sharply into the bulk solution. The growing crystals are observed to assemble at the droplet center, driven by the capillary force of the deformed liquid-air interface. The drying droplet now prefers to deposit into several small crystals instead of one. For a pinned drying droplet with a relatively high C_{surf} (see Figure 5.18 (c)), the liquid layer is quite low when the crystal occurs near the edge. As it grows

bigger, the crystal quickly immigrates to the center region and strikes out of the liquid-air interface. At the late drying stage, the solution shrinks towards the central crystals, left behind a colorful film (see Figure 5.19), which is a mixture of absorbed surfactant molecules and salt solutes. With the droplet drying approaches to the end, dendrites are then observed to emerge at one location of the thin film and then spread over the whole area very quickly.

Figure 5.18. Dynamics of the crystalline formation at (a) 10% NaCl 0 mM, (b) 10% NaCl 0.01 mM, (c) 10% NaCl 0.2 mM, and (d) 1% NaCl, 0.8 mM on silicon wafer. Images are captured under the dark field. The red scale bar indicates 0.4 mm.

Figure 5.19 Thin film color interference pattern around the central crystals. The droplet is 10% NaCl 0.2 mM. The red scale bar indicates 0.4 mm.

It should be noted that the adjacent region of the central crystal is in absent of dendritic deposits, which we would attribute to the crystallization induced flows. As shown in Figure 5.20, an overall inward motion of the liquid can be observed. It is reasonable to assume that the surfactant adsorption on the substrate would be weakened by the flushing effect of the flow. The vector field shows that the flow accelerates from the droplet edge to the center and evolves into strong vortices when it reaches the central growing crystal. As a result, we could expect a lesser amount of surfactant adsorption on the substrate where the liquid flow is stronger, especially near the crystal where continuous vortexes exist. This could help to explain the evolution trend of the dendritic structure from coarse to fine as shown in Figure 5.15 (a). Since the adsorbed surfactant could trap salt solutes, a weaker adsorption effect leads to a smaller amount of salt solutes and therefore fine crystals. Near the crystal, surfactant adsorption is inhibited by the flow and thus no dendritic deposits form at all. The precipitation feature holds the same for other saline droplets with high C_{surf} as listed in Figure 5.14 (b2-b4). However, if the salt concentration is quite dilute (see Figure 5.18 (d)), the droplet dries into a thin

liquid film while the crystallization occurs. This thin solution layer provides little flow channel for the supply of nearby salt ions to help the crystal to grow bigger. Instead, the crystals crawl on the substrate to reach the nearby liquid and grow into dendritic structures.

Figure 5.20 The flow field inside a drying surfactant saline droplet (10% NaCl 0.2 mM) at its 70% lifetime (after the crystallization happens). (a) Particle trajectories in 8 secs; (b) Vector field. The white scale bar indicates 0.4 mm.

5.4. Summary

In this chapter, the saline droplet drying has been performed on various flat substrates or with surfactant additives. On the various flat surfaces, the salt crystalline morphology was found to be greatly dependent on the substrate modulated droplet wetting and drying dynamics. On the silicon wafer and PMMA plate, the saline droplets experienced a unique depinning period in the middle of evaporation. The long depinning stage could guarantee a large liquid thickness for the crystalline cube to grow bigger and impel it to move inward, leading to the final pattern with one or more cubes locating at the droplet center. In contrast, the droplets dried in a pinned regime on the soda lime glass. The resulting crystalline deposit on the soda lime glass depended greatly on the initial salt concentration such that it was comprised of exterior cracked layers of salts and interior separated small cubes for low salt concentrations, while the large crystalline cubes formed near the droplet edge for high salt concentrations. The surfactant additive in the

saline solution was found to bring a big change to the droplet drying dynamics and the morphologies of crystallization. A small amount of surfactant additive could depin the droplet from the beginning of drying. However, with the surfactant concentration increasing, this initial autophobic effect weakens and the droplet gets pinned gradually. Crystals are found to first emerge near the rim and moving inwards as it grows bigger. Under a relatively high surfactant concentration, the dendritic precipitation patterns are observed to form around the central crystals. An increase in the surfactant concentration would make the dendritic structure thicker and wider, while a high salt concentration could inhibit the growth of the branched structures. In the following chapter, the colloidal droplet drying would be performed on the patterned substrate, to explore the possibility to control the droplet wetting and evaporation behavior.

Chapter 6. Wetting and evaporation dynamics of sessile droplets on patterned surface

6.1. Introduction

The wetting dynamics of sessile droplets on patterned substrates is closely related to the surface microstructure and the droplet liquid property. Here we investigate the wetting and evaporation dynamics of saline droplets and surfactant droplets on a patterned surface decorated with micropylamid pillars. With the presence of salt in the solution, the droplet surface tension increases both initially and during the evaporation process. While the droplet surface tension varies in the reverse direction with the adding of surfactant in the solution. The wetting dynamics of the droplet is revealed by the evolution of the wetting area and the contact line pinning and depinning behavior during the evaporation process. This study shows how the surface microstructure shapes the liquid wetting behavior and how the droplet evaporation dynamics are related to the different surface tensions, which could help to provide a method to control and maintain droplet wetting shape.

6.2. Effect of saline solutions¹

6.2.1. Experimental setup

The experimental setup is shown in Figure 6.1 (a). An optical microscope (Nikon Eclipse LV100ND) was used to record the droplet evaporation process from the top view and two cameras (HiSpec-2) from the two side views. Images were captured with

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¹ Published paper: X. Zhong, J. Ren, M. Lin, K. S. L. Chong, K.-S. Ong, and F. Duan, *Octagonal Wetting Interface Evolution of Evaporating Saline Droplets on a Micropylamid Patterned Surface*. ACS Applied Materials & Interfaces, 2017. **9**(33): 28055-28063.

1 fps. As shown in Figure 6.1 (b), the patterned surface used in this experiment is decorated with micropillar pillars. One side view observing direction is parallel to the groove between the micropillar pillars, indicated as line-of-sight “||”; the other one is along the diagonal ridge of the micropillar pillar, indicated as line-of-sight “∠”. These two observing directions form a 45° angle.

Figure 6.1. (a) Schematics of the experimental setup. Droplet is recorded at the same time from top view and from two side views of the two line-of-sights. (b) The microstructure of PMMA patterned substrate. The geometries of the micropillar pillar are characterized by the central height h , bottom side length d , and diagonal edge length l . The line-of-sight “||” is parallel to the groove between the micropillar pillars. The line-of-sight “∠” is along the diagonal ridge of the micropillar pillars.

The patterned surface used in this experiment is made by nanoimprint lithography with poly(methyl methacrylate) (PMMA) flat surface. The geometries of the micropillar pillars are summarized in Table 6.1, including the central height h , side length d , diagonal length l and roughness r denoting the ratio of the top surface area of a micropillar to its bottom surface area. The surface structure was measured by a 3D profiler confocal and interferometry microscope (DCM8, Leica) and shown in Figure 6.1 (b).

In order to form pillars, a nickel shim mold decorated with micropyramid cavities was made first. Then the PMMA flat surface was imprinted with the nickel shim mold at a temperature of 140 °C and a pressure of 20 bar for 10 min using an Eitre 6 nanoimprinter (Obducat). In this process, the PMMA polymer would fill up the cavities of the mold gradually. Finally, a demolding process was carried out at 50 °C. After the thermal imprinting process, each substrate was cleaned before tests to remove contaminants by rinsing under deionized water (Milli-Q) and drying under compressed nitrogen gas.

Table 6.1. Geometric parameters of the micropyramid pillars on PMMA patterned surface

h (μm)	d (μm)	l (μm)	r
11	30	13.89	1.24

The homogeneous saline solution samples were prepared by dissolving potassium chloride powders (KCl, Sigma Aldrich, >99%) in nano-filtered water with resistivity at 18.2 M Ω -cm. The initial concentration C_{KCl} of the KCl solutions were 0%, 5%, 10%, and 20%, which were lower than the KCl saturation concentration at roughly $C_{\text{sat}}=23.7\%$ [162]. As the evaporation goes on, the salt concentration increases gradually and finally reaches a supersaturation state. Then the formation of crystalline could be initiated. The moment when crystalline occurs is defined as crystallization time t_c . As the crystalline grows bigger, it may penetrate the droplet liquid-air surface and defects the three-phase line. But still, we report contact angle and base diameter both prior to and after the deformation of droplet spherical profile to provide full-spectrum information.

