Evaporation of sessile nanofluid droplet

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

EVAPORATION OF SESSILE NANOFLUID DROPLET

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**SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING**

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EVAPORATION OF SESSILE NANOFLUID DROPLET

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Abstract

Sessile nanofluid droplet evaporation is receiving increasing attention lately due to its potential in various applications requiring controlling of the solutes morphology after liquid drying. Despite extensive progress, the understanding still remains elusive about how the deposited morphology is affected and produced owing to the numerous interrelated factors of a nanofluid droplet system. I investigate sessile nanofluid droplet drying in respect to the domains of colloidal suspensions, base solutions and solid substrates. In respect to suspensions, the addition of mono graphite nanoparticles is found to reduce the droplet wettability, enhance the contact line pinning effect, and induce a slight spreading at the initial stage of evaporation. By using proper combinations of dual-sized alumina nanoparticles, the heterogeneities of the two single-sized nanoparticle patterns are eliminated, and a uniform mixture pattern is produced. Besides, the mixture pattern assembled by two nanoparticle species either exhibits both the features of the single-species patterns or resembles one of them. In respect to the base solution, we probe the flow paradigms during evaporation from two aspects. One is employing water-ethanol binary droplets to examine the effect of ethanol concentration. The binary droplets display three distinct flow regimes. The relative weighings of Regimes I and II are enhanced and Regime III is shortened upon raising the ethanol component. The ethanol dependent weighings of the three regimes determine the congregation and trajectories of the nanoparticles and thus the final deposition. The other study for base solution is probing the autophobic effect induced by cationic surfactant cetyltrimethylammonium bromide in sessile droplets. For the pure droplet, below the critical micelle concentration of the surfactant, the droplet dominated by the autophobic effect exhibits two distinct phases of depinning: Phase 1 featuring rapid droplet shrinkage, and Phase 2 characterized by slower droplet receding. The velocity of the three-phase contact line in Phase 1 shows a transition as the surfactant concentration increases above 0.042 mM, while such a transition is absent for Phase 2. Besides, the spreading of the sessile

droplets as they form before the retraction and the maximum contact angle led by dewetting are found regularly dependent on the surfactant concentration. For graphite nanofluid droplets, the autophobic effect is enhanced upon increasing the nanoparticle concentration. The deposited morphology evolves to a distinct coffee ring with a loading of the surfactant, owing to the surfactant adsorption at the nanoparticles surface and the liquid-solid interface, which repels the nanoparticles from the liquid-vapor and the liquid-solid interfaces. In respect to the solid surface, the substrate temperature was varied to find its role in controlling the flow patterns and the stain morphology. The deposited patterns transforms from a disk-like profile to a dual ring from cooling to heating of the substrate. The droplet on the substrate at low a temperature reveals three primary stages. Stage I features the outward transports of nanoparticles along the liquid-vapor interface near the droplet edge. Meanwhile some nanoparticles deposit on the solid surface with a distance to the contact line. In the central region, nanoparticles are dominated by Brownian motion, so they fluctuate irregularly around their positions. Stage II is characterized by the enhanced outward travellings of the nanoparticles in the bulk, leading to a pronounced coffee ring. Most nanoparticles in Stages I and II are central-concentrated, leaving an annular gap sparsely covered adjacent to the outer ring. In Stage III, the pattern is homogenized by filling the gap of the interior nanoparticles. Upon increasing the substrate temperature, the accompanied flow pattern displays a transition when the substrate is still remained cooler than the atmosphere. It is attributed to the evaporative cooling at the droplet apex counteractive to the applied temperature gradient by substrate cooling. Above the transition temperature, the induced inward Marangoni flow takes place earlier at a higher substrate temperature, and in conjunction with the outward radial flow, a dual ring pattern is formed. Recommended future works comprise the employments of dual-sized fluorescent spheres to examine the size-dependent motion of spheres, textured substrates for distinct droplet dynamics, and the infrared thermographic technique for detecting the temperature profile of droplet free surface.

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Nomenclature

Symbols

C_{nano}	Nanoparticle concentration [g/L]
C_{surf}	Surfactant concentration [mM]
C_0	Constant
D	Droplet diameter [mm]
D_0	Initial droplet diameter [mm]
E	Energy for pulling a particle away from a liquid-vapor interface [J]
E_0	Energy in precursor film of droplet [J/m ²]
f	Tension acting at contact line [dyn/cm]
F_b	Friction force [N]
F_{st}	Surface tension force [dyn/cm]
g	Gravitational acceleration [m/s ²]
h	Droplet height [m]
j	Evaporation flux [kg/m ² s]
j_0	Evaporation flux at droplet centerline [kg/m ² s]
K	Evaporation rate constant [mm ² /s]
k_L	Droplet conductivity [W/mk]
k_S	Substrate conductivity [W/mk]
k_R	The ratio of k_S to k_L
L	Capillary length [mm]
m	Mass [kg]
n	Constant
r	Distance from droplet center [mm]
R_0	Initial droplet radius [mm]
R_S	Particle radius [μ m]
S	Spreading coefficient [dyn/cm]
t	Time [s]

t_c	Time scale of evaporation [s]
t_i	Inertial time scale of contact line [s]
t_0	The time droplet stops spreading [s]
U	Contact line velocity [$\mu\text{m/s}$]
$\bar{U}_1$	Contact line velocity for Phase 1 [1/s]
$\bar{U}_2$	Contact line velocity for Phase 2 [$10^{-3}/\text{s}$]
V	Droplet volume [μL]

Greek symbols

α	Aspect ratio
γ_{LV}	Liquid-vapor surface tension [dyn/cm]
γ_{SL}	Solid-liquid surface tension [dyn/cm]
γ_{SV}	Solid-vapor surface tension [dyn/cm]
δ_0	Film thickness [nm]
θ	Contact angle [$^\circ$]
θ_{max}	Maximum contact angle [$^\circ$]
$\Delta\theta$	Contact angle increment [$^\circ$]
$\Delta\theta_0$	Contact angle increment at 0.14 mM of C_{surf} [$^\circ$]
$\hat{\theta}$	Contact angle [rad]
λ	Function of $\hat{\theta}$
μ	Dynamic viscosity [Pa·s]
$\Pi(e)$	Electrostatic disjoining pressure [dyn/cm ²]
$\Pi(m)$	Molecular structural disjoining pressure [dyn/cm ²]
$\Pi(\delta)$	Disjoining pressure [dyn/cm ²]
$\Pi(st)$	Structural disjoining pressure [dyn/cm ²]
$\Pi_0(\delta_0)$	Sum of capillary pressure and hydrostatic pressure [dyn/cm ²]
ρ	Droplet solution density [kg/m ³]

ρ_v	Vapor density [kg/m ³]
τ_{max}	Wetting tension [dyn/cm]

Overscripts

–	Average values of parameters
---	------------------------------

Superscripts

<i>crit</i>	Critical values of parameters
-------------	-------------------------------

Abbreviations

CA	Contact angle
CCA	Constant contact angle
CCR	Constant contact radius
cmc	Critical micelle concentration
CTAB	Cetyltrimethylammonium bromide
EDX	Energy dispersive X-ray spectroscopy
IPA	Isopropyl alcohol
PIV	Particle image velocimetry
p.z.c.	Point of zero charge
SEM	Scanning electron microscope
SDS	Sodium dodecyl sulfate

Chapter 1

Introduction

1.1 Background

A ring-shaped stain has been ubiquitously observed in our daily lives left from spilled coffee, soup and many other drinks. Deegan, et al. [1] examined such a phenomenon and explained the “coffee-ring effect” for the first time. Such a finding breaks the conventional impression that particle deposition from evaporating sessile droplets appears to be a rather simple problem. It involves plenty of interlaced factors, such as the interactions among phases of liquid, solid, vapor and particles, interfacial behaviors, flow paradigms, droplet evaporative dynamics, and so on. Initiated by various applications of particles assembly after liquid evaporation, such as micro-assay chip manufacturing [2, 3], miniature photonic band-gap materials [4], inlet-printing [5, 6] and DNA molecule deposition process [7], strategies and interventions in a variety have been invented to achieve desirable deposition patterns. But so far the field is still far beyond fully understanding, and further investigations are necessary especially for enriching the fundamental knowledge of sessile nanofluid droplet evaporation.

1.2 Motivation

Evaporation of a sessile droplet containing suspended nano/micro- or other sized particles is a complicated problem with numerous interrelated parameters. Through controlling these parameters the deposited solutes profile can be varied to meet the requirement of various applications. For instance, employing mixed solvents for ink-jet printing can improve printing quality by producing uniformly distributed ink solutes (silica particles), in contrast to the ring-like deposits from

conventional water-based ink droplets [8]. Despite of the plenty studies stressing on suspension droplets evaporation, many phenomena and problems are still remained unexplored. I decompose the field of nanofluid droplet evaporation into three major aspects frequently investigated: the particles suspended in the droplet, the base solution and the solid surface. For the suspended particles, mono-species is a common choice aiming to study the effects of particle size [9], shape [10], surface charge in an aqueous solution [11], hydrophobicity and concentration [12]. So far studies addressing the problem of particle mixtures are few, and most of which focus on the size effect of particles and the features of patterns formed by each mono-sized particles [13]. How the pattern is affected by the ratio of different sized particles, and how it is related to the droplet evaporative dynamics are rarely probed. Combinations of different nanoparticle species is another gap, particularly whether the mixture could be adopted to control the morphological profile after droplet evaporation.

The domain of base solutions has attracted much attention lately due to its effective control of the flow paradigms of droplets. Hitherto popular interventions include employing different liquids, liquid mixtures, and adding surface additives. Binary droplets of water and a more volatile liquid such as alcohol, for instance, have been shown to generate three evaporation regimes [14,15]. But it is unknown how each regime is affected by the ratio of the liquid mixture, and what is the deposited pattern resulting from such flow regimes if the droplet is added with nanoparticles. Employment of surfactant is another broadly adopted approach to vary the flow inside the droplet, mainly attributed to its reduction in liquid-vapor surface tension which could enhance liquid wettability and induce the associated Marangoni flows [16]. Surfactant adsorption at the solid-vapor interface which brings the autophobic effect [17, 18] has been rarely related to sessile droplet, especially if the droplet contains insoluble solutes. How the autophobic effect varies droplet dynamics and particles deposition is of great interests since it breaks a new path for the manipulation of the stain profile from droplet drying through

employment of surfactant.

Substrates with different properties exert great influence on droplet evaporation as well. Energy conduction through solid substrates in conjunction with non-uniform evaporation along the droplet free surface could result in local evaporative cooling effect at the liquid-vapor interface and the accompanied thermal Marangoni flows. It sheds light on the control of deposited patterns by simply varying the solid substrate temperature [19]. Plenty studies have reported the greatly enhanced inward Marangoni flows along the liquid-vapor interface by raising the substrate temperature. However, substrate cooling, which is expected to generate a reversed temperature gradient of a droplet, received not as much attention. It is stimulating to obtain the deposition evolution resulting from cooling to heating of the solid surface.

1.3 Objectives

The objectives of the study are to improve the understanding the phenomena of sessile nanofluid droplet evaporation under various experimental conditions, and to provide strategies with the potential to manipulate the deposition patterns of nanoparticles. We concern three major aspects of nanofluid droplet evaporation: the suspended particles, the base solution and the solid surface, and corresponding to which I investigate the single species and mixtures of nanoparticle, the base fluid in terms of water-ethanol binary liquids and aqueous surfactant solutions, and the substrate temperature from cooling to heating conditions, respectively. The present work examines the evaporative dynamics, the flow regimes inside droplets, nanoparticles trajectories, particle-particle interactions, the interplay among the particles and the liquid-vapor and the liquid-solid interfaces, and the energy transport correlated with phase change.

1.4 Scope

Chapter 2 is a literature review in the field of nanofluid droplet evaporation from two major aspects that how nanoparticles affect droplet dynamics including contact line dynamics, evaporation rate, and evaporation regimes, and that the flow patterns and the deposited profiles generated from colloidal droplet drying.

In chapter 3, nanoparticles of mono-, dual-species, and dual-size are employed to investigate nanoparticles role in the droplet wettability, the evaporative regimes, and the deposited pattern. For dual-sized nanoparticles, it is found how the pattern is homogenized under specific ratios of the particles with different size. For dual-species nanoparticle, the distribution of each species in the mixture pattern is examined, reflecting the role of each nanoparticle species in determining the evaporative dynamics and the final deposition.

In chapter 4, the base solutions are manipulated by using water-ethanol binary liquids with various ethanol concentrations, and the CTAB surfactant aqueous solutions with a wide range of the surfactant concentration including the critical micelle concentration (cmc). It is investigated about the dependence of flow regimes on the ethanol concentration, and how these regimes determine nanoparticles motion. The surfactant-induced autophobic effect is studied in relevance with the depinning behavior of the contact line and the stains evolution with an increase of the surfactant concentration.

In chapter 5 the substrate temperature is altered from cooling to heating conditions to impose a temperature gradient on the sessile droplets and create accompanied flows. The variation of the flow paradigms is obtained as the substrate changes from being cooler to warmer than the atmosphere, resulting in the deposited profiles of nanoparticles with distinctly different features.

Finally, chapter 6 presents the conclusions drawn from chapter 3 to chapter 5, and a few future recommendations. The future recommendations concern the employment of dual-sized fluorescent spheres with different size and emission

spectrums, textured solid substrates with applied temperature gradient, and thermographic technique to investigate the temperature profile of droplet free surface.

Chapter 2

Literature Review

It is a universal phenomenon that a liquid droplet evaporates when it is surrounded by its unsaturated vapor. The commonly observed cycle of water in nature is an example of the water vapor condensation and liquid evaporation of droplets or other forms [20]. When a droplet contains insoluble particles, a deposition pattern would be formed on the solid surface. The movement of particles is correlated with the mode of droplet evaporation and the dynamics of the three-phase line. The coffee ring, for instance, was formed by solutes or suspensions driven by an outward flow in a pinned droplet [1,21,22]; the uniform pattern could be produced by controlling the evaporation kinetics and particle interactions at the liquid-vapor interface [23]; the concentric rings were composed as a result of alteration of pinning and depinning behaviors of the three-phase line [24–26]. Thus, it is crucial to study the evaporative dynamics of a sessile droplet and the influence resulting from the solutes. Droplet shape, spreading dynamics, evaporation rate and evaporation regimes are the factors affected by the addition of particles. Controlling particles organization and final deposit patterns can be achievable from further understanding of droplet evaporative dynamics. Changing a number of intrinsic parameters and external conditions could generate diverse deposition patterns, including the central-congregated bump [27], combined structures and highly ordered organization of particles as well as the three aforementioned patterns. These distinctive patterns are presented in different applications. The coffee-ring effect, for example, was shown in the ink-jet printing [28], while a stretched individual particle was desirable in the DNA deposition process [7].

In this chapter, I primarily stress on the evaporation of droplets containing nano-sized particles, known as the nanofluids. Nanofluids are a kind of engineered colloidal suspensions that exhibit distinctive properties, such as thermal

conductivity [29, 30], heat capacity [31] and viscosity [32, 33], as compared with pure liquids. The dynamic drying and the evaporative-induced self-assembly in a sessile droplet significantly depend on the type, size and shape of nanoparticles. In addition to highlight nanoparticles role, I mainly emphasize the general concepts of sessile droplet and the major mechanisms controlling liquids flow. Spreading dynamics, evaporation rate and evaporation regimes are the three aspects exhibiting varieties due to the presence of nanoparticles. Afterwards, a series of experimental approaches to control flow paradigms, the transport and the self-assembly of nanoparticles via manipulating suspensions, base solution and solid substrates are explicated. It is worth noticing that some investigations concerned the effect of colloidal particles which were not nanoparticles, as they also shed light on the dynamics, the complex evaporation and the deposition processes of sessile droplets.

2.1 Dynamic Evaporation of Nanofluid Droplets

In comparison with pure liquid droplets, droplets containing nanoparticles show a great variation in spreading, evaporation and liquid flow. These variations caused by nanoparticles are mainly revealed here by static contact angle, contact line motion, evaporation rate and evaporation regimes of drying droplets.

2.1.1 Effect of Nanoparticles on Spreading Dynamics

There are two primary stages constitute the spreading of a sessile nanofluid droplet on a solid surface. Once a droplet is touched with a solid surface, it undergoes a rapid spreading driven by capillary force and gravity force, until it reaches an equilibrium state. The process is relatively short and the droplet could soon reach balance. Then it comes into the second stage when a wedged film ahead of the bulk droplet has formed. Nanoparticles tend to arrange orderly in the film, resulting in an additional pressure, known as the disjoining pressure which

enhances the spreading behavior. To elaborate the effect of nanoparticles on droplet spreading, more attention should be paid to both static wetting and dynamic wetting of droplets. To reflect them, static contact angle and contact line motion are investigated respectively.

2.1.1.1 Static Contact Angle

When a droplet sits on a smooth and homogeneous surface without any fluid motion, its contact angle in Fig. 2.1, is static contact angle, which is normally used to define the static wetting behavior of liquids on a substrate. The Young's equation in Eq. 2.1 was proposed to describe static contact angle and surface tensions at the contact line of a droplet under static state [34].

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

where γ_{LV} , γ_{SV} , and γ_{SL} are the liquid-vapor, solid-vapor, and solid-liquid surface tensions respectively. Noted that Young's equation describes an ideal situation with a smooth, rigid, and homogeneous surface. Contact angle hysteresis is neglected and the effects of droplet size and possible depositing ways are not considered. In reality, the defects of a solid surface are normally inevitable, and thus the observed contact angle on a non-ideal solid surface is within a range of value instead of solely one. However, the contact angle in Young's equation can still be used locally for both smooth and non-smooth solid surfaces, in order to reflect the relative strength of molecular interactions, known as the wettability among liquid, solid, and vapor phases. Strong wettability usually results in a relatively small contact angle while poor wettability leads to a larger contact angle. One key factor used to determine wettability and contact angle is whether the solid surface is hydrophilic or hydrophobic. Förch, et al. defined that the solid surface was hydrophilic if the contact angle was smaller than 90° ; otherwise, it was hydrophobic [35].

Adding nanoparticles into droplets has been widely found to vary static contact

Figure 2.1: The contact line and contact angle of a sessile droplet.

angle considerably. One essential reason was the deposition of nanoparticles that could vary the superficial characteristics of solid surfaces, such as local roughness and topography. Moreover, adsorption of nanoparticles in the vicinity of a three-phase line was experimentally found to modify the liquid-solid surface tension evidently [36]. The modified superficial characteristics and the liquid-solid surface tension were considered to be the main reasons for the greatly enlarged contact angles in the experiments of droplets with added titanium oxide (TiO_2) [37] and aluminium (Al) nanoparticles [36] at low concentrations as compared to the pure liquid droplets. The case of TiO_2 nanoparticles demonstrated that TiO_2 clusters were more likely to deposit at the location with a distance away from the contact line. The non-uniform deposition of TiO_2 clusters could form a heterogeneous surface: the area covered by TiO_2 clusters was more hydrophilic, while the contact line region was more hydrophobic due to less TiO_2 residuals. The hydrophilic area had higher surface energy than the hydrophobic contact line region, and thus the contact line tended to absorb towards the hydrophilic area, accordingly shrinking the wetting area and enlarging the contact angle [37]. This enlargement in contact angle due to nanoparticles was also observed by Vafaei, et al. [38]. Besides the altered surface tension and the nanoparticles assembly near the contact line, they concerned that the enlarged contact angle might also result from a repulsive force between the negatively charged carboxylic groups of the nanoparticles and the hydroxyl groups on the silicon wafer. The electrostatic-interacting force depended

on the nature of nanoparticles as they could be charged either positive or negative in suspensions. Notably herein the contact angle increased only when the nanofluid concentration was relatively low. At a relatively high nanofluid concentration, agglomeration and clustering of nanoparticles had a higher chance to occur, which had been corroborated by Radiom, et al. in their experiment [37] that the larger effective size of nanoparticles was able to prevent nanoparticle aggregates from accessing the wedged film region, so the number of available nanoparticles taking effect in varying the contact angle could be reduced. It was consistent with the experimental outcome obtained by Vafaei, et al. [38], that smaller-sized nanoparticles led to greater change in contact angle, and that as the nanoparticle concentration increased to a point the contact angle reached the apex and then declined. The ascending and then descending trend was observed as well by adding sub-micron polystyrene beads at different sizes [39], and bismuth telluride (Bi_2Te_3) [40].

2.1.1.2 Contact Line Motion

Contact line shown in Fig. 2.1 for a sessile droplet is a three-phase line where liquid, vapor and solid surfaces coexist. The dynamic motion of a contact line reveals the evolution of the droplet shape, and the deposition patterns if the droplet contains particles. Pinning, depinning, and stick-slip are three primary behaviors of a contact line, resulting in coffee rings, relatively uniform patterns, and concentric rings respectively [24, 41].

In order to detect liquid movement during droplet spreading, Dussan and Davis [42] added a dye into the upper surface of the wedge-shaped film of a droplet, and found that the dye transported to the edge first, and then got stuck to the solid surface, representing a rolling trajectory. Therefore, the energy burned in a way of viscous friction mainly in three regions [43]: (1) the wedged region representing the nominal contact line; (2) the precursor film ending up with a real contact line; and (3) the real contact line. The addition of nanoparticles was found to vary the energy

in Regions (1) and (3) through the particles deposition, and changed surface tension and viscosity accordingly [32]. The effect of nanoparticles on energy dissipation in the precursor film is primarily resulted from nanoparticles self-assembly in the thin film ahead of a droplet. Due to the narrow space of the film confined by the liquid-solid and liquid-vapor interfaces, there is an induced excess pressure, defined as the disjoining pressure, $\Pi(\delta)$, driving the liquid in the film into motion [44]. $\Pi(\delta)$ comprises three components: the structural component Π_{st} , the molecular component Π_m and the electrostatic component Π_e . Among them, Π_{st} could be induced by nanoparticles layer-by-layer assembly in the thin film, within which Π_{st} was found to dominate on scales larger than the effective diameter of a nanoparticle, and below which Π_e and Π_m were dominant [45,46]. The energy dissipated due to Π_{st} has an oscillatory exponential decay with the increasing film thickness, which corresponds to nanoparticles self-assembly in the thin film [45,47,48], as shown in Fig. 2.2.

Figure 2.2: Structural disjoining pressure over the film thickness of a droplet. Nanoparticles self-assemble orderly in the film [45].

The function of the energy in the precursor film, E_0 , can be expressed as,

$$E_0 = US, \quad (2.2)$$

$$S = \prod_0(\delta_0)\delta_0 + \int_{\delta_0}^{\infty} \prod(\delta)d\delta \quad (2.3)$$

where U is the liquid velocity; S is the spreading coefficient, identifying whether a droplet can spread or not; $\prod_0(\delta_0)$ is the sum of capillary pressure and hydrostatic pressure; and δ_0 is the equilibrium thickness of the film. Equation 2.3, known as the Frumkin-Derjaguin equation, indicates that any change in disjoining pressure would lead to the change in E_0 , and thus vary the spreading behavior of the droplet.

The induced structural disjoining pressure and the varied superficial characteristic of the solid surface due to nanoparticles deposition have been confirmed to promote the pinning effect of the droplet. Compared to that of a pure liquid droplet, the contact line of a nanofluid droplet might be prevented from receding since it would pass through nanoparticle residuals on the way of sliding back. Joanny and de Gennes [49] proposed a model to describe this phenomenon by considering a deformation of a contact line due to the presence of a single circular defect. It was found that the contact line deformed around the defect but stayed intact away from it. Many experimental studies verified the enhanced pinning effect led by nanoparticles [37, 51–55, 146]. In a study of microliter-sized droplets containing 250 nm gold particles, the droplet drying exhibited a second pinning stage rather than the behavior of a pure liquid droplet, revealing a significantly pronounced pinning effect [53]. This was possibly due to an increase in the disjoining pressure as a result of particle-ordering in the meniscus-film region [146].

One essential factor determining the pinning effect of the contact line is the geometry of the particle which affects the way the particles interact and organize. The commonly employed spherical particles are able to form a coffee ring effortlessly, as they are easy to transport to the periphery and fix the contact line. Marin, et al. investigated the orderly-formed coffee ring by spherical microspheres and found that the ring region displayed an order-to-disorder transition, as shown in Fig. 2.3. Spheres arrived at the outermost part of the ring organized as square,

Figure 2.3: Particle ordering in the coffee ring stain. (a) Overview of the different patterns in the ring. (b1)-(b3) A close-up reveals the sequence of patterns in the stain: square packing close to the contact line (b1), followed by hexagonal packing (b2), and finally disordered packing (b3) [56].

followed by a hexagonal arrangement, and then a disorder assembly [56]. This was attributed to the accelerated velocity of the spheres in the proceeding of evaporation of a pinned droplet. This transition was also observed by using hard spheres at microscale [57], silicon dioxide (SiO_2) nanoparticles [58, 59], and polystyrene latex [60]. The transition of self-organization at the contact line region was also manifested in the droplets containing spindly carbon nanotubes (CNTs) [61–63]. CNTs, in particular the single-wall carbon nanotubes (SWNTs), were observed to be driven by a capillary flow in the sessile droplet, and tended to align in parallel to the periphery to form a monodomain. In the region away from the contact line, nanotubes deposited more randomly [63]. Similar outcomes were found by Li, et al. The transition from parallel to random organization was related to the proceeding of the evaporation. At an early stage, CNTs preferred to direct themselves along the contact line due to a strong edge effect; as the deposition proceeded, the edge effect was less strong, thus CNTs began to orient along the direction of the radial outward flow [61]. Zeng, et al. ascribed the parallel and the perpendicular assemblies to capillary force and fingering instability at the contact line respectively. They obtained the desirable assemblies of CNTs based on manipulation of these two mechanisms with appropriate configurations of the wedge. [62]. In the above reports, the coffee-ring effect was present during the entire evaporation. With the

employment of ellipsoidal particles, however, the coffee-ring effect was suppressed as reported by Yunker, et al. The aspect ratio, α , was applied to represent the shape of the particles. The spherical particles, $\alpha = 1$, produced a typical coffee ring deposition. When α was 3.5, the ellipsoids particles organized into a uniform deposition. The elongated shape of the particles was found to enhance the long-ranged particle-particle interactions, and thus led to loosely-packed aggregates at a relatively large scale which prevented particles from transporting to the droplet edge. Besides, the ellipsoidal particles easily adhered to and thus deformed the liquid-vapor interface [10]. Although the droplets containing both kinds of the particles remained pinned on the solid surface during evaporation, the amount of the spherical particles depositing at the contact line region was way larger. It is extrapolated that the droplet containing spheres displayed a stronger pinning effect.

2.1.2 Evaporative Rate of Nanofluid Droplet

In most calculations of evaporation rate for pure liquid droplets, two assumptions are made: (1) the evaporation process is treated as a quasi-steady state, and (2) vapor is transported solely by diffusion (convection is neglected). These assumptions stemmed from the well-known Maxwell-assumption [64]. Under specific conditions, such as the liquids with large saturation vapor concentration values, transient and convection terms should be taken into account as they contribute a nontrivial portion to the evaporation [65]. Evaporation was found to occur non-uniformly along the droplet interface, resulting in varied temperature field and flow dynamics within the droplet [1, 66, 67]. The evaporation rate on the unit area of a droplet liquid-gas interface is defined as the evaporation flux, j , which was early solved by Deegan, et al. [1],

$$j = j_0 \left(1 - \left(\frac{r}{R_0}\right)^2\right)^{-\lambda(\hat{\theta})} \quad (2.4)$$

where j_0 is the evaporation flux at the centerline of the sessile droplet surface, R_0 is the initial radius of the droplet, r is the distance from the droplet center, and $\hat{\theta}$ is the contact angle in radians. λ is a function of $\hat{\theta}$ and is expressed as,

$$\lambda(\hat{\theta}) = \frac{\pi - 2\hat{\theta}}{2\pi - 2\hat{\theta}} \quad (2.5)$$

As illustrated in Fig. 2.4, Deegan, et al. showed that the evaporation flux increased along the surface from the centerline to the edge of the droplet, thus an outward flow was induced to replenish the evaporation loss there [1,21,68].

Figure 2.4: Evaporation flux j increases along the droplet interface from the center to the edge of the droplet [1]. R_0 is the initial droplet radius, j the evaporation flux, and $\bar{v}$ the radial velocity, and h is the droplet thickness.

Most of the subsequently developed formulas of evaporation rate were with different assumptions from Deegan, et al. [1,68]. By using the finite element method (FEM), Hu and Larson [69] numerically predicted the evaporation flux by applying the vapor concentration above the droplet as a boundary condition. The numerical solution was comparable with their experiments with 750 nm fluorescent particles in their experimental droplets.

Nanoparticles in a sessile droplet was considered to influence evaporation in three primary aspects: (1) the pinning effect of the contact line could be enhanced by nanoparticles. Different from that in a pure liquid droplet, such a pinned state in a drying nanofluid droplet was prolonged conspicuously on the planar substrate [70], rough heated substrate [36] or superhydrophobic surfaces [53]; (2)

a higher nanofluid viscosity than its pure liquid in most cases could slow down the outward flow mentioned by Deegan [21] in sessile droplets, and reduce the evaporation primarily occurring at the edge. The limiting effect due to the increased viscosity was verified in the investigations of gold nanofluid droplets [53] and the Al nanofluid droplets [36]. The evaporation rate of the nanofluid droplet at its pinning stage was slower than the relative pure liquid droplet with the same base diameter. But nanoparticle helped spreading the droplet base diameter and extending the pinning period, which is discussed later in this chapter. The relatively larger surface area would facilitate the overall evaporation rate of the nanofluid droplet [36]; and (3) nanoparticles could cover the liquid-vapor interface, resulting in a varied liquid-vapor surface tension and thus an affected evaporation rate. Therefore, with different types of nanoparticles, the evaporation rate could be either enhanced or attenuated as compared to the base fluid droplet. In the experimental investigation of Moghiman and Aslani [71], iron oxide (Fe_2O_3), zirconium dioxide (ZrO_2), or nickel/iron (Ni/Fe) nanoparticle addition into droplets was observed to reduce evaporation, while the presence of clay nanoparticles increased evaporation. The viscosity and surface tension of Fe_2O_3 nanofluids were both increased. Contrarily, the clay nanofluid had a reduced surface tension. Another experimental study with the employment of diverse types of nanoparticles showed different trends of evaporation rate as well [72]. Based on the D^2 -Law ($D^2=D_0^2 - Kt$, in which D is the instantaneous diameter, D_0 the initial diameter, K the evaporation rate constant, and t is the consuming time), the nanofluid droplets exhibited various K in comparison with the pure liquid droplet. It was deduced that the value of K was basically inversely proportional to the latent heat of vaporization. The presence of nanoparticles was found to enlarge the latent heat of vaporization so the K value was reduced. During the evaporation, as the nanofluids were concentrated, the K value exhibited a transition as the nanofluid concentration reached a critical value, and it was observed in both gold and Fe_2O_3 nanofluid droplets.

Combined with nanoparticles, the factors involving humidity, fluid convection,

and radiation have been taken into account as well. In respect to the effect of humidity, its variation along the droplet free surface was created by making droplets sit close to each other so the humidity was higher in the neighboring regions. It turned out that arches could be formed after evaporation. In the area with higher humidity the evaporation rate was slower while the particles agglomerated in the places where the drying was faster. It is suggested that the effect of humidity on the evaporation rate cannot be neglected [73].

Compared to the influence of humidity, the imposed force-convection affects droplet evaporation more evidently. In the study of Gan and Qiao, the evaporation obeyed the D^2 -law for the ethanol-based nanofluids under weak convection, but a deviation was observed likely at a higher particle concentration and for the base fluid with a higher boiling point under natural convection at a relatively low temperature. Therefore, evaporation lifetime could be an important indication to evaluate whether the deviation of the D^2 -law would happen. A long evaporative lifetime could increase the feasibility of particle aggregation, which could inhibit diffusion and slow down the evaporation rate [73, 74].

Radiation is another thermal factor exerting influence on droplets evaporation. Resembling the pure liquid droplet, the nanofluid droplets with Al, aluminum oxide (Al_2O_3), CNTs, multi-walled carbon nanotubes (MWCNTs), and carbon nanoparticles (CNPs) which have different radiation absorption levels were compared [31, 75]. The evaporation rates of the ethanol-based nanofluids containing MWCNTs and CNPs exhibited higher values than the others [75]. The radiation energy was discussed to be absorbed by nanoparticles, leading to an increased particle temperature and a temperature difference between nanoparticles and the surrounding liquids. Thus the convection in nanoscale took place and the radiation energy was dissipated accordingly. However, with a loading of the Al_2O_3 nanoparticles, the enhancement in evaporation rate was mitigated, which might result from a larger possibility of nanoparticle aggregation that could suppress the energy dissipation and diffusion. Different from Al nanoparticles, Al_2O_3

nanoparticles exhibited a smaller enhancement in evaporation due to a lower radiation absorption level [31].

2.1.3 Effect of Nanoparticles on Evaporation Regimes

A sessile droplet often follows two modes during evaporation or a combination of them: (1) constant contact radius (CCR) mode with a pinned contact line, and (2) constant contact angle (CCA) mode during which the contact area keeps reducing while the contact angle remains unchanged [114]. Hong, et al. [77] experimentally observed both CCR and CCA modes during evaporation of a water droplet deposited on a narrow planar solid surface. The droplet with the initial volume at 11 μL kept pinned with CCR mode until it reduced to 6 μL . From this moment on to 3 μL , the droplet shrank following CCA mode. Chon, et al. showed a sequence of evaporation phases of a strong pinned droplet containing 11 nm Al_2O_3 nanoparticles. As shown in Fig. 2.5, the droplet was pinned just on a micro-heated substrate at first. Induced by liquid evaporation, the strong pinning behavior drove the nanoparticles to the edge. With further evaporation of the base fluid, the contact angle reduced to its critical value, and the thin core liquid region began to break away from the rim, known as the depinning process. The depinned core liquid then shrank towards the center as it dried out further. Finally, the dried ring-shaped nanoparticle stain was formed along the rim [9].