The droplet initial volume was controlled at 0.5 μL using a micropipette. As the height of the salt droplet is at around 0.7 mm, which is much smaller than the capillary length (2.7 mm) of the water droplet and the capillary length (2.6 mm) of the KCl droplet (20%), the gravitational effect on the droplet shape is assumed to be negligible. The base

diameters from the two lines-of-sights and the solid-liquid wetting interface were analyzed by the software of NIS Elements. The snapshots of droplet profile captured from two side view directions were analyzed by ImageJ, to get the information of droplet contact angles. As shown in **Section 2.1**, the contact angle on patterned surfaces is usually denoted using θ^* , called the apparent contact angle. However, in this study, we use θ for simplicity to represent the apparent contact angle of the droplet on this micropyramid pattern surface. Three repeated experiments were carried out for each KCl concentration to ensure the reliability of the experiment. Standard deviations of the repeated results were calculated and plotted. The experiment was carried out in an open condition with the ambient temperature and humidity at 22 ± 1 °C and $55 \pm 2\%$. A summary of the experimental conditions is listed in Table 6.2.

Table 6.2. A summary of the experimental conditions

Solution type	Concentration (%)	Volume (μ L)	Substrate	Environmental condition	Pressure condition (mmHg)
Potassium chloride solution	0, 5, 10, 20	0.5	Micropyramid patterned surface	Temperature: 22 ± 1 °C Humidity: 55 ± 2 %	0

6.2.2. Evaporation dynamics

6.2.2.1. Droplets initial wetting state

Figure 6.2 gives the initial wetting state of the droplets from the top view and side view snapshots and the initial contact angle and base diameter from the two line-of-sights. Droplets sitting on the patterned surface were in the Wenzel wetting state, as no air bubbles were observed from the top view snapshots. It can be seen that the patterned surface is hydrophobic as the initial droplet contact angle is higher than 90°. Considering the fact that the corresponding droplet contact angle on the flat PMMA surface is smaller

than 90° , which means the traditional Wenzel equation cannot be used to describe the apparent contact angle in this case. The droplet initially beads up which makes the contact line not visible, but it still can be discerned that the contact forms an octagonal wetting shape, which can be confirmed after the contact angle decreases below 90° during evaporation. This octagonal wetting contact line shapes the droplet and makes it have different side view profiles from mainly two directions, line-of-sight “ $\angle$ ” and “ $\parallel$ ”. This is actually how the observing directions of the two side view cameras are set, as shown in Figure 6.1 previously.

It can be seen from Figure 6.2 (a) and (b) that the droplet initial contact angle from the line-of-sight “ $\parallel$ ” is higher than that from the line-of-sight “ $\angle$ ”. Figure 6.2 (c) shows that the droplet initial base diameter from the line-of-sight “ $\angle$ ” is larger than from that the

Figure 6.2. (a) The initial droplet snapshots taken from the top view and two side view directions. (b) The initial droplet contact angle θ_0 versus salt concentration C_{KCl} from both line of sights (c) The initial droplet base diameter D_0 versus salt concentration C_{KCl} from both line-of-sights.

line-of-sight “||”. A higher initial contact angle is corresponding to a lower initial base diameter. This observation holds also as the salt concentration C_{KCl} increases. The initial base diameter and contact angle versus C_{KCl} are plotted in Figure 6.2 (b) and (c) with the best linear fitting lines. As the presence of KCl in the solution could enhance the droplet surface tension, a higher C_{KCl} would lead to a larger initial contact angle. And because the droplets were controlled with the same initial volume, a larger initial contact angle corresponds to a lower initial base diameter.

6.2.2.2. Evaporation modes

The evaporation dynamics of KCl droplets were revealed by the evolutions of the contact angle and base diameter during the droplet evaporation process. The normalized contact angle and base diameter versus normalized time at various KCl concentrations were plotted from both line-of-sights, as shown in Figure 6.3. It can be seen from the figure that the droplet initially evaporates in a CCR mode with the contact angle decreasing and contact line pinned, regardless of the KCl concentration. After the contact angle θ reduces to a certain value, the droplet contact line begins to recede while the contact angle keeps almost constant, indicating the droplet enters a CCA evaporation mode. At the late stage of evaporation, the pure water droplet evaporates in a mixed mode with its contact angle decreasing and contact line receding simultaneously. While for saline droplets with C_{KCl} higher than 0%, the late stage evaporation would behave differently. Due to the presence of crystals at the late stage, liquids would stay at the sides of the crystals and thus maintain a relatively constant value till the end of evaporation. Despite the evaporation modes, droplet evaporation will also be affected by salt in the solution. As shown in Figure 6.3 (a1), the reducing rate of the contact angle

becomes lower at a higher KCl concentration, suggesting a suppression of droplet evaporation.

Figure 6.3. The evolution of normalized contact angle θ/θ_0 (a1, b1) and base diameter D/D_0 (a2, b2) versus normalized time t/t_f at various KCl concentrations from both line-of-sights. t_f is the total lifetime of the evaporating droplets. θ_0 and D_0 are the initial droplet contact angle and base diameter respectively.

6.2.2.3. Crystallization and droplet receding dynamics

It is also observed that the start depinning time of contact line and the corresponding contact angle θ_r is related with the different KCl concentrations, as shown in Figure 6.4. It can be seen from Figure 6.4 (a) that the normalized depinning time t_r is delayed at a higher C_{KCl} along both line of sights. One reason is that the larger initial contact angle θ_0 at a higher C_{KCl} requires more time to reach θ_r at the receding moment. Another

reason is the occurrence of crystallization prior to depinning at high C_{KCl} , as shown in Figure 6.4 (a) at 10% and 20% of C_{KCl} . The presence of crystalline could increase the local pinning effect and postulate contact line depinning.

Figure 6.4. (a) The normalized depinning time t_r from the two line-of-sights, and the normalized crystallization time t_c with respect to different C_{KCl} . (b) The contact angle θ_r at the onset of receding from the two line-of-sights with respect to different C_{KCl} . The inset indicates the contact angle reduction $\Delta\theta$ during the CCR evaporation mode with respect to different C_{KCl} .

The contact angle when the receding of contact line begins is plotted in Figure 6.4 (b). θ_r is found to increase moderately with C_{KCl} . This can be explained by the increase of the inward force f acting on the three-phase line, which can be expressed as $\Delta f = \gamma_{LV} (\cos \theta - \cos \theta_0)$, where θ_0 is the initial contact angle of the droplet. As γ_{LV} increases with raising C_{KCl} , a same decrease in the contact angle θ would bring a larger enhancement of Δf . The increase of initial contact angle θ_0 at higher C_{KCl} also contributes to a larger enhancement of Δf . These two factors help the contact line to acquire an inward force f large enough to depin at a higher θ_r . In addition, the θ_r along the line-of-sight “ $\angle$ ” is smaller than that along the line-of-sight “ $\parallel$ ”. This can be

attributed to the lower initial contact angle θ_0 along the line-of-sight “ $\angle$ ” which then requires a larger decrease in θ to reach the affordable f for depinning.

6.2.3. Wetting shape evolution

6.2.3.1. Initial wetting interface

As shown in Figure 6.2, the initial octagonal wetting shape of the droplet is partially blocked by its spherical cap. Once the droplet contact angle decreases below 90° , the octagonal interface becomes fully visible, as depicted in Figure 6.5. This octagonal shape has two kinds of side length “ $L_\angle$ ” and “ $L_\parallel$ ”, corresponding to the two line-of-sights “ $\angle$ ” and “ $\parallel$ ” respectively. A “side ratio” parameter $\tau = L_\parallel / L_\angle$ is set to quantify this octagonal shape. For each droplet, τ is calculated by dividing the summed length of the four “ $\angle$ ” sides by that of the four “ $\parallel$ ” sides. It can be seen from Figure 6.5 that the side length “ $L_\parallel$ ” is longer than the side length “ $L_\angle$ ”. Combined with Figure 6.2 (c), we can see that the longer side length “ $L_\parallel$ ” is corresponding to a shorter initial base diameter while the shorter side length “ $L_\angle$ ” is corresponding to a longer initial base diameter. This can be explained by the different pillar distributions from the two line-of-sights. Along the line-of-sight “ $\parallel$ ”, the pitch between two adjacent micropillar peaks is $30\ \mu\text{m}$ while from the line-of-sight “ $\angle$ ” that is $30\sqrt{2}\ \mu\text{m}$. Therefore, pillars along the line-of-sight “ $\parallel$ ” are considered to be more condensed, generating more resistance and pinning effect to liquid initial spreading and resulting a shorter initial base diameter. And because it is harder for liquid to spread along this direction, the side length “ $L_\parallel$ ” would become longer.