The frequently observed sequence of CCR mode followed by CCA is interesting to many researchers. Zhang, et al. established a model based on the pinning force of the contact line to study this sequence. The pinning force kept the droplet evaporating in CCR mode before the contact angle decreased to its critical value [78]. Another simulation predicted CCA and CCR modes of nanofluid droplets on textured surfaces. It showed that the pinning force was of the molecular origin, and it was the local liquid-solid interaction in the vicinity of the contact line dominating the wetting behavior. A greater characteristic width of the inhomogeneity of the textured surface would generate a larger energy barrier to avoid a hydrophilic

Figure 2.5: Evolution of 11 nm Al_2O_3 nanofluid droplet evaporation with sequential photographs and schematic sketches. Once the droplet is placed on the microheater substrate, it goes through stages of (a) pinning, (b) liquid dominant evaporation, (c) depinning, (d) dryout progress and (e) formation of nanoparticles [9].

pattern, and instead result in a larger pinning force. The pinning of the contact line took place at the beginning of evaporation owing to the large pinning force. While on the textured surfaces with a smaller characteristic width of the inhomogeneity, CCA and mixed modes occurred [79]. Besides, capillarity, Marangoni effects, evaporation and disjoining pressure were all indicated to influence the droplet evaporative regimes in the simulation based on the lubrication theory. The numerical results showed that the droplets exhibited a variety of behaviors including spreading, evaporation-driven retraction, contact line pinning, and the formation of “terrace” [80].

A key point to analyze droplet evaporation is the transition from pinning to depinning. The pinning time or the pinning period, before the contact line starts to recede, is affected by the factors involving the concentration and the size of nanoparticles, droplet sizes and thermal effects. The addition of Al nanoparticles to ethanol droplets, for instance, made the droplet recede at a lower critical contact angle and thus led to a longer pinning stage in comparison with the pure ethanol droplets [36]. The evaporation process could be quite complex, with more than one switch of pinning to depinning behaviors of the contact line, i.e. the stick-slip behavior. Fukai, et al. [81] experimentally investigated the effects of droplet sizes and particle concentrations on the depinning behavior. For the macroscale

xylene-polystyrene droplets, the contact angle at which the contact line began to recede decreased with increasing the initial solute concentration, while the relation between them was indistinct for the microscale droplets. The three-phase line receded even when the contact angle was above the receding contact angle. What is more, the dot-like and the ring-like deposits were produced at different initial particle concentrations. This fact showed that either the pinning duration or the receding distance was an important factor to determine the shape and the dimension of the film. Evaporation rate and surface hydrophobicity were found as another two factors controlling the depinning behavior of contact line. In the experiments of Au (gold) nanofluid droplets on substrates bearing different hydrophobicity, the dependence of the evaporation regimes on the evaporation rate at a superhydrophobic surface was weak. However, a second pinning of the contact line emerged as the evaporation rate was significantly reduced on a planar hydrophobic surface [53].

2.2 Deposition Patterns from Drying Droplet Suspensions

To obtain desirable deposition patterns, designing experiments to control the motion of nanoparticles is a major challenge in the study of nanofluid droplet evaporation. The major aspects of colloidal sessile droplet systems intensively studied are base solutions, colloidal solutes, and solid surfaces. Therefore, in this section it is explicated how droplet dynamics, evaporation and colloidal particle motion vary with diverse experimental conditions in respect to the three domains.

2.2.1 Base Solutions

Fluid flows inside and along the free surface of a sessile droplet are the main mechanisms driving particles travelling through drag forces and particle-interface

interactions. Capillary flows and Marangoni flows are the two primary flow regimes frequently observed in evaporating sessile droplets. As a droplet is placed on a solid surface, the pinned contact line would initiate a radially outward flow to replenish the evaporation loss at the periphery, known as the capillary flow [1, 82]. Consequently, particles in the bulk are driven outward and immobilized near the three-phase line, forming a coffee ring pattern [1] (Fig. 2.6 (a)). But in plenty of applications, uniform depositions are preferred instead of ring-shaped stains, and thus capillary flows need to be suppressed and even eliminated. A Marangoni flow orienting inwards along the liquid-vapor interface of a droplet could work. Marangoni flows induced by surface tension gradients can result from temperature gradients [83] or concentration gradients [16, 82] along the free surface of a droplet. For thermally induced Marangoni flow, namely the thermocapillary flow, its direction was found to be determined by the temperature profile along the sessile droplet surface. The temperature profile was related to the uneven evaporation rate along the droplet radius and the heterogeneous heat transfer from the substrate. A concept of k_R , the ratio of the substrate thermal conductivity k_S to the liquid thermal conductivity k_L , was introduced for determining flow directions [84], as illustrated in Fig. 2.6 (b). Besides the thermocapillary flow, the one arising from concentration gradients received as much attention. A concentration gradient was reported to be achieved by using binary base fluids [14] or adding surface active surfactant in the base solutions [16, 82]. And in the following elucidation I focus mainly on the influence of base solution compositions on the evaporation of sessile droplets.

The understanding of the wettability and the evaporation of pure sessile droplets consists of multi-component liquids has been greatly improved by the studies stressing on binary mixtures consisting of water and a more volatile liquid, such as methanol [85], ethanol [15, 86–89], and 1-propanol [90]. Since the volatile component evaporates faster than water, the evaporation rate exhibits a deviation such that it is more rapid for the former stage than for the latter one. The non-

Figure 2.6: (a) Description of the capillary flow from the center to the edge of a droplet, in which particles are driven outwards [82]; (b) droplets with different relative thermal conductivities $k_R = k_S/k_L$, and the consequent Marangoni flows and the temperature gradients along the droplet surface when $k_R > k_R^{crit}$ and $k_R < k_R^{crit}$. Arrows outside the droplets indicate directions of the increasing temperature; arrows inside the droplets indicate directions of the Marangoni circulations [84].

simultaneous evaporation of the binary components leads to three flow regimes of the droplet, as observed by Christy, et al. [14] shown in Fig. 2.7. The more volatile component in the binary solvent, ethanol, was found to dominate the first regime which was full of vortices. Evaporation in this phase was relatively rapid. In the second regime, Marangoni flows were induced, ascribed to the non-uniform local ethanol distribution at the droplet free surface. The third regime was indicated to be governed by the drying of the left water in the droplet, resembling the evaporation dynamics of a pure water droplet. These findings are consistent with the temporal volume change of a binary droplet that it decreased faster at the initial stage than at the late stage of droplet evaporation [12].

How the three flow regimes of a binary droplet influence nanoparticles motion and the deposited morphology, however, has been barely investigated. Solely one study from Zhong and Duan, [12] employed intermediate ethanol concentrations in aqueous binary droplets with suspended nanoparticles to examine their travelling and deposition. The left patterns of nanoparticles varied greatly upon changing the ethanol concentration. The dried pattern was a reflection of the flow regimes denoted by the movement of nanoparticles within the droplet. As presented in Fig. 2.8, at 10 % ethanol, the regime of vortices ends at around 25 % of the lifetime,

Figure 2.7: Velocity fields of a water-ethanol binary droplet for three flow regimes I, II and III [14].

during which the intense flow drives the nanoparticles to form sporadic aggregates at the droplet surface. Afterwards the fragments are transported to the centerline with the flow at the liquid-vapor interface until 70 % of the lifetime. At a higher ethanol component of 40 %, the termination of the vortices is at roughly 55 %, and the flow towards the centerline almost disappears at 83 % of the lifetime. The gap inside the nanoparticle deposition results from the depinning at the last stage. The distinction of the patterns from these two droplets was attributed to the ethanol-dependent flow paradigms. The induced vortices for the 10 % were not as strong as those for the 40 %, thus the formation rate of the aggregates was low. However, the more intensive flows lasting for a longer time for the 40 % ethanol led to more rapid assembling of the aggregates.

Surfactant addition to sessile droplets has been broadly approved to be an effective strategy capable of altering the deposited morphology of colloidal solutes. Its accumulation near the three-phase contact line has been shown to reduce the local liquid-vapor surface tension, and thus inducing an inward Marangoni flow which brought some solutes to the droplet center. Kajiya, et al. [91] and Still,

Figure 2.8: Snapshots of the water-ethanol binary droplets with suspended graphite nanoparticles and the ethanol concentrations at (a) 10 % and (b) 40 % [12].

et al. [16] reported similar outcomes from such a concentration gradient induced Marangoni flow by employing different types of surfactants. As presented by Fig. 2.9 (a), the presence of the surfactant F489 with a small concentration at 0.05 % alters the polymers film from a ring pattern to a homogeneous profile. They also confirmed that the role of such Marangoni flows, named the levelling effect, worked ubiquitously irrespective to the polymer concentration, droplet volume, and solvent material. Still, et al. [16] utilized the same mechanism and obtained central-concentrated deposits by adopting sodium dodecyl sulfate (SDS) surfactant. Fig. 2.9 (b) illustrates the Marangoni eddies which produce a depletion zone through reversing the orientation of the particles.

On the other hand, surfactant has been found to exhibit counteractive effects on the formation of uniform deposits under certain conditions. Fig. 2.10 demonstrates the deposition transition from an uniform pattern to an edge-concentrated one from two studies. Fig. 2.10 (a) illustrates that the uniformly distributed ellipsoids with the aspect ratio $\alpha = 3.5$ are carried outwards with the addition of surfactant SDS. It was attributed to the decrease in the energy for surface deformation of the liquid-vapor interface, and in the particle-particle interactions. Consequently, the ellipsoidal particles easily detached from the liquid-vapor interface, so they were prevented from assembling into long-chain aggregates [10]. The CTAB surfactant

Figure 2.9: (a1) Schematics of the Marangoni flow induced by concentration gradient of surfactant F489 and the accompanied capillary flow; (a2) the left stain profiles without and with 0.05 % F489 respectively [91]. (b1) Schematics of the Marangoni flow due to the uneven distribution of the surfactant SDS; (b2) the surfactant induced Marangoni eddies in the droplet with suspensions [16].

also has been shown to reduce the sticking force between graphite nanoparticles, as presented by Fig. 2.10 (b). The nanoparticle aggregates uniformly locate in the interior region from the droplet free of surfactant; while the pattern changes to a ring-shaped stain with a small amount of CTAB. The adsorption of CTAB surfactant at the particles surfaces reduced the attractions among them, and thus attenuated their agglomeration [92].

The aforementioned studies reveal that surfactants have non-monotonous effects on deposited patterns such that the pattern uniformity can be either enhanced or attenuated. The mechanism for the non-unidirectional variation of a deposition through adding surfactant is meaningful as it provides us a universal rule of employing surfactant to better control stain profiles. Anyfantakis, et al. [93] found a general character for the correlation between the deposited morphology and the surfactant concentration via an experimental study of various particle/surfactant mixtures. The deposited profile experienced a transition of ring-to-disk or vice versa upon increasing the surfactant concentration in specific particle/surfactant

Figure 2.10: (a) A uniform organization of ellipsoids with the aspect ratio α at 3.5 and (b) a ring formed by ellipsoids with the aspect ratio α at 3.5 when surfactant SDS is added in the droplet [10]. (b) A uniform deposition of nanoparticles from a droplet without surfactant CTAB and a coffee ring produced from a droplet with CTAB [92].

mixtures. Such a change in particle deposition was originated from the electrostatic interactions among particles and interfaces, and the hydrophobic bonding between the non-polar chains of surfactant molecules. Fig. 2.11 presents a general picture to explain the role of particle-interface interactions at low, intermediate and high surfactant concentrations in four combinations of the particle/surfactant mixtures either like-charged or oppositely charged.

At a low surfactant concentration, particles remain their initial surface charge since the adsorbed surfactant molecules oppositely charged are few (Fig. 2.11 (a)), or the adsorption barely takes place when the particle and the surfactant are like-charged (Fig. 2.11 (b)). Herein the electrostatic force attracts the particles to the solid surface and form a pattern with a ring and interior particles. At the same concentration region, electrostatic repulsion prevents the particles from depositing on the solid surface and thus a ring is produced (Fig. 2.11 (g, j)). For

Figure 2.11: Role of particle-interface interactions on the formation of patterns from droplets of different surfactant-particle mixtures either like-charged or oppositely charged [93].

an intermediate surfactant concentration, surfactant-decorated particles through electrostatic attractions lead to neutralization of the particles surface charge, so the particles become more hydrophobic and are directed to locate at the liquid-vapor interface, resulting in disk-like profiles (Fig. 2.11 (b, h)). In like-charged systems, as shown in Fig. 2.11 (e, k), particles maintain their initial charge so rings are generated. For high surfactant concentrations, particle charge reverses in oppositely charged systems (Fig. 2.11 (c,i)), while particles remain the initial charge for like-charged systems (Fig. 2.11 (f,l)). The rule applies to the charge of the solid surface as well. Consequently, particles and the solid surface are always like-charged, and the repulsion between them leads to a ring stain.

On the other side, the well-reported surfactant adsorption at the solid interface [94–97] which could lead to the autophobic effect, has received not as much attraction in terms of its influence in the dynamics of evaporating sessile droplet. Autophobicity can be represented by the shrinkage of aqueous solutions in contact with the solid surface resulting from the reduction of surface energy by surfactant

adsorption [98–100]. As a sessile droplet was made on the silicon substrate, the negatively charged silicon surface can attract the cationic heads of the surfactant molecules, and some of them assemble external to the contact line, leading to the reduction of the solid-vapor surface tension and dewetting of the droplet. So far the broadly employed system for examining the autophobic effect is the Wilhelmy plate technique which requires a vertical solid plate to be inserted into a surfactant solution at a slow rate to induce a stick-slip-retreat behavior of the three-phase line. Limited by the weak mobility of the surfactant molecules across the bare solid surface, the autophobic was widely reported to be irrelevant to the surfactant concentration at a low value for such configuration [101]. For sessile droplets, however, the mechanisms responsible for the dependence of droplet dewetting on surfactant still remain debated, such as the critical concentration of surfactant for the cessation of autophobic effect and the correlation between the contact line retreat and the surfactant concentration [17, 18, 157, 162]. Takenaka, et al [160] demonstrated that the droplet dewetting exhibited a monotonous dependence on surfactant below the critical micelle concentration (cmc), while which is inconsistent with the findings of Frank and Garoff [101] that the contact line retreat is irrelevant to the surfactant inventory below 0.45cmc.

2.2.2 Suspensions

Insoluble solutes suspended in evaporating droplets are proved capable of varying contact angle, evaporation regime, evaporate rate, liquid-vapor surface tension, interfacial deformation and the others, rather than being solely passive indicators for fluid flow trajectory. Numerous studies have found that the size and shape of particles, and their properties such as hydrophobicity and electrostatic charge in water exert great influences in their interactions with the interfaces, their motion during droplet drying, and hence the deposited profiles. A typical example is the alteration of the deposit from a coffee ring to a disk-like profile by replacing the spherical particles to ellipsoidal ones [10], as shown in Fig. 2.12. The shape of the

particle was described by the aspect ratio α , which is 1.0 for spheres and 3.5 for ellipsoids.

Figure 2.12: (a) A disk-like profile formed by ellipsoids with the aspect ratio α at 3.5 and (b) a coffee ring of spheres with the aspect ratio α at 1.0 [10].

Studies in a variety demonstrate different behavior of particles with various sizes in drying sessile drops. One found that microparticles and nanoparticles were transported separately that the smaller ones were driven outwards while the larger ones were carried inwards. The congregation of nanoparticles in the vicinity of the contact line enhanced the pinning effect, which induced a surface tension gradient that drove the microparticles to the droplet center [145]. Weon and Je stated that it was the capillary force that pushed the larger particles inwards [13]. The capillary force near the contact line was found positively proportional to particle size while negatively proportional to contact angle value. The thermal stability of aggregated structures and thus the occurrence of more complex patterns could be enhanced by smaller particles because assemblies of the smaller nanoparticles had much higher cohesion strength than those made of larger ones [103]. By applying the particle-size effect, Wong et al. succeeded in separating organic colloidal particles with different sizes [104]. They obtained patterns composed by proteins, micro-organisms, and mammalian cells which have different sizes. It showed that the particle with a smaller size located near the contact line (Fig. 2.13). These findings have direct implications for developing low-cost technologies for disease diagnostics. Similarly, Hendarto and Gianchandani sorted out the particles with different sizes by manipulating substrate temperature to control the Marangoni effect [105].

Glass cenospheres with different diameters at microscale were separated in the evaporating isopropyl alcohol (IPA) droplets on a smooth glass substrate. When the substrate temperature was at 55°C , larger spheres tended to deposit in the droplet center, but smaller spheres were found everywhere throughout the dried region. At the substrate temperature of 80°C (higher than the boiling point of IPA), most of the smaller spheres were found close to the droplet periphery. Also based on the particle-size effect, Sommer, et al. produced unique circular deposition patterns from binary suspensions containing two different nanospheres in size. It was found that the slow evaporation generated well-ordered structures on a smooth substrate, while the large particles self-assembled in dense hexagonal structures, forming apparently an external ring around the massive inner ring [106].

Figure 2.13: (a) Schematics showing the concept of size-dependent particle separation near the contact line of an evaporating colloidal droplet. (b) Optical fluorescence image showing the separation of 40 nm (green), $1\mu\text{m}$ (red), and $2\mu\text{m}$ (blue) particles after evaporation. (c) A semi-log plot showing the dependence of the coffee ring separation distance (edge-to-edge) on particle concentration. (d) Optical fluorescence image showing the separation of antimouse IgG antibodies (blue), Escherichia coli (green), and B-lymphoma cells (red) in a dried liquid drop [104]

However, opposite motion of particles with diverse sizes was observed in the experiments by using four nanofluids containing 2 nm Au, 30 nm copper oxide (CuO), 11 nm Al₂O₃, and 47 nm Al₂O₃ nanoparticles. The smaller nanoparticles had a tendency to form wider edge aggregation and more uniform central deposition while the larger particles were more likely to congregate at the contact line. To better understand the pattern formation, a schematic illustration of nanofluid droplet evaporation and drying process depending on the particle sizes is presented in Fig. 2.14. Smaller nanoparticles with a higher density and viscosity counteracted the thermally driven nanoparticle motion, resulting in a thicker and more uniform pattern in the central area with a loosely increased width of a ring around. On the other hand, larger nanoparticles with a lower viscosity tended to move to the rim due to the more active evaporation there, and thus led to a highly distinctive ring-shaped stain [9].

Figure 2.14: Schematic illustration of nanofluid droplet evaporation and dryout process depending on particle sizes: (a) a uniform distribution formed by nanoparticles with smaller size and (b) a coffee ring pattern formed by nanoparticles with larger size [9]

2.2.3 Planar Substrate

Solid substrates properties, particularly thermal conductivity and hydrophobicity, exert great impacts on the flow paradigms and the evaporative dynamics of sessile drops. The greatest evaporation at droplet edge correlated with decreased droplet thickness along the radius could result in a heterogeneous temperature profile

along the liquid-vapor interface [20, 107]. As introduced in the previous section, Ristenpart, et al. [84] proposed a quantitative criterion based on the relative thermal conductivities of the substrate to the liquid, k_R , to determine the direction of the thermal Marangoni flow along the droplet surface. The evaporative cooling at droplet rim was normally neglected when k_R was large, since for substrates with high conductivities energy could be provided instantly to the contact line region for mainly replenishing the heat loss resulting from phase change. This study of Ristenpart, et al. [84] implied the role of substrate properties in defining the flow pattern of sessile drops. Xu, et al. [108] further pointed out the dependence of Marangoni flow direction on the ratio of the substrate thickness to the droplet contact radius. The temperature profile along the droplet free surface was also affected by the droplet height. When the droplet was tall, the evaporative cooling could be great owing to the large thermal resistance [109]. Therefore, the effects of substrate thermal conductivity, substrate thickness and droplet height should be involved simultaneously as analyzing the issue of temperature distributions.

Figure 2.15: (a) The variation of the deposition from a disk to a dual ring and to a stick-slip pattern upon increasing the substrate temperature [19]. (b) The variation of the deposition pattern from a coffee ring to coffee eyes with raising the substrate temperature [111].

Although it is aware that a natural evaporation normally gives rise to vulnerable Marangoni flows, to my surprise, only a few studies imposed enhanced temperature

gradients by heating the substrate to strengthen the Marangoni flows. The warmer edge of the droplet and its cooler apex leads to an inward Marangoni flow which drives particles toward the droplet center, as a counteractive to the coffee ring effect. Parsa, et al. demonstrated that the deposit of nanoparticles evolved from a homogeneous profile to a dual ring and then a stick-slip pattern with raising the substrate temperature [19], as shown in Fig. 2.15 (a). The temperature gradient detected by an infrared thermographic technique was found to orient to the droplet edge for both the natural and heating conditions, being consistent with the one obtained by Girard, et al. [110]. In the study of Li, et al., the enhanced thermal Marangoni flow directed plenty of particles to form an interior “eye” enclosed by an exterior ring stain attributed to the radially outward capillary flow [111], as presented in Fig. 2.15 (b).

Figure 2.16: The deposited profile at 22 °C, 30 °C and 38 °C. (b) The height of the deposition along the droplet diameter at various substrate temperatures from cooling to heating conditions [112].

Besides substrate heating, so far solely one study has probed the substrate temperature below the atmospheric one [112]. As shown in Fig. 2.16 (a, b), at the substrate temperatures below the atmosphere, the left polymers are central-

concentrated. While the deposited pattern gradually alters to a ring-shaped profile upon increasing the substrate temperature above the room temperature. The experimental system revealed that the polymers inside the evaporating droplets at the end of evaporation changed directions depending on the substrate temperature.

2.3 Theoretical Studies on Nanofluid Droplet Drying

The theoretical investigation of the sessile nanofluid droplet evaporation mainly stresses on two parts: one is related to the evaporation dynamics around and within a sessile droplet, the other is the motion or deposition behavior of nanoparticles. In the previous sections it is briefly mentioned several theoretical results of evaporation flux and liquid velocity [113–115]. Now only the theoretical studies of the evaporation process and the drying patterns of nanofluid droplet are introduced. The approaches are the Navier-Stokes (N-S) equations, the Diffusion Limited Aggregation (DLA) approaches, the Kinetic Monte Carlo (KMC) methods, and the Dynamic Density Function Theory (DDFT). In most case studies, the initial droplet shape was treated as a spherical cap to simplify the simulation. While just before dryout of the droplet, the left solvent was instead treated as an ultra-thin film in which the particles were in rapid motion. Normally solving N-S equations was applied to describe macroscale droplet evaporation process; The DLA approach was often used to simulate nanoparticles aggregation process in a droplet while the KMC and DDFT models were used for both film and droplet with an unpinned contact line.

2.3.0.1 Navier-Stokes Equations

The analytical and numerical methods are two primary ways to obtain solutions from the N-S equations. In analytical methods, the approximation method and

the lubrication theory are generally employed. In the classic description from Deegan, et al. [1] of a small sessile droplet, the advective velocity, evaporation flux, and deposit growth with time were solved on the basis of an electrostatic analogy. Extensive works were conducted with comprehensive considerations. Hu and Larson described the flow dynamics within a sessile droplet under quasi-steady state [116]. They obtained a time-dependent full velocity field including radial and vertical velocities [115], and also obtained a numerical result by using FEM. Based on the solutions, Hu and Larson took the Marangoni effect into account. The energy equation was simplified to the Laplace equation and solved with combining with the boundary conditions related to force balance at the droplet interface and the finite element analyzed temperature profile along the droplet surface. The velocity affected by the Marangoni effect and the streamlines of the flow field were obtained, as shown in Figure 2.17. The results also indicated that when the surfactant concentration at surface was about $300 \text{ molecules}/\mu\text{m}^2$, the Marangoni effect induced by surfactant concentration gradients could suppress the outward radial flow [116].

On the basis of the solutions of Deegan, et al. [1, 68] and Hu and Larson [113, 115–117], Jung, et al. adopted the scale analysis to elucidate the drag, electrostatic, van der Waals and surface tension forces on a single particle [118]. At the pinning stage, the drag force mostly affected the particle motion. Once the depinning stage started, most of the particles have deposited on the solid surface and the dominate force was the surface tension force. Duun, et al. proposed a formula of the evaporation flux as a function of the vapor concentration and temperature at the saturation point [119]. The formula took account of the evaporation-induced cooling on the saturation vapor at the droplet free surface. Similarly to that in the study of Hu and Larson [113], the vapor concentration was solved by FEM with the assistance of COMSOL Multiphysics software.

The numerical methods can be applied to discretize the droplet domain and calculate the equations with iterations. Through the numerical methods both

Figure 2.17: Streamline plots of the flow field from the finite element model for the Marangoni-stress boundary condition at contact angle of 40° and Marangoni number of 841, from (a) FEM solution and (b) analytical solution. The inset is the corresponding velocity field [116].

Figure 2.18: Contours of the particle volume fraction in the left part of the droplet and velocity field in the right part of the droplet at two times ((a) and (b)) with consideration of a monolayer formed by particles on the droplet surface [122].

Figure 2.19: Vector representation of the internal flow field in a kinetically controlled evaporating droplet.(a) a pinned droplet and (b) an unpinned droplet [124].

evaporative dynamics and particles motion can be predicted. With the application of FEM, for instance, the motion of particles and the formation of different deposition patterns could be described [120]. Combined with the mass, N-S and energy equations, the particles concentration profile was obtained by solving a continuum advection-diffusion equation. The transition between a ring-like and an uniform deposit was explained by a FEM-based study of Bhardwaj, et al. [120], with the consideration of DLVO interactions such as the electrostatic and van der Waals forces. A phase diagram was developed as well to explain the competitions among the radial flow, the Marangoni flow and the DLVO interactions. The Galerkin method [121] was used in a study combined with FEM to discrete the spatial domain and an adaptive finite difference method (FDM) was applied to discretize the time domain. The ring-like deposit and the uniform pattern were predicted by this model. Types of the deposition patterns relied on on the convective and diffusive mass transfer in the bulk liquid phase and on the deposition rate along the solid surface. Maki and Kumar described a less numerically explored phenomenon of the formation of a layer of particles at the surface of the droplet [122]. Based on a thin colloidal droplet, the precursor films were considered instead of the pinned

contact line, for the sake of being fully consistent with the lubrication theory. Evaporation has been considered limited by the speed of the molecules escaping from the liquid phase rather than the vapor diffusion. The coupled equations were solved by FDM with a moving overset grid. The obtained contours of the particle volume fraction and velocity field at two times are shown in Figure 2.18. The particle aggregation at the droplet surface resulted from the presence of evaporation and a large Peclet number. Reducing the outward capillary flow, the Marangoni effect could pronounce the skin formation. Moreover, Sumardiono and Fischer used the molecular dynamics simulation to investigate the dynamics of a droplet when it was heated from its warm vapor side [123]. They indicated that the radial velocity had a trend to increase at first and then decrease, and the velocity value reduces with a greater number of time steps. Instead of only stressing on the pinned droplet for most cases, Petsi and Burganos derived velocity fields for both pinned and unpinned sessile droplets [124]. For pinned droplets, the liquid flow was oriented towards the edges, and therefore inducing the coffee-ring deposits. While for an unpinned droplet and contact angle less than $\pi/2$, the flow was oriented towards the droplet centerline, as shown in Figure 2.19.

2.3.0.2 Diffusion Limited Aggregation

DLA is a process by which a fractal can be formed by solutes undergoing a random walk induced by Brownian motion in a solution. It was proposed by Witten Jr and Sander [125], in which diffusion was the primary means of transport, but affected by the aggregation. DLA was combined with the other models to describe particles movement and aggregation [126, 127] while it could be used in such a plenty of systems as electro-deposition, Hele-Shaw flow, mineral deposits, and dielectric breakdown [128]. In the process, the irreversible aggregation of the particles occurred due to sticking. The two effects competed with each other in the process. In order to achieve a fractal in the aggregation process, the concentration of particles should be low enough so that particles could not come in contact with

each other simultaneously, but could slowly assemble together. In the drying of suspensions, the particles have possibility to meet and aggregate so the arms of the cluster may grow longer and produce branches. During the DLA process, the sticking coefficient, a chance of a particle to stick to a cluster, is an important factor taken into account. The nondimensional sticking coefficient is 1 if the particle always sticks to the existing cluster once the particle is the structure, otherwise the value is less than 1.

Based on the nature of nanoparticle in the base fluids in a drying droplet, the diffusion limited cluster-cluster aggregation (DLCA) process has been studied recently [129–133]. The DLCA model has been employed to investigate fractal aggregation in nanofluids, during which the aggregation between the clusters was considered. A formed cluster grew and got in touch with the other clusters or nanoparticles. The value of fractal dimension of formed clusters was of critical importance as the different aggregation processes had the different value of it. The theoretical results demonstrated that it was the thermal restructuring induced by their low bonding energies leading to a large fractal dimensions of clusters from small nanoparticles. But it is still unknown for the small fractal dimension value of clusters from large particles [129].

By coupling the 2D DLA method, the experimentally observed transition from the uniform pattern to the coffee ring from both graphite nanofluid droplets and Al_2O_3 nanofluid droplets as a result of adding surfactant was simulated [92, 134]. The simulation demonstrated that it was the sticking force between nanoparticles controlling the final deposition patterns. The simulated results were statistically in a good agreement with the images of the ultimate self-assembled structures recorded experimentally, as shown in Figure 2.20. Additionally, the 2D model has been developed into a three-dimensional (3D) layers model [135] and full 3D model [136] for the transition from the coffee ring to the uniform deposition. By coupling DLA with the biased random walk to simulate microparticle motion and aggregation during droplet evaporation [10], the simulation [135] presented the

Figure 2.20: Comparison of the experiments and simulation. The coffee rings display the particle distribution profiles in the simulated patterns (a, b), captured after 2500 MCS with the initial particle coverage at 5%, and the finally dried experimental graphite structure from 2% graphite nanofluid with CTAB (c); The mixed patterns display the particle distribution profiles in the simulated patterns (e, f), captured after 2500 MCS and the initial particle coverage at 10%, and the finally dried experimental graphite structure from 5% graphite nanofluid with CTAB (g) [92].

particle adsorption, long-range attraction, and circulatory motion for the transition. In the simulation, the capillary flow at the late stage of evaporation was shown strong enough to destroy particles organization at the initial stage.

2.3.0.3 Kinetic Monte Carlo Model

The classical KMC model was proposed by Rabani, et al. [137]. It has been extended to simulate the particles assembly and organization with a 2D square lattice domain. Based on the interaction between drying of base fluid and diffusion of nanoparticles, different nonequilibrium patterns are able to be produced. In the 2D model in Figure 2.21(a), the solvent was divided into an array of 2D square lattices with size dictated by nanoparticles. Each cell was considered occupied either with a nanoparticle, liquid or vapor, which could be effectively described by two variables n and l . The possible states are: liquid ($l = 1, n = 0$), nanoparticle ($l = 0, n = 1$), and vapor ($l = 0, n = 0$). This model was applied in a closed

domain firstly [137] and was used to simulate inner part of the wetted domain. The Hamiltonian corresponding to energy expression for an entire configuration can be expressed as,

$$E = -\frac{\varepsilon_{nn}}{2} \sum_{\langle i,j \rangle} n_i n_j - \frac{\varepsilon_{nl}}{2} \sum_{\langle i,j \rangle} n_i l_j - \frac{\varepsilon_{ll}}{2} \sum_{\langle i,j \rangle} l_i l_j - \mu \sum_i l_i \quad (2.6)$$

where $\sum_{\langle i,j \rangle}$ indicates a summation of adjacent pairs of cells, among which, ε_{nn} , ε_{nl} and ε_{ll} are the interaction energies for particle-particle, liquid-particle, and liquid-liquid cells respectively. The Hamiltonian energy function describes the energy profile and a balanced state of the system. The interaction energy values are calculated by the first three terms on the right side respectively. The extra-energy for the phase transition was expressed by the last term with the chemical potential. The energy calculated from this function for the i – th lattice cell represents the energy it contributes to the system.

In the closed-domain KMC model [137], the area was surrounded by wet substrate so the studied region was the inner part of the wetted domain that was far from the wetting front (“Closed domain” in Figure 2.21(b)). Based on this, Pauliac-Vaujour, et al. [138] simulated the experimentally observed fingering structures that formed behind the macroscopic wetting front. Different from the closed domain, an open domain method was proposed to simulate the condition of the final drying stage of thin layer [139], in which the edge was treated as the wetting front to describe square liquid surrounded by the empty substrate, as shown in the “Open domain” in Figure 2.21(b). From the method, the formation of fractal-like microstructures from nanofluid was investigated. The particles described in the model were isotopically deposited into the fractal-like structure that remained immobilized after the base fluid totally dried [139]. The formed fractal-like structures were not the same as the fractal “holes” obtained in the closed domain model. Afterwards, the 2D model was improved to simulate the evaporation of a nanofluid sessile droplet with a circular depinned moving contact line. The

Figure 2.21: (a) Schematics of the two-dimensional lattice-gas KMC model; (b) closed domain [137] and open domain [139] in KMC model; (c) symmetrical and asymmetrical drying patterns obtained by using KMC model [141].