As shown in Figure 6.5, there is no obvious trend of τ when the salt concentration C_{KCl} increases from 0% to 20%. This may be because the related liquid-vapor surface tension only changes from around 72.51 to 76.49 mN/m [167], which is not large enough to

bring evident changes compared with the structural difference between the two line-of-sights. This has also been shown in Figure 6.2 that the increase of initial contact angle with raising C_{KCl} is less than 5° from both line-of-sights.

Figure 6.5. The side ratio of droplet initial octagonal wetting interface at various KCl concentrations. The inset shows the two kinds of side lengths “ $L_{\perp}$ ” and “ $L_{\parallel}$ ”, corresponding to the line-of-sight “ $\perp$ ” and “ $\parallel$ ” respectively.

6.2.3.2. Wetting shape evolution during evaporation

Apart from the initial wetting shape of the interface, we also take a close view to its evolution during the evaporation process, as indicated in Figure 6.6. It is found that the contact line doesn’t start to recede simultaneously at different positions. The depinning starts from the two ends of the contact line sides from both line-of-sights, as indicated by the white arrows in Figure 6.6 (a2), (b2), and (c2). This makes the wetting interface become rounded. Then the depinning propagates into the central part of the contact line sides until they start to recede row by row, which are denoted by the white arrows in Figure 6.6 (a3), (b3), and (c3). As the “row by row” receding along the line-of-sight “ $\perp$ ” starts earlier than that along the line-of-sights “ $\parallel$ ”, the wetting interface could evolve

into a circular shape gradually (Figure 6.6 (a4, b4)). For droplets with 10% or 20% C_{KCl} , crystallization happens before depinning taking place and the formed crystal may change the wetting interface significantly. As shown in Figure 6.6 (c2, c3), the crystal makes part of the contact line keep pinned and makes the wetting interface evolve into an irregular circular shape (Figure 6.6 (c4)).

Figure 6.6. Evolution of droplet wetting interface during evaporation process with C_{KCl} at (a) 0%, (b) 5%, and (c) 20%. (a1), (b1), and (c1): the octagonal wetting interface right before depinning of contact line; (a2), (b2), and (c2): depinning starts from the two ends the contact lines from the two line-of-sights, indicated by the white arrows; (a3), (b3), and (c3): the central part of the contact lines start to recede also, indicated by the white arrows; (a4) and (b4) the wetting interface evolves into a circular shape; (c4) the wetting interface evolves into an irregular circular shape under the effect of the crystal.

6.2.4. Contact line topology

6.2.4.1. Initial contact line topology

In this section, we take a close view to the droplet contact line to see how the droplet wets the surface. As the droplet initial contact angle from both line-of-sights is larger

than 90° , the contact line is not fully visible from top view until the contact angle $< 90^\circ$. In order to get to know how the droplet wets the patterned surface initially near the contact line, we have set a side view camera whose lens forms a 15° angle with the patterned surface, as shown in Figure 6.7 (a). The surface has been put at different orientations so as to observe the contact line from both line-of-sights. Side view images captured from the two line-of-sights are shown in Figure 6.7 (b) and (c), where the contact line's projections onto the surface are also given. It can be seen that the droplet completely wets the microstructures of the surface and its contact line follows the local variations exactly. Along the line-of-sight “ $\angle$ ”, the droplet initial contact line follows the diagonal ridges of the micropyramid pillar and intersects with the pillar peak. Along the line-of-sight “ $\parallel$ ”, the droplet initial contact line follows the slant triangle edges of

Figure 6.7. Initial droplet contact line topology along the two line-of-sights. (a) Schematics of the side view camera and the direction of two line-of-sights; (b) Contact line along the line-of-sight “ $\angle$ ” and its projection onto the surface; (c) Contact line along the line-of-sight “ $\parallel$ ” and its projection onto the surface. The red dashed lines in the figure mark part of the contact line. Pure water droplet is used here.

the micropillar, whose projection forms a “W” shape. These edges of the micropillar act as defects which provide strong pinning effects and contribute to the global hydrophobic behavior of the pattern surface. As shown by the red dashed lines in Figure 6.7 (b) and (c), the pillar density along the line-of-sight “||” is more condensed, which accounts for the higher initial contact angle and longer contact line side length.

6.2.4.2. Depinning contact line

Beside the initial wetting details of the contact line, its receding dynamics during evaporation is also investigated. Figure 6.8 shows the typical dewetting features of the contact line along the two line-of-sights. For both line-of-sights, receding of the contact line starts with a “slow slip” process, where the contact line depins from its initial wetting position gradually. Then a stepwise receding motion starts. Along the line-of-sight “||”, the stepwise receding motion consists of a “slow slip” and a “fast slip” process. During the “slow slip” process, the contact line retreats within the surface structures gradually until its wetting front reaches the bottom grooves. Then a “fast slip” process happens where the contact line quickly jumps and pins at the surfaces of the next micropillar row. While along the line-of-sight “⌞”, only “fast slip” receding is observed in the stepwise motion, where the wetting front jumps row by row in a “stick slip” manner. The contact line repeats the two receding processes along the two directions until the droplet height decreases beneath the micropillar height, after which the remaining liquid dries out in the grooves between pillars.

Figure 6.8. Top view depinning features of the droplet contact line from the line-of-sight “∠” and “||”. (a) Initial “slow slip” of contact line; (b) Stepwise receding motion of contact line; (c) The corresponding snapshots of the receding contact line taken from the video.

6.2.5. Surface energy analysis

The octagonal wetting interface of the droplet as shown in Figure 6.5 could be explained by the analysis of the free surface energy difference near the contact line, which was previously applied in the case of the wetting on hydrophobic cylindrical micropillar arrays [69]. This energy difference describes the energy barrier generated by the micropillars. Here we modify the expression of the free surface energy difference to make it suitable for this case of wetting on pyramid micropillar arrays. In the previous section, we have examined the initial wetting behavior of contact line. As shown in Figure 6.9, along the line-of-sight “∠”, the three-phase line intersects with the diagonal ridges, AE and AC, of the micropyramid pillar. The presence of the micropyramid pillar distorts the local wetting interface from a planar liquid-air interface S_{ACE} to two triangle

faces of the micropillar, S_{ABC} and S_{ABE} . The resultant surface energy difference could be expressed as:

$$E_{d\angle} = \frac{1}{2} d \sqrt{d^2 + 4h^2} \gamma_{SL} - \frac{\sqrt{2}}{2} h d \gamma_{LV} \quad (6.1)$$

Along the line-of-sight “ $\angle$ ”, the pitch between two adjacent pillar peaks is $\sqrt{2}d$. Then the change in free surface energy per unit length of the contact line is

$$\frac{E_{d\angle}}{\sqrt{2}d} = \frac{\sqrt{2}}{4} \sqrt{d^2 + 4h^2} \gamma_{SL} - \frac{1}{2} h \gamma_{LV} \quad (6.2)$$

Figure 6.9. Intersection of three-phase line on the micropillar along the two line-of-sights

Along the line-of-sight “ $\parallel$ ”, the three-phase line slant triangle edges, AD and AC, of the micropillar. The presence of the micropillar distorts the local wetting interface from a planar liquid-air interface S_{ACD} to three triangle faces of the micropillar, S_{ABC} , S_{ABE} , and S_{ADE} . The resultant surface energy difference could be expressed as:

$$E_{d\parallel} = \frac{1}{4} d \sqrt{d^2 + 4h^2} (3\gamma_{\text{SL}} - \gamma_{\text{LV}}) \quad (6.3)$$

Along the line-of-sight “||”, the pitch between two adjacent pillar peaks is d . Then the change in free surface energy per unit length of the contact line is

$$\frac{E_{d\parallel}}{d} = \frac{1}{4} \sqrt{d^2 + 4h^2} (3\gamma_{\text{SL}} - \gamma_{\text{LV}}) \quad (6.4)$$

In order to calculate $E_{d\perp} / \sqrt{2}d$ and $E_{d\parallel} / d$, we need to know the solid-liquid surface tension γ_{SL} and liquid-vapor surface tension γ_{LV} . As there is no direct technique to measure the solid-liquid surface tension, here we use the method developed by K. Szymczyk et al. [168] that γ_{SL} can be estimated by

$$\gamma_{\text{SL}} = \gamma_{\text{SV}} - \gamma_{\text{LV}} \cos \theta \quad (6.5)$$

where $\gamma_{\text{SV}} = \gamma_c$, γ_c is the critical liquid surface tension required to give zero degrees contact angle. For PMMA substrate, the critical liquid surface tension ($\gamma_c = 33.13 \text{ mN/m}$) is used [169]. The liquid-vapor surface tension of DI water (72.51 mN/m) is used, and that of the saline solution with different C_{KCl} is taken from the reference [167]. We have measured the contact angle of the KCl droplet on the smooth PMMA substrate, then we can calculate the solid-liquid surface tension γ_{SL} , as shown in Table 6.3.