2D circular domain was selected to describe the top view of the spherical-cap-shaped sessile droplet. Coupling with the non-uniform chemical potential function and the thickness profile of a droplet, a pseudo-3D Monte Carlo simulation model was introduced. A fractal-like structure was formed due to the evaporation of nanofluid and was comparable to the recorded images of nanoparticle-assembled structures from the experiments [140]. The KMC model was also used to simulate the observed symmetric and asymmetric drying patterns formed during the drying of sessile nanofluid droplets suspended with nanoparticles, as shown in Figure 2.21 (c) [141]. Figure 2.22 shows a predicted sequence of the drying process of a droplet, in which the receding drying front induced particles into fingering structures toward the centerline of the droplet. The parameters, such as domain diameter, chemical potential distribution, particle interaction energy, particle coverage, moveability, etc., were shown to have great effects on the ultimately formed patterns [141]. The simulation was comparable with the experiments. Then, the KMC model was used to simulate the process of formation of a well-distinguished fingering structure inside a coffee-ring pattern from a millimeter-sized sessile nanofluid droplet on a silicon substrate [126]. The simulation indicated that the nucleation and growth process that started inside the ring resulted in the observation of emergence of branched structures connected to the inner side of the ring [141].

Figure 2.22: Intermediate steps of the simulation process for the uniform droplet evaporation. The images are captured after (a) 2000, (b) 4000, (c) 6000, (d) 8000 and (e) 10000 MCS, respectively [141].

Although the KMC model is effective in description of various patterns formation from evaporation of nanofluids, the limitations brought by a 2D

assumption without considering liquid thickness should be amended. In an investigation of a local controlling of dewetting-induced 2D pattern formation from nanofluids, Vancea, et al. [142] revealed that certain kinds of structures could not be simulated and which were of significant importance to the study of directed-dewetting by the purely 2D KMC approach. They made a change to the original KMC model by coupling the chemical potential with the global solvent coverage. The results showed that the evaporation rate of solvent was inversely proportional to its coverage and agreed well with the experimental images. Sztrum and Rabani [143] and Stannard [?] extended the 2D KMC model to 3D under different conditions. Sztrum and Rabani found that the assembled structures in the 3D model were in a good agreement with those of the 2D model when liquid evaporated in a manner of layer by layer and solvation forces were strong [143]. The researchers also confirmed that the 3D model was indispensable to predict the formation of nano-stalagmites. Furthermore, in order to produce dual-scale structures resulting from the nonequilibrium nanoparticles-assembly, Stannard simulated it with a pseudo-3D lattice gas-based Monte Carlo model with the coupling chemical potential to solvent density [144]. Dual-scale cellular networks, ring and fingering structures with small-scale patterning were produced by this extended model.

2.4 Summary

In this section, it is highlighted sessile nanofluid droplet evaporation from experimental and theoretical investigations. The role of nanoparticles concentration, size and shape in influencing the spreading, the evaporation rate, the evaporation mode and the flow dynamics of a sessile droplet have been elucidated by reviewing diverse experimental strategies. Aiming to control particles motion and deposition process, diverse interventions have been adopted to guide particles assembly and create preferable residue patterns. Studies stressing on parameters effect on

particles motion and aggregation serve as the foundation for better manipulation of the transport of nanoparticles. However, droplet evaporation with suspensions is very complicated, and further studies are needed to facilitate the understanding in the field of nanofluid droplet evaporation. The continuous studies might be on mixing particles with different shape, size and properties, making base fluids by using liquids of various thermal properties, designing novel confined geometries, controlling contact line motion by using substrates with different level of wettability, etc.

Chapter 3

Effects of Mono-Species, Dual-sized and Dual-Species Nanoparticles Suspended in Sessile Droplets at Room Temperature

3.1 Introduction

Evaporation of a sessile droplet with suspended nanoparticles is a complex process. These nanoparticles cannot be simply treated as passively driven dissolved indicators, but they could exert great impact on the wetting dynamics and evaporation of a droplet, and may interact with the liquid-vapor and the liquid-solid interfaces, accordingly vary the deposited profiles. In this chapter, I experimentally investigate the effects of mono-, dual-sized, and dual-species of nanoparticles on the deposit morphologies from dried sessile droplets.

3.2 Experimental Methods

3.2.1 Nanofluid Preparation

Deionized water with resistivity at 18.2 M Ω -cm generated by Milli-Q was used for all the samples. Nanoparticles of graphite at 2-3 nm (purity 93.0%), aluminum oxide at 5 nm (γ -Al₂O₃, purity 99.9%), aluminum oxide at 40 nm (α -

Al₂O₃, purity 99.0%), and 5-10 nm titanium oxide (TiO₂, purity 99.9%) listed in table 3.1 were purchased from SkySpring Nanomaterial, Inc. These four types of nanoparticles were with irregular shapes. They exhibited relatively high hydrophilism and thus weak adsorption at the liquid-vapor interface, such that the particles preferably remained suspended in the bulk solution without evident sedimentation for at least 24 hours. The evaporation substrates were brand new 4” prime one-side polished silicon wafers with 100 mm diameter and 100 orientation purchased from Latech Scientific Supply Pte. Ltd. and Bonda Technology Pte. The wafers were ultrasonically cleaned in water for 1 hour and then dried by compressed dry nitrogen prior to each test.

Table 3.1: The properties of the nanoparticles employed in the mono-species, dual-size and dual-species experiments.

Nanoparticle	Chemical formula	Size	Purity
Graphite	C	2-3 nm	93%
Alumina	γ -Al ₂ O ₃	5 nm	99.9%
Alumina	α -Al ₂ O ₃	40 nm	99.9%
Titanium oxide	TiO ₂	5-10 nm	99.9%

The nanofluids were prepared by the two-step method. Proper amounts of deionized water and nanoparticles were mixed in clean glass bottles, and the samples were placed in the ultrasonic bath (Fisher Scientific model 500) at first and then underwent magnetic stirring to ensure well-mixed suspensions.

3.2.2 Droplet Deposition and Characterization

Evaporative dynamics of the droplets were characterized by a “Wet Angle” Theta Optical Tensiometer for recording the evolution of the droplet from a side-view (see Fig. 3.1). The tensiometer is equipped with a controlling dosing system for droplet generation, a mechanical stage enabling droplet placement on the substrates, a high-resolution digital camera for capturing droplet images as fast as 1 frame per second, and a LED cold light source for illumination. The entire evaporation times ranged from 20 to 30 mins. Ball calibration was conducted before each

experiment to minimize experimental error. After the evaporation experiments, all the images were post-processed by the graphic analysis of the program, through which contact angle (CA), baseline diameter (D) and droplet volume (V) were obtained. The measurement accuracy of contact angle or volume was $\pm 0.1^\circ$ or $\pm 5\%$. The uncertainties of the post processing were evaluated within $\pm 5\%$.

Figure 3.1: A tensiometer used to capture sessile droplet evaporation from a side view. The magnified image indicates the recording of a droplet deposited on a silicon wafer.

To examine nanoparticles transport and the resulting deposition patterns, a real-time optical microscopy (LV100D-U, Nikon Inc.) as illustrated in Fig. 3.2, was employed to visualize droplets from a top view. The microscopic system consists of a high resolution scientific color CCD camera, an anti-vibration optical stage and a program for recording and post-processing. The left particle profiles were analyzed by the function of “Inverted Grayscale Intensity Analysis” to reveal the variation of nanoparticles along the droplet radial line. In addition, in section 3.5 for the study of dual-species of nanoparticles, the distribution of each species at specific locations was analyzed by the “Scanning Electron Microscope” (SEM, JEOL JSM-7600F)

equipped with an “Energy Dispersive X-ray Spectroscopy” (EDX). Evaporation experiments were conducted in an open condition with the temperature at $24\pm 1^\circ\text{C}$ for section 3.3, and $22\pm 1^\circ\text{C}$ for sections 3.4 and 3.5 respectively. The relative humidity ranged within $50\pm 5\%$. Each experiment was conducted for several times to ensure the repeatability.

Figure 3.2: Schematics of the experiment with an evaporating nanofluid droplet under the visualization of a microscope. After evaporation completed, the nanofluid droplet leaves a deposition pattern.

3.3 Evaporation of Sessile Droplets Affected by Mono-Graphite Nanoparticle Concentration

Adding graphite nanoparticles into a droplet is found to influence its wettability, the evaporative dynamics and the evaporation rate. Therefore, herein I varied the graphite nanoparticle concentration from 0.5 g/L to 2 g/L, together with a pure water droplet to examine how the droplet profile evolves during the evaporation and how the deposition pattern changes in respect to the nanoparticle concentration.

Fig. 3.3 shows the snapshots taken from a side view during the droplets drying and the resulting deposition patterns at the intermediate nanoparticles concentrations. At 0 s, the pure water droplet exhibits a flatter shape as compared to those containing nanoparticles. Afterwards, the water droplet retracts from the initial position, while the nanofluid droplets remain pinned for most the

Figure 3.3: Drying sequences of droplets with (a) 0 g/L, (b) 0.5 g/L, (c) 1 g/L, (d) 1.5 g/L and (e) 2 g/L nanoparticle concentrations C_{nano} at 0 s, 20 s, 100 s, 500 s and 1100s. The vertical lines are aligned with the edges of droplets at 0 s. The deposition patterns are shown in the bottom row.

lifetimes. The deposited profiles of nanoparticles at the intermediate concentrations are shown in the bottom row of Fig. 3.3. The patterns feature a central-concentrated stain circumscribed by an exterior ring. As the graphite nanoparticle concentration increases, both the interior residual and the outer coffee ring are intensified, reflected by the darker deposition color. Agglomeration of nanoparticles is enhanced at a higher nanoparticle concentration as exemplified by the large aggregates formed in the deposited pattern of the 2 g/L droplet.

All the patterns, regardless of the nanoparticle concentration, display different extent of nanoparticles accumulation in the interior region of the droplet area (Fig. 3.3). It was observed that at the late stage of evaporation, nanoparticles were carried inwards until immobilized at the solid surface. The descending liquid-vapor

interface could lead to a narrow space between the liquid-vapor and the liquid-solid interfaces, and when it was comparable to agglomerations, the aggregate would be in contact with the liquid-vapor interface. The body force, proportional to the friction force, $F_b = mg$ in which m is the mass and g is the gravitational acceleration was estimated to on the order of 10^{-12} for a $5\text{ }\mu\text{m}$ spherical aggregate, and the surface tension force $F_{st} = 2\pi R_S \gamma_{LV}$ in which R_S is the radius and γ_{LV} is the surface tension is on the order of 10^{-6} [145]. Consequently, the aggregate would be driven oriented to the droplet center due to the tensile strength of the liquid. Another reason for the inward motion of nanoparticles at room temperature could be the thermally-induced Marangoni flow, and it is elucidated in Chapter 5 of this study.

Interestingly, the droplets containing graphite nanoparticles exhibit a slight spreading at the very beginning of evaporation. Such an initial spreading was indiscernible for the pure water droplet. The nanoparticles could account for the initial spreading. Nikolov, et al. [45, 146] observed a nanoparticles-induced slow spreading of the nanofluid in a wedge film confined by a glass slide and an oil droplet which was emersed in the nanofluids. The spreading of sessile droplets led by the nanoparticles, however, has not been observed extensively. Here I provide both a direct observation and quantitative analysis for the initial spreading behavior.

To investigate the impact of the nanoparticles on evaporation, I plot Figs. 3.4 and 3.5 to show the evolution of the baseline diameter D and the contact angle CA for each nanoparticle concentration C_{nano} . As demonstrated in Fig. 3.4 (a), the base diameter of the deionized water droplet initially is much longer than those of the nanofluid droplets, suggesting its stronger wettability. Nanoparticles sedimentation at the solid surface could vary the superficial structure and roughness of the wafer [36]. The roughened surface particularly in the vicinity of the contact line could lead to an inhomogeneity of the surface energy, and thus attract the contact line to a new site [36, 37]. However, the droplet spreading at the initial stage is solely found in the nanofluid droplets instead of the pure water droplet, and

Figure 3.4: (a) Baseline length D as a function of time in the water-based nanofluids with graphite nanoparticle concentrations C_{nano} at 0 g/L, 0.5 g/L, 1.0 g/L, 1.5 g/L and 2.0 g/L; (b) the maximum baseline spreading ΔD with nanofluid concentrations C_{nano} .

such a spreading is sensitive to the graphite nanoparticle concentration. Fig. 3.4 (b) demonstrates the initial droplet spreading at each nanoparticle concentration by plotting the increment of the droplet base diameter. The addition of nanoparticles extends the base diameter, and such an extension is further enhanced as the nanoparticle concentration increases to 1.5 g/L. It could be attributed to the arrival of nanoparticles at the three-phase line. The nanoparticles there could self-assemble into ordered structures which lead to excess energy in the wedge film, known as the structural disjoining pressure which was able to drive the three-phase line into motion [45]. Upon increasing the nanoparticle concentration, a greater amount of

nanoparticles were able to access the thin wedge film and hence the associated base diameter extension was promoted. As the nanoparticle concentration is increased to 2.0 g/L, however, the initial elongation of the base diameter is reduced. As reported by Vafaei, et al. [38], although the structural disjoining pressure was pronounced with smaller nanoparticles, a larger number of nanoparticles could actually inhibit the film spreading due to a larger chance for them to agglomerate into large clusters [147]. These large sized cluster were normally unable to fit into the thin film space, thus the total number of nanoparticles capable of enhancing the droplet spreading was reduced. The non-unidirectional change of the spreading behavior with the nanoparticle concentration is determined by the two competing mechanisms, resulting in a apex of the base diameter increment at 1.5 g/L.

The droplet wettability is expressed by the baseline diameter shown in Fig. 3.4 (a) and the contact angle shown in Fig. 3.5. The base diameter of the pure water droplet maintains constant at the initial stage of evaporation. Afterwards, at about 400 seconds, the baseline begins to reduce until the end of evaporation. The corresponding contact angle in Fig. 3.5 demonstrates a rapid and linear decrease until at around 400 seconds, and from the moment the contact angle barely decreases. Such behaviors suggest that the water droplet went through a constant contact radius (CCR) mode at first, and then an approximate constant contact angle (CCA) mode. It is found from the normalized contact angle curves in Fig. 3.5 (b) that the transition occurs only in the pure water droplet. With the addition of 0.5 g/L, 1.0 g/L, 1.5 g/L, or 2.0 g/L graphite nanoparticles, the contact angle keeps reducing at an approximately constant rate before the ultimate dry-out, and such a declining slope is greater at a higher nanoparticle concentration. Besides, the base diameter of the nanofluid droplets maintains nearly unchanged throughout the evaporation except the spreading at the beginning stage. It indicates that the nanofluid droplets solely experienced CCR mode. The considerably enhanced pinning effect was related to the forces acting on the contact line. The local forces at the three-phase line included the depinning force responsible for the retracting

Figure 3.5: (a) Contact angle changes with time in the water-based droplets with graphite nanoparticle concentrations C_{nano} at 0 g/L, 0.5 g/L, 1.0 g/L, 1.5 g/L and 2.0 g/L; (b) the relative contact angle change with time. The inset is the initial contact angle for droplets with various nanoparticle concentrations C_{nano} .

behavior, and the pinning force, which were found to be dependent on the contact angle, the roughness and the heterogeneity of the solid surface [148]. The deposited nanoparticles roughened the substrate, which acted like obstacles in the retracting path of the contact line.

The initial contact angle of the nanofluid droplet is larger than that of the pure water droplet (see the inset of Fig. 3.5 (b)). But the initial contact angle is insensitive to the nanoparticles loading. It recalls the discussion about the enhanced pinning effect of nanoparticles. Deposition of nanoparticles on a substrate would modify and roughen its surface, resulting in an attraction of the contact line to new sites on the substrate [36, 37]. It was clarified by Blake and De Coninck that

Figure 3.6: (a) Droplet volume as a function of time for droplets with 0 g/L, 0.5 g/L, 1.0 g/L, 1.5 g/L and 2.0 g/L graphite nanoparticle concentrations; (b) the average evaporation rate of the nanofluid droplets with different graphite nanoparticle concentrations. The data are compared with the pure water experiments [150,151].

the advancement of liquid on a solid surface was a successive-attaching process that the liquid molecules were inclined to be absorbed on sites with a preferable orientation [149]. Therefore, the deposited nanoparticles created new sites for liquid molecules to be attracted and consequently changed the contact angle [36]. The accumulated deposits at the contact line strengthened anchoring of the contact line on the substrate and prevented its macroscopical from shrinking as the pure water droplet.

Fig. 3.6 (a) demonstrates the evolution of the droplet volume over the lifetime at various nanoparticle concentrations C_{nano} . The volume change of the deionized water droplet in respect to time is much slower, so the lifetime is longer compared

to that of the droplets suspended with graphite nanoparticles, implying a smaller evaporation rate of the pure water droplet. The steeper curves of the other nanofluid droplets suggest an enhanced evaporation at a higher nanoparticles concentration. Fig. 3.6 (b) presents the averaged evaporation rate for each nanoparticle concentration. The averaged evaporation rate of the pure water in my study is comparable to the counterparts in the studies of Cheng, et al. [150] and Liu, et al. [151]. The evaporation rate basically increases linearly with the graphite concentration ranging from 0.0 g/L to 1.5 g/L. However, the increasing trend at 2.0 g/L slows down despite that it is still higher than that of the water droplet. As illustrated by Fig. 3.4 (a), the depinning behavior of the pure water droplet does not take place in the nanofluid droplets attributed to the greatly enhanced pinning effect. The evaporation is stronger in those nanofluid droplets with a nearly pinned contact line. Furthermore, as the graphite nanoparticles had a higher thermal conductivity compared to that of water, the great loading of graphite nanoparticles may enhance the heat conduction for phase change and lead to faster evaporation. However, adding nanoparticles into base fluids also could result in a higher fluid viscosity [147], which could inhibit the outward radial flow serving as the replenishment of the high evaporation loss at the droplet edge; and more particle aggregations at surface or in the vicinity of contact line may also suppress liquid evaporation. The combination of the aforementioned reasons determines that the enhancement of evaporation could be attenuated as the nanoparticle concentration reaches 2.0 g/L.

3.4 Effects of Dual-Sized Nanoparticles

Table 3.2: The weight ratio of the 5 nm to the 40 nm Al_2O_3 nanoparticles for each experiment of multi-sized nanoparticles. The nanofluid concentration is 1 g/L for all the samples.

Exp. No	1	2	3	4	5	6	7	8
5 nm:40 nm	0:1	1:19	1:9	2:8	3:7	4:6	5:5	1:0

In this section, it is probed how the combination of two different sized nanoparticles with the same material influences the deposition profiles. 5 nm and 40 nm Al_2O_3 nanoparticles were mixed with various ratios as listed in Table 3.2. All the droplets generated by the micropipette (Thermo-Fisher) have the initial volumes fixed at 2.0 μL .

Figure 3.7: (a1) and (a2) are the deposition patterns from evaporating sessile droplets with the weight ratio of the 5 nm to the 40 nm Al_2O_3 nanoparticle at 0:1, 1:19, 1:9, 2:8, 3:7, 4:6, 5:5, and 1:0; (b1) and (b2) are the normalized inverted grayscale intensity profile along the radial line at each corresponding ratio of the 5 nm to the 40 nm Al_2O_3 nanoparticles.

Top views of the deposition patterns captured by the microscopy for the different ratios of the 5 nm to the 40 nm Al_2O_3 nanoparticle mixtures are shown in Figs. 3.7 (a1, a2). Figs. 3.7 (b1, b2) present the corresponding normalized grayscale intensity profile at each size ratio. It is worth mentioning that with the ratio from 0:1 to 2:8, the droplets receded in the middle of the evaporation, while those droplets with the ratio of 3:7 and above maintained pinned for nearly the lifetime. The deposited nanoparticle profiles for high percentages of the 40 nm

Al_2O_3 nanoparticles (Fig. 3.7 (a1)) exhibit similarities in the interior region where nanoparticles are accumulated into thick wire-like assemblies. Fig. 3.8 (a) reveals such a structure formation by the time-lapse photographs for the ratio at 2:8. As the droplet shrinks, the contact line becomes irregular and it alternates between depinning and pinning, namely the “stick-slip” behavior. The depinning contact line brings along the nanoparticles, and as long as the contact line re-pins, some of the nanoparticles are sucked into the slim regions and organize into fractal-like structures. The large-sized nanoparticles with weak pinning effect are drift in the bulk and are easily swept inwards by the moving contact line (Fig. 3.8 (b)). Contrary to it, the coffee ring is greatly enhanced by adding the 5 nm Al_2O_3 nanoparticles at a small fraction of 10%.

The pattern alters completely as the weight fraction of the 5 nm Al_2O_3 nanoparticles increases from 20% to 30%. The locally accumulated structure changes to a rather uniform distribution. The interior homogeneity is further enhanced as the 5 nm nanoparticles increases to 40% and 50%. At 100% of the 5 nm nanoparticles, however, a heterogeneous deposit profile emerges again reflected by the gap covered with sparse nanoparticles between the central thick deposition and the outside coffee ring. Therefore, the co-existing 5 nm and the 40 nm Al_2O_3 nanoparticles could suppress the non-uniform effects led by both of them. On the one hand, the strong pinning effect of the 5 nm nanoparticles ensures the formation of a robust coffee ring (Fig. 3.8 (c)) and it could prohibit droplet shrinkage from taking place upon evaporation. Therefore, the accumulated branched structures forming along the receding contacting line would not appear. On the other hand, the interaction between the small and the large sized Al_2O_3 nanoparticles limits the free transport of the small ones. It is observed that the inward transport of nanoparticles in the mono 5 nm Al_2O_3 nanoparticle suspension droplet is almost eliminated in the presence of the 40 nm nanoparticles. The isolated small nanoparticles are bonded with the large ones, as shown in Figs. 3.9 (I, II), and such a coalescence limits the the freedom of the 5 nm nanoparticles to

Figure 3.8: (a) The formation of a fractal-like deposition from the sessile droplet containing the mixture with the weight ratio of the 5 nm to the 40 nm Al_2O_3 nanoparticles at 2:8. (b) The receding contact line which brings some nanoparticle aggregates inwards for the mono 40 nm Al_2O_3 nanofluid droplet. (c) The formation of a robust coffee ring from the 5 nm Al_2O_3 nanofluid droplet.

“climb” toward the droplet apex [152]. With the reduction of the 40 nm Al_2O_3 nanoparticles, nanoparticle agglomeration is attenuated, and the vacancies are increasingly covered with nanoparticles and small congregates (Figs. 3.9 (III, IV)). Therefore, the particle-dependent droplet dynamics coupling with particle-particle interactions determines the deposit structure of multi-sized Al_2O_3 nanoparticles. Based on the results of nanoparticle size effect, I am concerned that it is possible to vary the deposition homogeneity by varying the recipe of small and large-sized nanoparticles, which sheds light on controlling deposition patterns particularly for the purpose of generating a uniform profile.

Figure 3.9: Nanoparticle assemblies in the interior region of the deposition profile formed from sessile droplets with the ratio of 40 nm to 5 nm Al_2O_3 nanoparticles at (I) 3:7, (II) 4:6, (III) 5:5 and (IV) 1:0.

3.5 Effects of Dual-species Nanoparticles

As each species of nanoparticles produces a distinct profile after droplet evaporation completed (the left two patterns in Figs. 3.10-3.12 (a)), it is interesting to probe the combined effect, whether synergetic or counteractive, of mixtures consisting of dual-species of nanoparticles on their final distribution. The solutions of nanoparticle mixtures are listed in Table 3.3. The corresponding mixture patterns shown in Figs. 3.10-3.12 (b) are resulting from the combination of the 2-3 nm graphite and the 5-10 nm TiO_2 nanoparticles, the 2-3 nm graphite and the 40 nm Al_2O_3 nanoparticles, and the 2-3 nm graphite and the 5 nm Al_2O_3 nanoparticles, respectively. Through comparing the mixture pattern with the ones formed by its constituent single species, it is found that the mixture pattern either exhibits both the features of the two single species patterns, or resembles solely one of them, suggesting that the other one lost its characteristics in the mixture pattern. To find out the role of each species in generating the final deposition, I employed the “Elemental Mapping Analysis” of the EDX to examine the weight fraction of each nanoparticle species at specific locations of the mixture pattern (see Figs. 3.10-3.12 (b)).

Table 3.3: The combination of different species of nanoparticles for the experiment of multi-species nanoparticles. The nanofluid concentration is 1 g/L for all the samples.

Exp. No	9	10	11	12	13
Al ₂ O ₃ 5 nm	-	-	-	-	0.5 g/L
Al ₂ O ₃ 40 nm	-	-	-	0.5 g/L	-
Graphite 2-3 nm	1 g/L	-	0.5 g/L	0.5 g/L	0.5 g/L
TiO ₂ 5-10 nm	-	1 g/L	0.5 g/L	-	-

The mixture pattern formed by the graphite and the TiO₂ nanoparticles appears to reflect the characteristics of both the single species patterns (Fig. 3.10 (a)). The relatively uniform profile of the 2-3 nm graphite nanoparticles was formed from a pinned droplet, while the dendritic structure of the TiO₂ was caused by the depinning contact line and thus the pattern lacks a coffee ring. The mixture pattern, however, exhibits both a loose ring-shaped residual and a heterogeneous interior deposit analogous to a “stick-slip” structure. At the initial stage of evaporation, the droplet containing the mixture of nanoparticles remained pinned thanks to the stronger pinning effect of the graphite nanoparticles, so a ring-shaped stain was produced. But the pinning stage did not last long and the droplet entered into a stage with alternating depinning and pinning behaviors. Therefore nanoparticles congregated into wire-like aggregations when the repinning of the contact line occurred.

The EDX results confirmed the supposition that the graphite nanoparticles contributed more to the ring-shaped stain while the interior deposition was dominated by the TiO₂ nanoparticles. In Fig. 3.10 (b), I present the elemental mapping images for carbon (C) and titanium (Ti) to identify the graphite and the TiO₂ nanoparticles, respectively. Three areas are selected involving the ring-shaped stain, the wire-like aggregation and the central deposition to conduct the EDX mapping analysis for the graphite-TiO₂ mixture pattern. The SEM image and the mapping images for C and Ti are provided corresponding to each location. As shown in Fig. 3.10 (b), at the ring region denoted by “1”, the distribution of carbon element is more obvious to detect than that of Ti, implying that the

Figure 3.10: (a) The single 2-3 nm graphite nanoparticle pattern, the single 5-10 nm TiO₂ nanoparticle pattern, and the mixture pattern formed by these two species of nanoparticles. (b) Left: the positions numbered 1, 2 and 3 at the mixture pattern. Right: the corresponding SEM view and the EDX elemental mapping of carbon C and titanium Ti for each position.

ring-shaped deposition is contributed more by the graphite nanoparticles. At the position where the contact line exhibited the “stick-slip” behavior noted by “2”, more Ti is detected which uniformly distributes in the region, implying that a greater amount of TiO₂ were transported toward the repinning contact line during droplet evaporation. The central region denoted by “3” where the ultimate drying process took place is covered with interlaced graphite and TiO₂. The elemental map shows a clear spread of Ti, suggesting that most TiO₂ nanoparticles were carried to the interior deposition, which is consistent to their distribution in the single TiO₂ nanoparticles pattern.

As the 2-3 nm graphite nanoparticles are mixed with the 40 nm Al₂O₃

Figure 3.11: (a) The single 2-3 nm graphite nanoparticle pattern, the single 40 nm Al₂O₃ nanoparticle pattern, and the mixture pattern formed by these two species of nanoparticles. (b) Left: the positions numbered 1, 2 and 3 at the mixture pattern. Right: the corresponding SEM view and the EDX elemental mapping of carbon C and aluminum Al for each position.

nanoparticles, the mixture pattern resembles the single graphite pattern while it is with an intensified coffee ring (Fig. 3.11 (a)). The dendritic structure of the single Al₂O₃ pattern was resulted from contact line receding and repinning. The didisperse nanofluid droplet and the single graphite nanofluid droplet were alike because both of them remained pinned on the substrate for nearly the lifetime. Therefore, the interior-concentrated structure produced in the single Al₂O₃ pattern was eliminated with the presence of graphite nanoparticles.

Fig. 3.11 (b) presents the SEM and the elemental mapping results at areas from the droplet rim to the center denoted by numbers “1”, “2” and “3”. The amount of aluminum (Al) is smaller near the edge and it increases as reaching the droplet

center. Increased Al emerging at Areas 2 and 3 implies that the distribution of Al_2O_3 is homogenized as compared to its single pattern, and it may be attributed to the greatly prolonged pinning stage due to the graphite nanoparticles. The anchored contact line ensured an outward capillary flow by which some Al_2O_3 nanoparticles could be more evenly dispersed and some of them may have reached the perimeter. In other words, the inward motion of the 40 nm Al_2O_3 nanoparticle was constrained with the presence of the graphite nanoparticles. The profile of carbon shows no surprise that it increases from the droplet rim to the center, being consistent with the single graphite profile.

Figure 3.12: (a) The single 2-3 nm graphite nanoparticle pattern, the single 5 nm Al_2O_3 nanoparticle pattern, and the mixture pattern formed by these two species of nanoparticles. (b) Left: the positions numbered 1, 2 and 3 at the mixture pattern. Right: the corresponding SEM view and the EDX elemental mapping of carbon C and aluminum Al for each position.

The mixture pattern consists of the 2-3 nm graphite and the 5 nm Al_2O_3 nanoparticle is similar to the Al_2O_3 profile while with an aggravated center-

concentrated deposition (Fig. 3.12 (a)). The gap is expanded between the interior stains and the outside coffee ring. The EDX map (Fig. 3.12 (b)) shows that the amount of Al increases from the droplet edge (Area 1) to the center (Areas 2 and 3). Therefore, the 5 nm Al_2O_3 nanoparticles behaved similarly in the evaporating single Al_2O_3 nanofluid droplet and the didisperse Al_2O_3 -graphite nanofluid droplet.

Comparison of the mixture pattern and the patterns formed by the constituent single species of nanoparticles indicated a restrictive or a collaborative correlation between the two types of nanoparticles. The 2-3 nm graphite nanoparticles, for instance, had a stronger enhancement in the pinning effect than for the TiO_2 and the 40 nm Al_2O_3 nanoparticles. Therefore, the mixture pattern exhibited a more or less pronounced coffee ring than for the single TiO_2 or the 40 nm Al_2O_3 profile. The intensified pinning effect suppressed the inward motion of the TiO_2 and the 40 nm Al_2O_3 nanoparticles so the structures given rise by the contact line depinning in their single species pattern was either mitigated or deprived. Here it can be seen that the combination of the 2-3 nm graphite/ TiO_2 or the 2-3 nm graphite/40 nm Al_2O_3 exemplified the restrictive relation between the two species of nanoparticles. The combination of the 2-3 nm graphite and the 5 nm Al_2O_3 showed a collaborative effect on the mixture pattern. They did not limit each other but rather retained their position as in their single species patterns.

3.6 Summary

Effects of insoluble nanoparticles in terms of the concentration of mono-species and the combination of dual-sized or dual-species particles are probed in this chapter on the evaporative dynamics, particle-particle interactions and the resulting deposited profiles.

In the mono graphite nanofluid droplet, the initial spreading was intensified first and then attenuated with a loading of graphite nanoparticles. In the drying process, the droplet with the graphite nanoparticle basically showed a stronger pinning

effect and enlarged contact angle in comparison with the pure water droplet. The intensified evaporation was mainly due to a prolonged pinning stage and higher thermal conduction for phase change led by the nanoparticles. However, the graphite nanoparticles with the concentration at 2.0 g/L terminated the increasing trend of the evaporation rate.

For the study of droplets with dual-sized Al_2O_3 nanoparticles, the pattern organized either by the 5 nm or the 40 nm Al_2O_3 nanoparticles was heterogeneous; while such heterogeneities were eliminated with a proper combination of the them. The small-sized nanoparticles enhanced the pinning effect so the aggregation of the large-sized nanoparticles at the depinning-repinning contact line would not occur. The collision of the small-sized and the large-sized Al_2O_3 nanoparticles constrained the freedom of the small nanoparticles so their center-toward movement could be suppressed. These two phenomena probably accounted for the uniform spread of the mixture nanoparticles observed in the study.

The mixture pattern assembled by two species of nanoparticles either displayed the features in both the single deposition patterns or was analogous to solely one of them. The EDX analysis confirmed that each species of nanoparticles behaved similarly for its mixture pattern and its single species pattern. The nanoparticles with a greater pinning effect mitigated the inward transport of the other species; the two nanoparticle species with similar behaviors in their single patterns repeated their respective features in the mixture pattern. Therefore, the competition or the coordination depending on the two nanoparticle species could vary the evaporation regimes of the droplet and determine the ultimate deposition morphology.

It turns out that the stains morphology can be controlled, such as suppressing or even eliminating deposit heterogeneities, through simply adopting proper recipes of different nanoparticles. This study sheds lights on the manipulation of dissolved solutes depositions from drying droplets solely through interfering intrinsic parameters.

Chapter 4

Effects of Base Solutions on Pure/Nanofluid Sessile Droplets Evaporation at Room Temperature

4.1 Introduction

The base solution of a droplet is a broadly manipulated domain owing to its effectiveness in varying the flow paradigm, the accompanied solutes transport and the resulting deposited profile. In this chapter the influence of base solutions is examined in respect to binary liquids and aqueous surfactant solutions. Such combinations of water and another material, whether alcohols or surfactant, as the base solution produces distinctly different fluid flows and deposited morphologies, as compared to water-based droplets.

4.2 Effects of Binary Mixture Base Solutions

4.2.1 Experimental Methods

The objective of this study is to investigate the effect of the ethanol component on the flow field of a droplet and the deposition pattern formed by Al_2O_3 nanoparticles. Considering that the trajectory of the non-luminous Al_2O_3 nanoparticles hard to be captured opposed a limitation on flow analysis, I therefore apply the assumption that the flow pattern of the water-ethanol binary droplet resembles that of the same

base solution droplet suspended with nanoparticles. The fluorescent microspheres were employed to probe the evaporation of pure water-ethanol binary droplets through the Particle Image Velocimetry (PIV) technique. Since the study requires a fairly dilute fluorescent solution to minimize solute effect on pure fluid flow, the fluorescent microspheres were reckoned as solely visual indicators for the flow field during the droplet evaporation.