Table 6.3. Contact angle of KCl droplet on smooth PMMA surface and the corresponding solid-liquid surface tension

C_{KCl}	0%	5%	10%	20%
Contact angle ($^\circ$)	68.73	72.78	74.70	77.71
γ_{SL} (mN/m)	6.82	11.47	13.62	16.85

The free surface energy difference per unit length $E_{d\angle} / \sqrt{2}d$ and $E_{d\parallel} / d$ are calculated and shown in Table 6.4.

Table 6.4. The free surface energy difference per unit length of the contact line

C_{KCl}	0%	5%	10%	20%
$E_{d\angle} / \sqrt{2}d$ (mN·mm)	-0.309	-0.251	-0.227	-0.199
$E_{d\parallel} / d$ (mN·mm)	-0.484	-0.360	-0.308	-0.241

With the above data, we can get

$$\frac{E_{d\parallel}}{d} < \frac{E_{d\angle}}{\sqrt{2}d} < 0 \quad (6.6)$$

The negative value of $E_{d\parallel}$ and $E_{d\angle}$ shows that adhesion of contact line to a pillar provides a free energy profit. The lower $E_{d\parallel} / d$ means larger energy barrier exists along the line-of-sight “ $\parallel$ ”. As a result, liquid prefers to spread along the line-of-sight “ $\angle$ ”, generating a larger base diameter D_0 and shorter side length “ $L_\angle$ ”.

6.3. Effects of surfactant solutions^{1,2}

6.3.1. Experiment setup

The experiment setup is the same as what have been shown in Figure 6.1. What’s different here is that surfactant droplets are used instead of saline droplets. The surfactant solutions were prepared by dissolving cetyltrimethylammonium bromide (CTAB, Sigma-Aldrich) in the nanofiltered water (18.2 MΩ cm). The critical micelle concentration (CMC) of the surfactant in the solution is 0.92 mM. Various solutions

¹ Published paper: X. Zhong, J. Ren (equivalence first author), K. S.-L. Chong, K.-S. Ong, and F. Duan, *Controlling Octagon-to-Square Wetting Interface Transition of Evaporating Sessile Droplet through Surfactant on Microtextured Surface*. ACS Applied Materials & Interfaces, 2018, **10**(14): 11425-11429.

² Published paper: X. Zhong, J. Ren, K. S.-L. Chong, K.-S. Ong, and F. Duan. *Wetting Transition at a Threshold Surfactant Concentration of Evaporating Sessile Droplets on a Patterned Surface*. Langmuir, 2019, **35**(13), 4509-4517.

have been prepared with the initial surfactant concentrations, C_0 , at 0, 0.04, 0.08, 0.2, 0.4, 0.8, 1.0, and 1.5 mM respectively. The droplets were deposited onto the surface with their initial volume controlled at $0.3 \mu\text{L}$ by a micropipette. As the height of the surfactant droplet is smaller than 0.6 mm, which is much smaller than the capillary length (2.7 mm) of the water droplet and the capillary length (2.0 mm) of the surfactant droplet (1.0 mM), the gravitational effect on the droplet shape is assumed to be negligible. The experiment was carried out in the open conditions with the ambient temperature and humidity controlled at $22 \pm 1 \text{ }^\circ\text{C}$ and $51.8 \pm 4.4\%$. A summary of the experimental conditions is listed in Table 6.5.

Table 6.5. A summary of the experimental conditions

Solution type	Concentration (mM)	Volume (μL)	Substrate	Environmental condition	Pressure condition (mmHg)
CTAB solution	0, 0.04, 0.08, 0.2, 0.4, 0.8, 1.0, 1.5	0.3	Micropyramid patterned surface	Temperature: $22 \pm 1 \text{ }^\circ\text{C}$ Humidity: $51.8 \pm 4.4 \%$	0

The time when the droplet made its first contact with the surface is denoted as t_0 . Once the sessile droplet was deposited onto the surface, it underwent a fast spreading process before the droplet stabilized. The moment when this fast spreading process finished was treated as the starting point of the natural evaporation process of the droplet. The droplet lifetime is denoted as t_f and the normalized time $\tilde{t} = t / t_f$ is used here, where t is the instantaneous evaporation time. The beginning of the natural evaporation is denoted as $\tilde{t} = 0$. To capture the fast spreading process, an inverted Nikon Eclipse Ti high-speed camera was used to record from the bottom of the droplet, with the framerate set at 1000 fps. The droplet formed an octagonal wetting interface gradually on the patterned

surface during the initial fast spreading period. The whole natural evaporation process lasted about 5 to 10 min for droplets under different values of C_0 .

6.3.2. Droplets initial wetting profile

The initial wetting states of the droplets with different surfactant concentrations are shown in Figure 6.10. Results under three concentrations, 0 mM, 0.4 mM, and 0.8 mM, are given, with the droplet snapshots taken from top view and droplet profiles extracted from the two line-of-sights “ $\angle$ ” and “ $\parallel$ ”. The droplet forms an octagonal wetting shape initially, regardless of the surfactant concentration, C_0 . However, the initial octagonal

Figure 6.10. The initial droplet top view snapshots (a1, b1, c1), and the corresponding droplet side view profiles (a2, b2, c2) extracted from the two line-of-sights. (a1, a2) 0 mM, (b1, b2) 0.4 mM, (c1, c2) 0.8 mM. The red dashed line indicates the line-of-sight “ $\parallel$ ” and the black dashed line indicated the line-of-sight “ $\angle$ ”.

wetting shape becomes closer to square as C_0 increases, showing different spreading preferences along the two line-of-sights. A viscous force exists to balance the initial spreading process until the equilibrium wetting state of the droplet is reached. For unit length of the wetting line, the viscous force can be written as $\eta Ux/h$, where x represents the wetting displacement, U is the velocity of the wetting front, and η is the viscosity of the droplet liquid [76]. The viscous force is expressed as $\eta U d / h$ along line-of-sight “||”, corresponding to the one row wetting from apex to apex, and $\sqrt{2}\eta U d / 2h$ along line-of-sight “Z”, corresponding to the one row wetting from the apex to the next corner of a micropillar. As the viscous force along line-of-sight “Z” is smaller, the droplet is able to spread more along this direction. An increase of C_0 would enhance the initial spreading, leading to a more inequilateral droplet profile.

This evolution in the wetting interface can be revealed by the changes of droplet side view profiles also. For the pure water droplet, its two side view profiles almost coincide with each other, which is consistent with the almost regular octagonal wetting interface. The droplet beads up and exhibits a hydrophobic wetting state. As C_0 increases, the deviation between the two side view profiles arises. This mainly originates from the preferred droplet spreading along the line-of-sight “Z” at a lower surface tension, corresponding to the evolution of wetting shape from octagonal to square. At the same time as shown in Figure 6.10 (a2), (b2), and (c2), with the increase of C_0 , the hydrophilicity along the two line-of-sight “Z” becomes different, with one remains hydrophobic and one evolves to hydrophilic.

In Figure 6.10, The octagonal wetting interface of the droplet has four “||” sides, corresponding to the line-of-sight “||”, and four “Z” sides, corresponding to the line-of-sight “Z”. In order to quantify the evolution of the initial wetting shape at different initial

C_0 , a side ratio parameter $\tau = L_{\parallel}/L_{\angle}$ has been defined. For each droplet, τ is calculated by dividing the summed length of the four “ $L_{\parallel}$ ” by that of the four “ $L_{\angle}$ ”, as shown in Figure 6.11 (a). The favored spreading along the line-of-sight “ $\angle$ ” results in the prolong of the “ $\parallel$ ” sides and the shorten of the “ $\angle$ ” sides, exhibit an evolution from octagonal to square. The side ratio τ was found to increase greatly with the raising of C_0 prior to 1.0 mM, which is quite different from that shown in Figure 6.5. This is mainly because there

Figure 6.11. The side ratio of droplet initial octagonal wetting interface at various CTAB surfactant concentrations. The two kinds of side lengths “ $L_{\angle}$ ” and “ $L_{\parallel}$ ” are corresponding to the line-of-sight “ $\angle$ ” and “ $\parallel$ ” respectively. (b) Snapshots of initial fast advancing three-phase line along the line of sights “ $\parallel$ ” and “ $\angle$ ” taken at $t_0 + 10$ ms, $t_0 + 14$ ms, $t_0 + 18$ ms, $t_0 + 22$ ms, $t_0 + 26$ ms, and $t_0 + 30$ ms, where t_0 indicates the moment when the droplet made the first contact with the substrate.

is a large decrease in the liquid-vapor surface tension γ_{LV} and solid-liquid surface tension γ_{SL} as C_0 changes from 0 mM to 1.0 mM, which could generate obvious changes in wetting behavior along the two line-of-sights. It is interesting to find that when C_0 increases above 1.0 mM to 1.5 mM, the rising trend of τ becomes flattened. This is consistent with the flattened increasing trend of γ_{LV} and γ_{SL} with C_0 once it is above CMC (0.92mM).

The preferred spreading along the line-of-sight “Z” can be explained further by taking a close recording of the initial fast spreading process, as shown in Figure 6.11 (b). It is seen that the droplet spreads with its contact lines advancing row by row in a stick-slip manner. Along the line-of-sight “||”, the advancing contact line crosses one row of micropillar pillars from $t_0 + 10$ ms to $t_0 + 14$ ms, and remains pinned from $t_0 + 14$ ms to $t_0 + 18$ ms. The advancing distance is d for crossing one row. While along the line-of-sight “Z”, the advancing contact line crosses one row of micropillar pillars from $t_0 + 10$ ms to $t_0 + 14$ ms, and another row from $t_0 + 14$ ms to $t_0 + 18$ ms. The corresponding distance is $\sqrt{2}d$ for two rows. Such an advancing manner makes the liquid propagate more distances along the line-of-sight “Z” during the initial spreading process. A higher C_0 would enlarge the advancing differences between the two line-of-sights, generating a larger side ratio τ . It also can be seen from $t_0 + 10$ ms to $t_0 + 30$ ms, the “||” side becomes longer and longer while the length of the “Z” side remains almost unchanged, leading to an increase in τ . What’s more, the central part of the “||” side advances ahead of its two ends, as indicated by the white arrows in Figure 6.11. This results from the longer distance from the end of the “||” side, compared with the central part, to the droplet center point.

6.3.3. Evaporation dynamics

6.3.3.1. Drying sequences

The drying sequences of droplets at various surfactant concentrations are shown in Figure 6.12. When the droplet solution is free of surfactant, the initial octagonal solid-liquid wetting interface recedes to a circular shape during the depinning stage. While once surfactant is added in, the droplet contact line never recedes. Conversely, it may advance. At a low concentration, $0\text{mM} < C_0 \leq 0.08\text{ mM}$, the droplet remains its initial octagonal interface until the end of drying. When $0.08\text{ mM} < C_0 < 0.8\text{ mM}$, the octagon wetting interface is found to first transform to square and then a stretched rectangle in the evaporation process. As shown in Figure 6.12 (c, d), the droplets with C_0 at 0.40 mM and 0.80 mM complete their “octagon-to-square” transition at around $0.52t_f$ and $0.18t_f$ respectively. Further evolution of the wetting interface happens along line-of-sight “||” only, making the droplet shape evolve from square to an irregular rectangle, which is called the “square-to-rectangle” transition. For $C_0 \geq 0.8\text{ mM}$, the droplets undergo a fast “octagon-to-square” transition at the very beginning of drying, followed by the greatly suppressed “square-to-rectangle” transition. The square wetting profile of the droplets can be maintained to the end of drying. After the surfactant droplet dries out, a ring pattern is found to form, as shown by the dried pattern in Figure 6.12 (b, c, d, e). This is due to the existence of outward flow inside the droplet, surfactant molecules can be carried to aggregate at the droplet contact line. The shape of the surfactant residuals is the same with the final wetting interface of the droplet, and with most surfactant accumulating along the rim.

Through the repeated experiments with C_0 at 0.08 mM, the droplets are found to mainly follow the “octagon-remained” mode. However, there are occasional cases that the

droplet spreads along line-of-sight “Z” and undergoes an incomplete “octagon-to-square” transition. This inconsistent evolution behaviour indicates that 0.08 mM could be the critical separating point between the “octagon-remained” and “octagon-to-square” drying schema. Similarly, for C_0 at 0.8 mM, the repeated tests show that the “octagon-to-square” transition is mainly followed by the limited “square-to-rectangle” transition. While the unlimited one (for occasional cases) also takes place, making the droplet develop an irregular rectangle. This means that C_0 at 0.8 mM is another critical separating point that if C_0 rises higher than 0.8mM, then the “square-to-rectangle” transition would be greatly suppressed.

Figure 6.12. Drying sequence of droplets with different initial surfactant concentrations C_0 at (a) 0 mM, (b) 0.08 mM, (c) 0.4 mM, (d) 0.8 mM, and (e) 1.0 mM. The red and white arrow symbols shown in the first snapshot of (a) 0.00 mM indicate the two line-of-sights. t_f represents the droplet lifetime. The red scaled bar indicates 200 μm .

As shown in Figure 6.12, under various C_0 , the evolution of droplets wetting interface are significantly different, which depend on the different combinations of three drying modes (“octagonal retention” mode, “octagonal-to-square” transition and “square-to-rectangle” transition). The development the surfactant droplets in their wetting profiles are basically determined by whether and when the latter two transitions occur. As a result, the study is focused on the droplets drying dynamics with the surfactant accumulation effect, to reveal onset mechanisms of both transitions.

6.3.3.2. Threshold of the wetting shape transition

It can be seen from Figure 6.12 that the “octagon-to-square” transition starts with the advance along line-of-sight “ $\angle$ ”, which moment is denoted by t_{O-S} , while the “square-to-rectangle” transition begins with the spread along line-of-sight “ $\parallel$ ”, which moment is denoted by t_{S-R} . These two normalized time points are plotted in Figure 6.13 (a). The results show that both transitions are observed to occur earlier with the increase of C_0 . In addition, regardless of the various C_0 , the “octagon-to-square” transition always occurs before the “square-to-rectangle” transition, indicating a wetting preference along line-of-sight “ $\angle$ ”. At a dilute surfactant concentration (0.08 mM), the “octagon-to-square” transition starts quite late at around 90% of the droplet lifetime ($0.9t_f$). At a high surfactant concentration (0.8 mM), such a transition happens at the very beginning. A similar evolution trend can be observed in the “square-to-rectangle” transition that it starts from $0.8t_f$ with C_0 at 0.2 mM and is shifted to $0.2t_f$ with C_0 increases to 0.8 mM. The above wetting transition feature can also be revealed by the dynamic contact angle θ_{O-S} and θ_{S-R} , which are measured at t_{O-S} and t_{S-R} respectively. As shown in Figure 6.13 (b), both contact angles are larger at a higher C_0 . The large variation of these two

contact angles at various C_0 indicates that both transitions are not sensitive to the dynamic contact angle. Instead, they may be related to the surfactant accumulation effect, suggested by the earlier occurring transitions under a higher surfactant concentration C_0 .

Figure 6.13. The threshold of the “octagon-to-square” and the “square-to-rectangle” wetting transitions. (a) The corresponding normalized time, t_{O-S} and t_{S-R} , (b) the corresponding dynamic contact angle, θ_{O-S} and θ_{S-R} , as a function of the initial surfactant concentration, C_0 . (c) The corresponding temporal volume-averaged surfactant concentration, C_{O-S} and C_{S-R} , at various C_0 from repeated experiments (E.N.). C_t indicates the temporal volume-averaged concentration at each moment.

To test the hypothesis, here we calculate the temporal volume-averaged surfactant concentration, C_{O-S} and C_{S-R} , at the onset of the “octagon-to-square” and the “square-to-rectangle” transitions, and plot them in Figure 6.13 (c). It should be noted here that when calculating C_{O-S} , the cases with C_0 at 0.8 mM and 1.0 mM are not included. This is because in these cases, the “octagon-to-square” transition starts from the very beginning of drying, indicating their surfactant concentrations have exceeded C_{O-S} . Therefore, C_{O-S} is estimated based on the cases with C_0 ranging from 0.04 mM to 0.4

mM. The “octagon-to-square” transition is considered to be triggered by the condensing of surfactant in the solution. As the surface tension of the droplet liquid decreases with the increase of the surfactant concentration, the droplet will have a higher wettability with the condensing of the surfactant. When the surface tension becomes low enough, the droplet liquid would propagate within the forests of the micropillar pillars and thus trigger the wetting transition. Similarly, C_{S-R} is calculated from the cases where the “square-to-rectangle” transition exists during the evaporation process, with C_0 ranging from 0.2 mM to 0.8 mM. Figure 6.13 (c) shows a relatively narrow range of C_{O-S} (0.62 ± 0.065 mM) and C_{S-R} (0.94 ± 0.061 mM) for different values of C_0 . Droplets with a lower C_0 need to experience a longer period of drying to concentrate the solution to the transition threshold.