Two batches of solutions, each of which contained Al_2O_3 nanoparticles or fluorescent microspheres, were prepared with the concentrations at 2 g/L and 0.1 g/L, respectively. The Al_2O_3 nanoparticles were purchased from SkySpring Nanomaterials Inc. with a diameter of 5 nm in average. 1000 nm Red FluoSpheres carboxylate-modified microspheres from Technologies Holdings Pte Ltd were used as received. The concern for the size difference between the nanoparticle and the fluorescent microsphere is elucidated later in this section. The nano-filtered water and ethanol ($\text{C}_2\text{H}_5\text{OH}$, Reagent ACS Grade) were employed to prepare the base solvents for droplets. The brand new silicon wafers (Latech Scientific Supply Pte Ltd) with the orientation of 100 and average roughness at $0.106\ \mu\text{m}$ were used as the substrate for sessile droplet evaporation. The wafers were ultrasonically cleaned in water for 1 hour and then dried by compressed dry nitrogen prior to each test.

For the Al_2O_3 nanofluids, the base binary solutions had five ethanol concentrations in volume at 0 %, 10 %, 20 %, 40 % and 50 %. The fluorescent fluid samples contained 0 %, 10 %, 20 % and 40 % ethanol concentrations in volume. It is found that as the ethanol concentration was above 40 %, the fluorescent fluids could not form a droplet but spread as a film, unlike the alumina nanofluids which could self-develop into a droplet with 50 % ethanol because the enhanced pinning effect led by nanoparticles. All the samples were prepared just before the evaporation experiments.

Experiments were performed by employing the microscopy system (LV100D-U, Nikon Inc.) to examine the drying process of the droplets from a top view. The microscope with the brightfield schema was applied to examine the nanoparticles

motion during evaporation and the formed deposited profiles after the evaporation completed. In respect to the fluorescent droplet evaporation, the mercury lamp of the microscopy emitting at 527 nm was utilized to excite the fluorescent microspheres to fluoresce at 605 nm. The initial volume for both the nanofluid droplets and the fluorescent solution droplets was controlled at 0.2 μL by the micropipette (Thermo-Fisher). The snapshots of the fluorescent droplets were analyzed by the PIV program LaVision, DaVis 8.04 with the time interval set at 0.5 s for every image pairs. By combining the deposition patterns formed by the Al_2O_3 nanoparticles and the transport of the fluorescent microspheres during evaporation, the effect of the binary fluids on the relation of fluid flow and the resulting particles deposition is explicated. The droplets evaporation was under an open conditions with the pressure at 1 atm, the temperate at 23 $^\circ\text{C}$, and the relative humidity at $50\pm 5\%$. To ensure the repeatability of the outcomes, repeated tests were conducted for each experimental condition.

4.2.2 Results and Discussion

The deposition patterns of the nanofluid droplets as shown in Fig. 4.1 vary greatly with the ethanol concentration. At 0 % ethanol, nanoparticles with no visible aggregates deposit uniformly in the interior region enclosed with a distinct coffee ring. With the ethanol at 10 %, aggregates of nanoparticles are produced which either are driven to the edge or stay at the central region of the droplet. At 20 %, the interior uniformity of the stains is broken such that there has an evident gap to the exterior coffee ring. As the ethanol component increases to 40 %, the disorder of the interior distribution of nanoparticle is increased reflected by evident agglomerations of nanoparticles interlaced with vacancies. Meanwhile, however, the outside coffee ring is weakened. Such behaviors are intensified at 50 % of ethanol. The interior region is randomly covered with nanoparticle aggregates, and the exterior stain is so loosely-packed that it is hardly a ring anymore. Therefore, increasing ethanol component intensified nanoparticles agglomeration, the vacant area interlaced with

Figure 4.1: The images of the evaporating nanofluid droplets containing (a) 0 %, (b) 10 %, (c) 20 %, (d) 40 % and (e) 50 % ethanol concentrations. The evaporation time 2 %, 25 %, 45 %, 60 %, 80 %, and 100 % is normalized with the droplet lifetime. The scale bar indicates 0.2 mm.

nanoparticles, and the non-uniformity of the interior nanoparticle distribution, and it attenuated the coffee ring.

Although solely based on the final deposited profile of nanoparticles cannot determine the flow regime, the snapshots of the evaporating droplet from a top view can shed some light, as presented in Figs. 4.1 (a)-(e). However, it is still difficult to reveal the flow field by the nonluminous nanoparticles and these stationary images. Only from the droplets with 40 vol % and 50 vol % it can be roughly identified that the nanoparticle aggregates are formed from the edge toward the center at the initial stage of evaporation, and then some of them detach from the contact line owing to the furious flow. Afterward they randomly stay at the interior region during the late drying stage. Therefore, aiming to understand the relation between the flow regime, particle motion and the deposition pattern, I then used

fluorescent microspheres as an indicator to reveal the flow field influenced by the binary solutions.

Fig. 4.2 presents the evaporation process of the droplets containing fluorescent microspheres under the intermediate ethanol concentrations. The entire evaporation process of the binary solution droplet showed three distinct flow regimes. At the initial regime, strong vortices emerged with random orientation and numbers. We found that in this regime microspheres gathered into aggregates which were immobilized near the sessile droplet edge. The microspheres driven by the rapid flow had a higher opportunity to interact and collide to form agglomerations. The transition from the first regime to the second one was identifiable, revealed by the abrupt slowing motion of the microspheres. In the second regime, the initially produced aggregates near the perimeter of the droplet started to transport toward the droplet apex and cover the central liquid-vapor interface. This regime observed in my experiments lasted for dozens of seconds, rather than the instant period lasting for several seconds reported in the study of Christy, et al. [14]. The possible reason was that a much lower ethanol concentration at 5 % was used in Ref. [14]. The second regime finished when the aggregates stopped moving inwards and the third regime began. During the third regime, the ethanol fraction had been almost evaporated, and the evaporation of the left droplet resembled that of a pure water droplet. The microspheres and the small aggregates have been observed to transport to the droplet edge by capillary flow due to the pinning effect. The large aggregates covering the droplet free surface descended toward the substrate in this regime. At the ultimate moment, some aggregates deposited onto the substrate were along with the depinning contact line. The patterns of the microspheres formed under ethanol concentrations at 10 %, 20 % and 40 % exhibit various degrees of aggregation interiorly enclosed by a coffee ring, in contrast to the uniform deposition without visible aggregation from the water-based fluorescent solution droplet.

In order to quantify the results illustrated in Fig. 4.2, the PIV analysis has been

Figure 4.2: The images of the evaporating fluorescent droplets containing (a) 0 %, (b) 10 %, (c) 20 % and (d) 40 % ethanol concentrations. The drying time is normalized with the lifetime for each droplet. The Regimes I, II and III are indicated for the droplet with ethanol component. The scale indicates 0.2 mm.

conducted for each ethanol concentration during the entire evaporation process. In this study, I used the one at 20 % ethanol concentration to elucidate the evolution of the velocity field as one example (see Fig. 4.3). In Regime I, the furious flow primarily takes place near the periphery of the droplet. Strong vortices, indicated by the velocity vectors, emerging with random orientations and numbers. Regime I lasts for about 19 % of the entire lifetime. Afterwards, the droplet enters into Regime II during which the vortices disappear and the fluid flow suddenly slows down. The flow shows a more regular pattern that it directs inwards, namely the Marangoni flow. Due to the evaporative cooling effect the substrate might have a higher temperature [66]. In addition, the local ethanol concentration can also be

Figure 4.3: Particle image velocimetry results of velocity field for the droplet with ethanol at 20 % for the three flow regimes.

different, but it cannot be measured during droplet evaporation at this stage. Based on the inward Marangoni flow, the surface tension near the droplet apex should be higher than for the droplet edge. It is likely since ethanol evaporates prior to water and the local evaporation flux is higher at the three-phase line [1,66], which could result in a nonuniform distribution of the ethanol along the liquid-vapor interface [14]. I reckon that the combined effects can lead to a surface tension gradient along the liquid-vapor interface and a resulting Marangoni flow directing the droplet centerline. Regime II lasts for roughly 42 % of the lifetime for this case, and the temporal Marangoni flow is weakened with the evaporation. Regime II is finished when ethanol has almost evaporated. Regime III is dominated by the evaporation of the left water.

In light of the flow patterns indicated by fluorescent microspheres, nanoparticles motion and the deposition pattern can be explained to some extent by concerning their size difference. The nano-sized Al_2O_3 particles can easier fill in the thin wedge film in the vicinity of the contact line, and thus can enhance the pinning effect. Indeed it was observed that the nanofluid droplets with intermediate ethanol concentrations kept pinned for nearly the entire lifetime. The fluorescent microspheres with a larger size barely had enhancement in the droplet pinning, so the droplets retracted at the latest stage. However, it would not affect the present results much. At the late stage the droplet flow has been developed into Regime III, mainly dominated by water evaporation. The major stages, targeted in the present study, are Regimes I and II affected by ethanol, during which the droplets

Figure 4.4: The normalized duration of Regimes I and II over the ethanol concentration range from 0 % and 40 %.

containing fluorescent microspheres were pinned on the solid surface. Given that both the nanofluid droplet and the fluorescent solution droplet underwent constant contact radius mode during Regimes I and II, I can make an analogy for the two flows to explain nanoparticle movement and the deposited profile.

The combined three regimes and the relative weighing for each regime result in various patterns of nanoparticles [12]. Therefore, the duration of Regimes I and II is normalized with the entire droplet lifetime at each ethanol concentration (Fig. 4.4). Both Regimes I and II are basically prolonged with an increase of the ethanol concentration (Regime III is relatively shortened with increasing the ethanol fraction). It is reasonable since the vortices appearing in Regime I and the Marangoni flow in Regime II were generated due to the presence of ethanol in the base solutions. Based on the understanding, It can be analyzed how each pattern of nanoparticles was formed under various ethanol concentrations.

Employing the ethanol-dependent flow regimes and the flow intensity revealed by the fluorescent microspheres, it can be analyzed the formation of the nanoparticle deposition patterns. The stains of nanoparticles uniformly distributed at the interior region were found to decrease with a loading of ethanol. As ethanol triggered furious flows which intensified nanoparticle agglomeration, the number of isolated particles was reduced. Another phenomenon was that the

aggregates of nanoparticles were near the droplet contact line at relatively low ethanol concentrations, in contrast to those staying in the interior area for higher ethanol concentrations. The aggregates assembling near the droplet edge in Regime I were observed to easier detach from the coffee ring driven by the furious flows at a high ethanol concentration. The prolonged Regime II with a higher ethanol component as well promoted the inward transport of the aggregates by Marangoni flows, as demonstrated by the interior residual of nanoparticles with a gap to the outside ring for the droplet with 20 % ethanol (Fig. 4.1 (c)). Another noticeable feature was that the coffee ring was abated with ethanol at 40 vol % and 50 vol %. The flow patterns in regimes I and II suppressed the outward capillary flow, so the nanoparticles accessible to reach the contact line of the droplet decreased. Another reason was that the high ethanol concentration led to a rapid evaporation rate. As the droplet flattened, the evaporation flux was so high that the replenishment from internal flow could be insufficient to maintain the contact line on the substrate. At the late stage of drying, the droplet with 50 % ethanol exhibited a slight depinning behavior, therefore the coffee ring effect was attenuated accordingly. Generally, the ethanol opposed a non-monotonous effect on the fluid flow and the deposited profile of the particles. But the mechanism was rather complex that ethanol could influence the relative weighting of each flow regime and the intensity of the flow, leading to diverse deposition patterns.

4.3 Effects of Cationic Surfactant in Aqueous Base Solutions

4.3.1 Experimental Methods

Herein I probed the autophobic effect of pure sessile droplets in section 4.3.2, and how nanoparticles affect the autophobic effect in nanofluid droplets in section 4.3.3. The accompanied deposition patterns produced at various surfactant

concentrations was also examined in section 4.3.3.

For the pure sessile droplets in section 4.3.2, I studied the effect of the cationic surfactant CTAB (Cetyltrimethylammonium bromide, $C_{19}H_{42}BrN$, Sigma-Aldrich) concentration, C_{surf} , on the spreading, the retraction, and the evaporation of sessile droplets on silicon wafer substrates. The tensiometer introduced in chapter 3 was also utilized herein to capture the dynamic evaporation of the droplet from a side view. Controlled by the mechanical stage of the tensiometer at the slow downward speed, the surfactant-water solution droplet was made gently touched with the horizontal substrate to minimize the impingement. Once the droplet detached from the pipette, it spread to some degree to reach the maximum wetting area, and then retracted rapidly. I set the moment at which the droplet stopped spreading at $t_0 = 0$ s in the following analysis. Accordingly, I can measure the initial diameter, D_0 , and the initial contact angle, θ_0 . The droplet volume at $2.75 \pm 0.14 \mu L$ used in the experiments was controlled by the dosing-system of the tensiometer.

To investigate the role of nanoparticles in the autophobic effect in sessile droplets evaporation, I prepared four batches of solutions, each of which had 0.0 g/L, 0.5 g/L, 1.0 g/L and 1.5 g/L graphite nanoparticle concentration, C_{nano} , in section 4.3.3. Noted that we assumed that the low concentration of nanoparticles barely affects the critical micelle concentration (cmc) of CTAB (0.92 mM [154]) in water [153]. Evaporation of the droplets from a side view was also observed through the tensiometer, the same as the pure surfactant solution droplets in section 4.3.2. The instantaneous contact angle, θ , the base diameter, D , and the droplet volume, V , were evaluated by the post-processing program, and the measurement accuracies were $\pm 0.1^\circ$, ± 0.1 mm, and $\pm 5\%$, respectively. For recording of the deposition patterns, the microscope (LV 100D-U, Nikon Inc.) was employed with the brightfield schema to present the spatial distribution of nanoparticles after the droplets drying.

Table 4.1: The value of the liquid-vapor surface tension, γ_{LV} , at the listed surfactant concentration, C_{surf} .

C_{surf} (mM)	0.014	0.028	0.042	0.06	0.084	0.14	0.28	0.42	0.84
γ_{LV} (dyn/cm)	69.6	68.5	68.4	68.4	66.3	64.2	58.1	53.2	40.5

4.3.2 Autophobic behavior of pure droplets

In this section, water-based CTAB solutions were prepared to examine the effect of cationic surfactant on droplet dynamics during evaporation. CTAB was added in nano-filtered water to prepare solutions with the concentration C_{surf} ranging from 0.014 mM to 1.4 mM. The surfactant solutions were employed within 10 hours in avoidance of any decrease in surface activity [155]. The liquid-vapor surface tension, γ_{LV} , of the CTAB-water solution was measured using the “pendent droplet” method with a consistent droplet volume at 2 μ L by the tensiometer. The γ_{LV} value of the solutions, listed in Table 4.1, strongly agrees with the reported data [17, 156].

Figure 4.5: The schematic of autophobic effect for a sessile droplet.

As the sessile droplets were made on the silicon substrate, the negatively charged silicon surface can attract the cationic heads of some surfactant molecules, and a few of them assemble external to the contact line, leading to a reduction of the

solid-vapor surface tension and thus dewetting of the droplet. Figure 4.5 shows a schematic of autophobic effect on a sessile droplet. Surfactant molecules can arrive at the three interfaces and thus reduce the surface energy there. When such a reduction of solid-vapor surface tension overcomes the decrease in solid-liquid and liquid-vapor surface tensions, the spreading coefficient would be reduced, leading to a depinning of the droplet, namely the autophobic effect. Such autophobic-induced depinning behaviors occurring at the initial stage of evaporation depend greatly on the surfactant concentration, C_{surf} . Fig. 4.6 shows the side view of the droplet by its images taken at 0 s and 40 s at intermediate C_{surf} to reveal the initial droplet behavior led by surfactant. The pure water droplet (Fig. 4.6 (a1)) with a small contact angle keeps pinning on the solid surface, and its contact angle decreases due to evaporation. The droplets with a lower range of C_{surf} from 0.014 mM to 0.6 mM (Fig. 4.6 (a2-a5)) autophobe intensively such that the contact angles increase and the base diameters decrease rapidly, while the one with a high C_{surf} at 0.84 mM (Fig. 4.6 (a6)) no longer retracts but maintains pinning on the substrate from the very beginning.

Figure 4.6: The images at 0 s and 40 s for sessile droplets with the surfactant concentration, C_{surf} , at (a1) 0 mM, (a2) 0.014 mM, (a3) 0.084 mM, (a4) 0.14 mM, (a5) 0.6 mM, and (a6) 0.84 mM. The scale in the images indicates 0.5 mm.