The relatively similar threshold of surfactant concentrations at the “octagon-to-square” and “square-to-rectangle” transitions can be explained by carrying out a surface energy analysis over the spreading process on the patterned substrate along lines-of-sights “ $\angle$ ” and “ $\parallel$ ”. The wetting theory developed for hemiwicking in rectangular grooves is extended to apply in the current situation[76]. The surface energy difference is calculated between two quasi-steady states, corresponding to the spreading position from the current row to the next row of micropillar pillars, along both line-of-sights. The liquid spreading along the line-of-sight “ $\angle$ ” is shown in Figure 6.14 (a1) from t to $t + 35$ s, which detailed wetting manner is illustrated in Figure 6.14 (b1, c1). As the contact line of $2l$ in length (confined by the two dashed lines) invades a $\sqrt{2}d/2$ distance to the next row, it destroys a solid-vapor interface of area $4S_{\Delta}$ and an energy $4S_{\Delta}\gamma_{SV}$ is gained, it forms a solid-liquid interface of area $4S_{\Delta}$ and an energy $4S_{\Delta}\gamma_{SL}$ is expended. Here S_{Δ} represents the area of a triangular side of the micropillar pillar. The increase

in the liquid-vapor interface before and after the spreading can be shown by the difference between the triangular area “ABC” and the area “ABDEC”, which can be roughly estimated by d^2 . Then an energy $d^2\gamma_{LV}$ is expended in the invading process. As a result, the surface energy, $\Delta E_{\angle}$, expended for unit length of wetting line can be written as

$$\Delta E_{\angle} = \frac{4S_{\Delta}\gamma_{SL} - 4S_{\Delta}\gamma_{SV} + d^2\gamma_{LV}}{2l} \quad (6.7)$$

Figure 6.14. Schematic illustrations of the spreading process along lines-of-sight “Z” and “||”. (a1) Liquid propagates to reach the next row of micropillar pillars along the line-of-sight “Z”. (b1, c1) Schematic illustration to indicate the wetting status before and after the contact line proceeds a distance of $\sqrt{2}d/2$ to the next row of pillars along the line-of-sight “Z”. (a2) Liquid propagates to reach the next row of pillars along the line-of-sight “||”. (b2, c2) Schematic illustrations to indicate the wetting status before and after the contact line proceeds a distance of d to the next row of pillars along the line-of-sight “||”.

As the contact line spreads a distance of $\sqrt{2}d/2$ to reach the next row, the surface energy change for unit distance of spreading along the line-of-sight “Z” can be written as

$$\Delta e_{\angle} = \frac{\sqrt{2}}{2} \frac{(4S_{\Delta}\gamma_{SL} - 4S_{\Delta}\gamma_{SV} + d^2\gamma_{LV})}{dl} \quad (6.8)$$

The liquid spreading along the line-of-sight “||” is shown in Figure 6.14 (a2) from t to $t + 5$ s, which detailed wetting manner is illustrated in Figure 6.14 (b2, c2). The contact line of $2l$ in length (confined by the two dashed lines) invades a d distance to the next row. Similarly, the surface energy, $\Delta E_{||}$, expanded for unit length of contact line can be written as

$$\Delta E_{||} = \frac{4S_{\Delta}\gamma_{SL} - 4S_{\Delta}\gamma_{SV} + d^2\gamma_{LV}}{2l} \quad (6.9)$$

As the contact line proceeds a distance of d to reach the next micropylramid row, the surface energy change for unit distance spreading along the line-of-sight “||” can be expressed as

$$\Delta e_{||} = \frac{1}{2} \frac{(4S_{\Delta}\gamma_{SL} - 4S_{\Delta}\gamma_{SV} + d^2\gamma_{LV})}{dl} \quad (6.10)$$

From the above calculations we can see that the change of surface energy in one row spreading is the same for the two lines-of-sights, $\Delta E_{||}$ is equal to $\Delta E_{\angle}$. However, the corresponding surface energy change for unit distance of spreading is different, which holds a relation

$$\Delta e_{\angle} = \sqrt{2}\Delta e_{||} \quad (6.11)$$

By extracting the values of γ_{LV} , γ_{SL} and γ_{SV} from Ref. [168], the actual values of $\Delta e_{\angle}$ and $\Delta e_{||}$ can be calculated, which variation has been plotted in Figure 6.15 as a function of the increasing surfactant concentration. The decreasing trend indicates that $\Delta e_{\angle}$ and

$\Delta e_{\parallel}$ decreases upon decreasing γ_{LV} and γ_{SL} , or during the evaporation process as the surfactant keeps concentrating.

As shown in the inset of Figure 6.15, when the surfactant concentration, C_t , increases to 0.76 mM, the values of $\Delta e_{\perp}$ and $\Delta e_{\parallel}$ become negative, which would then initiate the spreading along the two line-of-sights. It has been observed that the “octagon-to-square” transition occurs before the “square-to-rectangle” transition, which can be explained by the fact that $\Delta e_{\perp}$ decreases in a speed $\sqrt{2}$ times as fast as $\Delta e_{\parallel}$ (see Eq. (6.11)). However, when the “octagon-to-square” transition occurs, the corresponding surfactant concentration is 0.62 mM, which is lower than the predicted threshold at 0.76 mM (see Figure 6.12). This is mainly due to the local higher surfactant concentration near the edge, resulting from the continuous outward flows inside the droplet. The detailed transportation and local accumulation behavior of surfactant molecules will be illustrated in next section.

Figure 6.15. The energy difference, Δe , for unit length of contact line and unit distance of spreading along the two line-of-sights. The region marked by the blue rectangle is enlarged and plotted in the inset, where Δe reverse its sign at 0.76 mM.

6.3.4. Surfactant transportation and accumulation

To verify the presence of outward flows inside the droplet, a particle image velocimetry (PIV) analysis has been carried to examine the flow field inside the drying surfactant droplet with C_0 at 0.8 mM throughout its lifetime. The velocity fields as shown in Figure 6.16 (a) are captured 30 μm above the patterned surface. An overall acceleration of the flow field can be observed with the normalized evaporation time. To show this evolution trend more clearly, a 3D map of the velocity magnitude has been plotted in Figure 6.16 (b), which is extracted along the radial position from droplet center to its corner with C_0 at 0.8 mM. During the evaporation process, the flows become stronger with time and exhibit a spike at last. Besides the strong outward flows, there also exist two other flows. One is the corner-directed flow toward the droplet side center, the other is the axisymmetric orientated recirculation flows near the four corners. It can be seen from the velocity fields at $0.3t_f$, $0.6t_f$ and $0.9t_f$ in Figure 6.16 (a) that the outward flow and the corner-directed flow are much stronger than the recirculation flows. And at $0.95t_f$ the recirculations are found to disappear. Under this flow feature, the surfactant molecules are mainly transported to the sides of the droplet, especially to the four corners. Then a continuous accumulation of surfactant molecules would happen, enabling the spread along line-of-sight “ $\angle$ ” and the associated “octagon-to-square” transition to occur in advance.

In contrast, there exists a delay in the “square-to-rectangle” transition which occurs with C_{S-R} at 0.94 mM (much higher than the predicted threshold at 0.76 mM). This may be explained by the fact that the previous “octagon-to-square” transition takes some time to be completed. When the “octagon-to-square” transition is completed, the volume-averaged surfactant concentration is $C_t = 0.88 \pm 0.076$ mM, which is calculated from

cases with $C_0 \leq 0.80$ mM. This value of C_i is quite close to C_{S-R} (0.94 mM), indicating the “square-to-rectangle” transition follows the former one almost instantly. In addition, the droplet is in a quasi-steady state between these two transitions, during which period the surfactant molecules take time to reach the new position of the contact line and accumulate to break the in-situ equilibrium state.

Figure 6.16. The flow field inside the drying surfactant droplet with C_0 at 0.8 mM. (a) The velocity fields at $0.3t_f$, $0.6t_f$, $0.9t_f$ and $0.95t_f$. (b) A 3D map for the magnitude of outward flows extracted along the radial position from the center to the corners and plotted over the normalized droplet lifetime.

For droplets with $C_0 \geq 0.8$ mM, the “octagon-to-square” transition starts from the beginning of drying and completes very quickly. In the latter evaporation period, the droplets keep pinned almost all the time (see Figure 6.12), suggesting that the “square-to-rectangle” transition is greatly suppressed. For C_0 at 0.8 mM, the droplet solution quickly concentrates to the CMC point at $0.13t_f$. Then the surfactant molecules assemble into micelles and are continuously transported by the outward flow to aggregate near the droplet edge and thus affecting the contact line dynamics.

To reveal the nonuniform distribution of the surfactant, we have measured the surface profile of the deposition pattern after the droplet dries out. Figure 6.17 (a) presents the final surfactant residuals left by the droplet with C_0 at 0.8 mM. It can be seen that most surfactant accumulates along the edge of the wetting interface, especially at the four corners. A zoom-in view of the lower-left corner is shown in Figure 6.17 (b). The surface height, h_{surf} , along the grooves over nine micropyramid pillars has been measured and plotted in Figure 6.17 (c). The height profile starts from one pillar distance away from the wetting area, thus the profile line is initially flat, representing the bare groove and is set at 0 μm . As h_{surf} moves into the wetting area, an acute increase can be observed, showing there are large amount of surfactant residuals. Further movement is

Figure 6.17. (a) The final surfactant residuals left by droplets with C_0 at 0.8 mM. (b) A close view of the surfactant residuals of one corner. (c) The surface height, h_{surf} , measured along the bottom sides of the micropyramid pillars as marked by the red arrow in (b) with C_0 at 0.08 mM, 0.2 mM, 0.4 mM, 0.8 mM, and 1.0 mM.

with a gradual decrease in h_{surf} , reflecting the fact that surfactant prefers to aggregate near the corner. Along the three micropylramids from the left of the wetting corner, h_{surf} increases upon increasing C_0 from 0.08 mM to 0.8 mM but barely changes once C_0 reaches 1.0 mM. However, h_{surf} is greatly enhanced for the other five micropylramids for C_0 at 1.0 mM.

It is assumed that the surfactant accumulation at the edge of the droplet would affect the motion of the wetting line. The hemiwicking force that drives the “square-to-rectangle” transition can be expressed as $F = -dE / dx$, where $dE = \Delta e_{\parallel} dx$ calculates the surface energy change due to the liquid invasion of a distance dx along the line-of-sight “||”. With the previously established expression of $\Delta e_{\parallel}$ (see Eq. (6.10)), F can be written as

$$F = \gamma_{\text{LV}} \left(\frac{\sqrt{4h^2 + d^2} \cos \theta_{\text{E}} - d}{2l} \right) \quad (6.12)$$

where θ_{E} is the equilibrium contact angle. As shown by the variation trend in the inset of Figure 6.15, F increases with C_{t} under the CMC, and becomes flattened when C_{t} goes beyond the CMC. What’s more, the “square-to-rectangle” transition is found to evolve into a complete wetting state (see Figure 6.12), so $\theta_{\text{E}} = 0$ and F can be expressed as

$$F = \gamma_{\text{LV}} \left(\frac{\sqrt{4h^2 + d^2} - d}{2l} \right) \quad (6.13)$$

By balancing the hemiwicking force with the viscous force, $\eta Ux / h$, we then have

$$Ux \sim \left(\frac{\gamma_{\text{LV}}}{\eta} \right) f(h, d) \quad (6.14)$$

where

$$f(h, d) = \frac{h(\sqrt{4h^2 + d^2} - d)}{2l} \quad (6.15)$$

Eq. (6.14) shows that the wetting dynamics of the contact line is proportional to the ratio γ_{LV} / η . The liquid-vapor surface tension γ_{LV} decreases with the increase of C_t , which trend becomes flattened once C_t exceeds the CMC. On the contrary, the viscosity η remains almost unchanged below the CMC but increases significantly over the CMC[170]. Therefore, at least above the CMC, the viscous force begins to take effect to resist the wetting transition. As the “square-to-rectangle” transition happens after the “octagon-to-square” transition, the local surfactant concentration at the end of the “octagon-to-square” transition near the contact line is critical for the wetting resistance. For $C_0 \geq 0.8$ mM, when the “octagon-to-square” transition is completed, C_t reaches 1.01 ± 0.081 mM, which is higher than the value of 0.88 ± 0.07 mM obtained for $C_0 \leq 0.8$ mM. What’s more, because surfactant assemblies prefer to accumulate near the droplet edge, the local surfactant concentration there should be further enhanced for a higher C_0 . And after the “octagon-to-square” transition is completed, the contact line is observed to change little for different C_0 (see Figure 6.12). The above analysis shows that a higher C_0 (≥ 0.8 mM) means a larger amount of surfactant accumulation near the edge, which raises the local viscous force to resist the hemiwicking path towards the “square-to-rectangle” transition.

As the surfactant continuously accumulates in the grooves between micropillar pillars, an obstacle effect could be established gradually which prevents the liquid from further imbibition. The height profile h_{surf} crossing the micropillar apex and groove alternatively is plotted in Figure 6.18 (a), corresponding to C_0 at 0.8 mM. The

Figure 6.18. (a) The height profile, h_{surf} , of surfactant residuals measured along the red arrow shown in the inset image of (b), this inset in (b) gives a close view of the surfactant residuals at one corner of the droplet with C_0 at 0.8 mM. (b) The variation of Δh_{surf} versus C_0 .

measuring position of the profile is marked by the red arrow in the inset of Figure 6.18 (b). The first “V” shape of the height profile represents the bare groove structure of the surface with its height range equals to the micropylar pillar height, h . From the second “V” shape of the height profile, the bottom position of the profile is elevated by Δh_{surf} (see Figure 6.18 (a)), resulting from the surfactant deposition in the grooves. Δh_{surf} is plotted as a function of C_0 in Figure 6.18 (b), which variation reflects the greatly enhanced surfactant aggregation at the high surfactant concentrations. By

combing $l = \sqrt{h^2 + \frac{1}{2}d^2}$ with Eq. (6.14), we have

$$Ux \sim f(h, d) = \frac{h(\sqrt{4h^2 + d^2} - d)}{\sqrt{4h^2 + 2d^2}} \quad (6.16)$$

It is easy to find that $f(h, d)$ holds a monotonic variation trend with h . As the surfactant accumulation on the substrate brings a decrease in h , the contact line motion evaluated by Ux would be suppressed. Therefore, the pinning effect would be enhanced. It can be concluded that with the preferred surfactant accumulation at the contact line, the enhanced local viscosity and the obstacle effect of the blocked groove channel could inhibit the liquid invasion and help to maintain the wetting shape.

6.4. Summary

In this chapter, the evaporation of a complex solution droplet has been explored on an ordered topographic surface. The study focuses on the evaporation dynamics and evaporation induced wetting transition. The findings could provide a further step toward liquid pattern control on patterned substrates.

In Section 6.2, it is showed that the saline droplets wet the pillar arrays completely. During the evaporation process, the pure water droplet undergoes CCR, CCA, and a mixed mode at the very late stage. While with the presence of KCl in the droplet solution, only CCR and CCA are observed. Initially, the droplet forms an octagonal wetting interface. After the CCR evaporation mode ends, the octagonal shape gradually evolves into a circle one in the CCA mode. No observable changes have been found on the initial octagonal wetting shapes when the salt concentration increases. A close view to the droplet edge reveals that the contact line retreats row by row, experiences “slow slip - fast slip” manner along the line of sight “||” and “stick-slip” manner along the line-of-sight “⌞”. A surface free energy analysis has been carried out to reveal the preferred spreading along the line-of-sight “⌞”.

In Section 6.3, the wetting evolutions of surfactant droplets have been studied on the patterned surface. The different drying schemas were found to be dependent on the initial concentration of the surfactant. At a dilute surfactant concentration, the droplet retained its initial octagonal shape to the end of drying. At the intermediate initial surfactant concentration, the droplet underwent the “octagon-to-square” transition first and then the “square-to-rectangle” transition, evolving into a stretched rectangle at last. At the high initial surfactant concentrations, the droplet quickly finished the “octagon-to-square” transition at the very beginning and kept the square shape to the end. Regardless of the various initial surfactant concentrations, the “octagon-to-square” transition was found to occur at a similar temporal volume-averaged surfactant concentration, which was determined by the surface energy difference for hemiwicking. A PIV analysis has been carried out on the flow field to reveal the surfactant transportation inside the droplet. The preferred surfactant accumulation near the droplet periphery could trigger an earlier “octagon-to-square” transition. At the high initial surfactant concentrations, the large quantity of surfactant assemblies near the contact line could bring an evident enhancement on the viscous force, which resisted the hemiwicking force and generated a strong suppression effect to the “square-to-rectangle” transition. The obstacle effect brought by the surfactant accumulation in the grooves also helps to suppress the “square-to-rectangle” transition.

Chapter 7. Conclusions and future work

7.1. Conclusions

The pattern formation of evaporating colloid droplets was numerically simulated under both pinning and dewetting drying conditions. The wetting and evaporation dynamics of colloid droplets were experimentally investigated on flat and patterned substrates. The major conclusions are drawn as follows:

1. Disk-ring pattern formation during the evaporation of pinning droplets

The pattern formation of colloidal droplets under the pinning drying condition was studied both numerically and experimentally. For a pinned drying droplet with an obvious Marangoni effect, a 3D DLCA model has been developed to simulate the deposition process of drying nanofluid droplets. With modeling the thermal Marangoni effect, particle adsorption at the liquid-air interface, and particle aggregation behaviors, the formation of the disk pattern inside a coffee ring has been simulated. Under a stronger Marangoni effect, the disk region of the simulated pattern was smaller and more concentrated. With an increase of the initial particle concentration, the disk-ring pattern was found to evolve into uniform coverage, with the enlargement of the disk region and the outer ring becoming taller and wider. The qualitative agreement was found in the comparison of local deposition distribution between the related experiments and simulations.

2. Dendritic pattern formation during the evaporation of dewetting droplets

For a drying nanofluid droplet with a dewetting contact line, a 3D lattice-gas KMC model has been developed to simulate the particle self-assembling behavior. The simulation results show the dried-in particle assemblies exhibit a dendritic pattern

connecting the sprawling branches with a central core structure. Parameter study shows that particles prefer to aggregate into more compact structures with fewer branches upon either increasing the mobility of particles, lowering particle-particle interaction, or under a lower chemical potential. Experiments of nanofluid droplet drying have been performed under different initial particle concentrations, which have similar 3D pattern structures and branch numbers with the simulated ones.

3. Evaporation and crystallization characteristics of saline droplet on flat surface

The dynamics of saline droplet evaporation and crystallization have been experimentally investigated on various flat surfaces. On the silicon wafer and PMMA plate, the droplets exhibit a unique period in the middle of drying with the contact angle keeps increasing and the contact line keeps receding. The lower wettability and the weaker pinning effect of silicon wafer and PMMA result in the morphology of crystalline cubes at the droplet center. On the soda lime glass, the droplets keep pinned all the time. The high wettability and strong pinning effect of the surface lead to precipitation throughout the wetted area.

With surfactant additives in the saline solution, the variations of droplet drying and precipitation are experimentally investigated. An initial autophobing effect can be observed at dilute surfactant concentration, while the droplet gets pinned gradually with the surfactant concentration rising. The precipitations are usually found to occur at more than one site near the rim with the crystals growing in a branched way. As the adsorbed surfactant molecules could trap salt solutes, under relatively high surfactant concentration, dendritic precipitation patterns are observed to form around the central crystals.

4. Evaporation and wetting dynamics of sessile droplets on micropyramid patterned surface

The evaporation dynamics and wetting shape evolution were studied with different droplet liquids on micropyramid patterned surface. By adding KCl salt and CTAB surfactant into the pure water, the droplet liquid property was controlled with one increasing the liquid surface tension and the other one decreasing the liquid surface tension.

When a saline droplet was deposited on the micropyramid patterned substrate, it formed an octagonal wetting interface and was in a hydrophobic Wenzel wetting state. During the evaporation process, the saline droplet experienced CCR and CCA evaporation mode before crystallization happened. The evolution of wetting interface from octagonal to circle was found to exist, which was brought by the receding of contact line. A close view to the contact line receding behavior revealed that the contact line retreated row by row, experienced “slow slip-fast slip” manner along the line of sight “||” and “stick-slip” manner along the line-of-sight “∠”. A surface free energy analysis had been carried out to reveal the different wetting preferences along the two line-of-sights.

For the surfactant droplets on a micropyramid patterned surface, the study is mainly focusing on the wetting shape evolution. An “octagonal-to-square” wetting transition was found to exist both initially with the increase of initial surfactant concentration and during the evaporation process with the surfactant enriching with time. The octagon-to-square transition occurs at a similar temporal volume-averaged surfactant concentration for the various initial surfactant concentrations. It can be explained by the change of surface energy brought by the spreading over the micropyramid structure. The maintenance of droplet octagonal wetting shape could be attained at a dilute surfactant concentration and square shape at a high surfactant concentration. At the high initial surfactant concentrations, the large quantity of surfactant assemblies near the contact

line could bring an evident enhancement on the viscous force and an obstacle effect of the blocked groove, generating a strong suppression effect to the “square-to-rectangle” transition.

7.2. Future works

Based on the present study, improvements can be made in future work to carry out the quantitative analysis on the observed phenomenon, to obtain controllable particle deposits on patterned surfaces and to simulate the related droplet drying process and particle self-assembly behavior.

1. Quantitative analysis of saline droplet drying

In this study, most of the work on saline droplet drying is observational and qualitative. In the future, a quantitative analysis should be carried out, such as the 3D profiles of the final deposition pattern. Since the crystalline is transparent, the residual patterns cannot be measured directly by the optical 3D profiler microscope (DCM8). As a result, surface treatment needs to be carried out to increase the reflectivity of the pattern. In addition, the detailed growth of the crystalline can be analyzed, especially with the presence of surfactant molecules.

2. Controllable particle depositions on patterned surfaces

With the ability developed to control the wetting shape of droplets on the micropylamid substrate, the next step of work would be to exam the corresponding particle deposition pattern. With suspended particles in the solution, the wetting and evaporation dynamics of the droplet could be changed. As uniform coverage is usually preferred in the real application, the spatial distribution of particles needs to be checked, such as the “coffee ring” effect and the crack formation. And considering the relative scale between the size

of the suspended particles and the surface structure, it remains an interesting topic that how the particles deposit into the local surface asperity.

3. Simulation of droplets drying on patterned surfaces

In this study, the wetting behavior on the patterned surface was studied by experimental observation and surface energy analysis. The droplet wetting preference was found to vary a lot along different surface orientations. In the case of a drying droplet with multicomponent solution, the wettability of the liquid changes as the solutes enrich. This complexity in surface structure and liquid property calls for more accurate modeling of the wetting phenomenon. In the future, simulation work can be carried out to model the droplet wetting state on this micropyramid pillar surface. This can improve our understanding of how the wetting behavior is correlated with the local surface structure and can help us to explore more wetting behaviors on various structures easily.

Achievements

1. Published papers

- [1] **J. Ren**, A. Crivoi, and F. Duan, Dendritic nanoparticle self-assembly from drying a sessile nanofluid droplet. *Physical Chemistry Chemical Physics*, 2021.
- [2] **J. Ren**, F. Duan. Recent progress in experiments for sessile droplet wetting on structured surfaces. *Current Opinion in Colloid & Interface Science*, 2021, 101425.
- [3] M. B. Tanis-Kanbur, V. Kumtepli, B. B. Kanbur, **J. Ren**, and F. Duan. Transient prediction of nanoparticle-laden droplet drying patterns through dynamic mode decomposition. *Langmuir*, 37(8): 2787-2799.
- [4] **J. Ren**, A. Crivoi, and F. Duan, Disk-Ring Deposition in Drying a Sessile Nanofluid Droplet with Enhanced Marangoni Effect and Particle Surface Adsorption. *Langmuir*, 2020, 36(49): 15064-15074.
- [5] L. Shen, **J. Ren**, and F. Duan, Surface temperature transition of a controllable evaporating droplet, *Soft Matter*, 2020, 16(41): 9568-77.
- [6] **J. Ren**, X. Zhong, L. Shen, and F. Duan, Hydrodynamic pattern in drying saline droplet with suspended nanoparticles, *Journal of Bionic Engineering*, 2020, 17(4): 802-808.
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- [8] X. Zhong, **J. Ren** (equivalent first author), K. S.-L. Chong, K.-S. Ong, and F. Duan, Controlling Octagon-to-Square Wetting Interface Transition of Evaporating Sessile Droplet through Surfactant on Microtextured Surface. *ACS Applied Materials & Interfaces*, 2018, 10(14): 11425-11429.
- [9] X. Zhong, **J. Ren**, M. Lin, K. S. L. Chong, K.-S. Ong, and F. Duan, Octagonal Wetting Interface Evolution of Evaporating Saline Droplets on a Micropyramid Patterned Surface. *ACS Applied Materials & Interfaces*, 2017, 9(33): 28055-28063.
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2. Awards

- (1) Best paper award of The 7th International Multidisciplinary Conference on optofluidics 2017.

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