To analyze the correlation of the droplet dynamics and C_{surf} , we quantify the evolutions of the contact angle and the normalized base diameter over the full-spectrum of the droplet lifetime. As shown in Fig. 4.7, droplets with different C_{surf} exhibit varieties in the contact angle at t_0 , the sudden depinning occurring mainly

from 0 s to 100 s reflected by the jump of the contact angle and the reduction of the base diameter, and the subsequent attenuated retraction till the end of drying. It is discussed about the droplet dynamics at time t_0 and the initial depinning behavior later. Once the initial depinning ceased, the droplets with C_{surf} below 0.084 mM (0.09cmc) display the constant contact angle mode (CCA) and the mixed mode; as C_{surf} is above 0.084mM, only the mixed mode takes place; while for the one with C_{surf} higher than 0.84 mM (0.9cmc) the initial depinning disappears and the droplet maintains pinned on the solid surface at t_0 . Therefore, the pinning effect is greatly enhanced by raising C_{surf} represented by the flattening trend of the normalized base diameter. The one with C_{surf} at 1.4 mM (about 1.5cmc) shows a base diameter with indiscernible decrease except at the ultimate stage of drying.

The prominent stage of dewetting affected by C_{surf} is from 0 s to approximately 100 s of the lifetime, during which the droplet evolves from the utmost spreading (0 s) to the initial depinning. The maximum spreading of the droplet before retraction is presented with D_0 in Fig. 4.8 (a) and θ_0 in Fig. 4.8 (b). The extent that the droplet utmost advances basically reduces with an increase in C_{surf} , presented by the shorter D_0 and the larger θ_0 at a higher C_{surf} . Marmur and Lelah [157] reported similar results that the growing surfactant inventory suppressed the initial droplet spreading (the circular symbols in Fig. 4.8 (a)). Although surfactant reduces the liquid-vapor surface tension, γ_{LV} , of the solutions (see Table 4.1) which reinforces the spreading, it is overwhelmed by the counteractive autophobic effect. As the droplet is placed on the silicon wafer, some surfactant molecules in the thinning front transport across the contact line and locate at the bare solid-vapor interface to form a hydrophobic barrier. When the barrier is sufficiently built up it can halt the contact line motion immediately. Indeed, increasing C_{surf} can facilitate the establishment of such a hydrophobic barrier. The area covered by surfactant at the bare solid-vapor interface was proportional to C_{surf} as reported by Frank and Garoff [158,159]. Therefore, any further spreading of the droplet can be terminated responsively with an increasingly effective arrival of the surfactant beyond the

Figure 4.7: (a) Contact angle, θ , and (b) the normalized base diameter, D/D_0 , as a function of time for the sessile droplets with different surfactant concentrations.

contact line.

The sufficiently established hydrophobic barrier halted the spreading and meanwhile initiated the contact line depinning abruptly. We observed that such a depinning stage displayed two distinct phases: at first the contact line retreated rapidly for less than several seconds, and then the velocity abruptly reduced and sustained to about 100 s. Therefore, the depinning stage is divided into Phase 1 featuring quick retreating and Phase 2 of slower shrinkage. After that the droplet contact line moved even slower till the droplet dried out. The evolution of the base diameter for the first 100 s featuring intense depinning is shown in Fig. 4.9 (a). Through directly differentiating the base radius with time, it is obtained the

Figure 4.8: (a) The initial base diameter, D_0 , in this study and from Ref. 157 as a function of C_{surf} . (b) The change of the initial contact angle, θ_0 , with C_{surf} .

instantaneous retreat velocity, U , of the contact line at various C_{surf} (Fig. 4.9 (b)). U falls sharply during the first several seconds, and then its declining trend slows down and towards flattening with small oscillations over a longer period. I plot the best-fitting line in the inset of Fig. 4.9 (b) as an example to determine the cut-off point for Phases 1 and 2. The average velocity with the reference to $D_0/2$ for Phase 1 and Phase 2 are denoted by $\bar{U}_1$ and $\bar{U}_2$. As shown in Fig. 4.10 (a,b), $\bar{U}_1$ is one order of magnitude higher than that of $\bar{U}_2$. Besides, the trend of $\bar{U}_1$ and $\bar{U}_2$ are surprisingly inconsistent with an increase of C_{surf} . They suggest that either the mechanisms controlling the contact line motion or the relative weight for each mechanism altered from Phase 1 to Phase 2.

In respect to Phase 1, $\bar{U}_1$ rises firstly and then declines with the increase of C_{surf} . The velocity apex falls at around 0.042 mM (0.043 cmc), which is near the point of zero charge (p.z.c.=0.05 cmc) [18]. On the basis of Young's equation, as the droplet is out of equilibrium, the tension, f , acting at the contact line and driving it into motion can be expressed as

$$f = \gamma_{LV}\cos\theta + \gamma_{SL} - \gamma_{SV}, \quad (4.1)$$

where θ is the dynamic contact angle, γ_{SL} and γ_{SV} are the solid-liquid and the solid-vapor surface tensions. The transition of $\bar{U}_1$ was attributed to the combined results of the surfactant-dependent surface tensions at the three interfaces. Below p.z.c., γ_{LV} (Table 4.1) remains relatively stable against the increase of C_{surf} . At the solid-liquid interface, as the adsorption is in the form of monomers (the left schematics of the inset of Fig. 4.10 (a)) obeying the two-step adsorption model [154], the adsorbed amount shows nuance with an increase of the surfactant and thus the resulting γ_{SL} remains nearly invariable. But since a higher C_{surf} enhances the amount of surfactant arriving at the bare solid-vapor interface beyond the contact line (the left schematics of the inset of Fig. 4.10 (a)) and thus the reduction of γ_{SV} [158], it dominates and reinforces the inward motion.

Above the p.z.c., the monomers at the solid-liquid interface have reached saturation. Surfactant molecules in the bulk start to assemble with the monomers to form admicelles (the right schematics of the inset of Fig. 4.10 (a)). It could lead to a roughly ten-folded adsorbed amount particularly when it approaches the cmc, and thus a substantial decrease of γ_{SL} [18]. The synergetic reductions of γ_{SL} and γ_{LV} (Table 4.1) compete and eventually overwhelm the decrease of γ_{SV} , so the increase of the inward velocity $\bar{U}_1$ is terminated and turned into downwards. Besides, $\bar{U}_1$ has been examined as well for the CTAB droplets [157] and the HTAB (Hexadecyltrimethylammonium bromide) droplets on glass slides [160] (Fig. 4.10 (a)). The velocity for either CTAB or HTAB on glasses increased monotonously

Figure 4.9: (a) Base diameter, D , versus time for the initial 100 s. (b) The retreat velocity, U , of the contact line versus time for the initial 20 s at surfactant concentrations. The inset in (b) is an example to show the transition from Phase 1 to Phase 2 from the best linear fitting.

with C_{surf} and no transition emerged. It may be attributed to the different property of the glass slide or the smaller range of C_{surf} .

As illustrated in Fig. 4.10 (b), such a transition of $\bar{U}_1$ does not show up in $\bar{U}_2$ which decreases monotonously with an increase of C_{surf} . It implies that the comprehensive effects of the surface tensions at the three interfaces varied by surfactant adsorption could not afford an increase of $\bar{U}_2$ below the p.z.c. Unlike the bare solid-vapor interface in Phase 1, Phase 2 has the solid-vapor interface used to

Figure 4.10: The averaged velocity $\bar{U}_1$ in Phase 1 as a function of C_{surf} in this study and from Refs. 157, 160. The inset is $\bar{U}_2$ in Phase 2 of early evaporation stage.

be covered by the solution and it is formed through the withdrawal motion of the contact line, as depicted by the arrows in the inset of Fig. 4.10 (b). Surfactant on such a surface has a “standing up” structure while the counterparts for Phase 1 are “lying down” assemblies [158, 161]. The sensitivity of the two types of structures to C_{surf} should be different and thus led to different degrees of reduction in γ_{SV} . Additionally, with C_{surf} being lower than the p.z.c., It is noticed that the dynamic contact angle, θ , was larger at a higher C_{surf} at a same moment. The resulting smaller horizontal component of γ_{LV} , $\gamma_{LV}\cos\theta$, possibly accounted for the

unidirectional decrease of $\bar{U}_2$.

The entire retraction of the droplet can be controlled either by autophobing, evaporation, or both [162]. The role of each mechanism can be evaluated by comparing their characteristic time scales as reported by Qu, et al. [161]. The duration of the unsteadiness of the moving contact line is on the inertial time scale and is described as $t_i = \rho L^2 / \mu$, in which ρ is the solution density, L is the capillary length, and μ is the viscosity. In the vicinity of the contact line, the evaporation time scale can be expressed as $t_e = L\mu\rho / (\gamma_{LV}\rho_v)$, in which ρ_v is the vapor density. In my experiment, t_i ranged from 4 to 7 s, and t_e was approximately 1 s. The unsteadiness, t_i , was highly compatible with the duration of Phase 1 for the surfactant solution droplets. The time scale of evaporation, t_e , suggests that the evaporation reached stability within around 1 s, coincident with the linear reduction of the droplet volume over time. The withdrawal velocity of the contact line solely driven by evaporation can be estimated under the CCA mode from the measured average evaporation rate and the initial base diameter at each C_{surf} . The evaporation induced contact line velocity was around $0.1 \mu\text{m/s}$, agreeing with the study of Qu, et al. [161]. We found that the evaporation-driven contact line motion was approximately 2 orders and 1 order of magnitude lower than $\bar{U}_1$ and $\bar{U}_2$, respectively. Therefore, the autophobic effect dominated the initial rapid retraction and it very likely controlled the second phase as well.

By the end of the initial depinning the droplet entered either the CCA or the mixed mode. No matter in which mode the maximum contact angle θ_{max} was reached. Fig. 4.11 (a) illustrates θ_{max} as a function of C_{surf} . θ_{max} rises at first and then declines, leaving its apex at 0.084 mM of C_{surf} . By assuming that the droplet with θ_{max} has almost approached equilibrium, the wetting tension at θ_{max} , formulated as τ_{max} , can be expressed with $\gamma_{LV}\cos\theta_{max}$. Therefore, τ_{max} exhibits an opposite trend as compared to θ_{max} (Fig. 4.11 (b)). The transition in θ_{max} and τ_{max} implies that the dominant mechanism for them should be the same for $\bar{U}_1$.

It is worthy noticing that the transition point of θ_{max} is delayed to 0.06 mM

Figure 4.11: (a) The maximum contact angle, θ_{max} , as a function of surfactant concentration, C_{surf} in the study and from Refs. 18, 17. (b) The wetting tension, τ_{max} , with the surfactant concentration, C_{surf} , in this study and for Refs. 18, 17.

as compared to 0.042 mM for $\bar{U}_1$. The inward tension f at t_0 in Phase 1 was partially determined by the initial contact angle, θ_0 , which positively depended on C_{surf} . Therefore, the horizontal component of γ_{LV} at t_0 was smaller at a higher C_{surf} . Thus the upward trend of $\bar{U}_1$ can be terminated more responsively and then turned to downwards as C_{surf} increases over the p.z.c. I compare the results with those from Refs. 18, 17 in Fig. 4.11 (a,b). The system employed in Ref. 18 was a vertical silica plate partly immersed in a CTAB solution, and the other in Ref. 17 was a sessile droplet on a horizontal mica plate. In Ref. 18, as the plate was forced

into the solution, the contact line exhibited a stick-jump and then an autophobic behavior. For both systems the results exhibited resemblance to the ones for my study. But for the mica surface the trends of θ_{max} and τ_{max} shift leftwards than the ones for the silica and silicon surfaces, which possibly resulted from a variation of the surface tension with C_{surf} . The larger equilibrium contact angle implies a more intense autophobic of the droplet on mica than on the silica or silicon surface.

4.3.3 Autophobic Behavior of Nanofluid Droplets

In this section, four batches of solutions were employed, each of which had 0.0 g/L, 0.5 g/L, 1.0 g/L or 1.5 g/L graphite nanofluid concentration, C_{nano} . Each batch of the nanofluids contained eight surfactant concentrations C_{surf} ranging from 0 mM to 2.1 mM. The effect of surfactant on the deposition patterns were explored in particle/surfactant solutions with the nanoparticle concentration fixed at 1 g/L and C_{surf} with the same eight concentrations. The 2.10 ± 0.13 μ L droplet produced by the micropipette (Thermo-Fisher) was placed on the clean silicon wafer, and the resulting deposition patterns of nanoparticles are shown in Fig. 4.12.

The droplet free of surfactant (0 mM) in Fig. 4.12 produces a central-concentrated deposit circumscribed by a typical coffee ring. With 0.042 mM surfactant added in, nanoparticles in the interior region become sparsely distributed and plenty of them are accumulated near the droplet perimeter. Such a transition in the particle profile is further enhanced with a loading of the surfactant. At and above 0.14 mM, the droplet forms a typical coffee ring, and it becomes insensitive to C_{surf} . Such a dramatic change of the particle profile suggests the role of surfactant in varying nanoparticles motion upon droplet evaporation.

Nanoparticles behaving differently in the droplets with and without surfactant were presumably correlated with surfactant adsorption at the particle surface and the liquid-solid interface. Such adsorption via electrostatic attractions or hydrophobic bonding modified the interplay among nanoparticles, and between the particles and the liquid-solid & liquid-vapor interfaces. For the droplet free

Figure 4.12: Deposition patterns of graphite nanoparticles formed from aqueous CTAB surfactant solution droplets with the surfactant concentration at 0 mM, 0.042 mM, 0.14 mM, 0.42 mM, 0.84 mM, and 1.96 mM. The scale bar indicates 400 μm .

of surfactant, although the graphite nanoparticles used in my study exhibited relatively strong hydrophilicity, some of them were found still to be trapped at the liquid-vapor interface. At the late stage of evaporation, the nanoparticles previously trapped at the liquid-vapor interface were pushed inwards to form a compact skin which rested on the solid surface with the descending droplet surface, leading to the central-concentrated particle morphology. Meanwhile, the evaporation-induced radial flow carried nanoparticles in the bulk to reach the droplet edge. In such a droplet system, both the graphite particles and the substrate have negatively-charged surfaces, as illustrated in Fig. 4.13 (a). Particles are either transported to the liquid-vapor interface or driven towards the contact line. The electrostatic repulsion presumably repels the nanoparticles from depositing on the substrate to some extent.

Figure 4.13: (a) In a water-based droplet without surfactant, the negatively-charged graphite particles either are trapped at the liquid-vapor interface or carried to the contact line; (b) at a low surfactant concentration C_{surf} , graphite nanoparticles become more hydrophilic due to the adsorbed surfactant, and the solid surface could be neutralized; (c) at a high C_{surf} , the positively charged nanoparticles could be easily driven to the rim due to the repulsion between them and the solid surface with reversed charge.

Surfactant in the droplet has a propensity to adsorb to the surface of

nanoparticles and the substrate. As reported by Paruchuri, et al. [153], CTAB surfactant molecules were bonded with the graphite particulate surface through hydrophobic interactions, with the cationic heads towards to the solution. Contrary to it, the amphiphilic surfactant molecules were electrostatically attracted to the silicon surface, thus with their hydrocarbon tails striking into the bulk. Fig. 4.13 (b) demonstrates the result of such adsorption at low surfactant concentrations. Surfactant adsorption in a manner of mono-layer may lead to a decrease of the anionic charge or even neutralization of the graphite nanoparticles and the substrate. The graphite nanoparticles could become more hydrophilic owing to the coverage of the hydrophilic heads of the surfactant molecules and hence their affinity to the liquid-vapor interface could be weakened. Considering a particle with radius R_S trapped at a liquid-vapor interface with surface tension γ_{LV} and forming with it a contact angle θ , the energy E required to pull the particle back into the solution is $E = \pi R_S^2 \gamma_{LV} (1 - \cos\theta)^2$ [93]. As a result, the reduction in particle hydrophobicity leading to a decrease in θ should be accompanied by a decrease in E , therefore the probability for nanoparticles trapping would be reduced. Skin formation of nanoparticles would no longer emerge in droplets with surfactant, and nanoparticles could either transported outwards or resting on the substrate. The possibly anionic or neutralized substrate could still seize some nanoparticles, in accordance with the patterns produced at 0.042 mM and 0.14 mM of the surfactant as shown in Fig. 4.12.

At a high C_{surf} approaching cmc, surfactant molecules start to assemble with the mono-layer via hydrophobic bonding to form hemimicelles or micellar structures on the solid-liquid interface, thus the substrate surface would be cationized. The electrostatic repulsion between the like-charged graphite particles and the liquid-solid interface repels the particles from depositing on it. Instead, they are carried to form a coffee ring by the evaporation induced capillary flow, as illustrated in Fig. 4.13 (c). Another reason for the enhanced coffee ring effect by adding surfactant in the droplet is the decrease in particle-particle sticking force via surfactant

adsorption at the particle surface. Nanoparticles with weakened sticking force bore greater freedom, so they could be easily driven by the outward flow to reach the contact line, rather than being bonded together to form aggregates [92]. As the particle is enclosed by the cationic heads of the amphiphilic surfactant, the repulsive interaction among the particles is increased and thus they maintain a certain distance away from each other, resulting in a lower probability of agglomeration.

Figure 4.14: Contact angle changes over time for the 0.0 g/L, 0.5 g/L, 1.0 g/L, and 1.5 g/L nanofluid droplets with the initial surfactant concentration at (a) 0.28 mM and (b) 0.56 mM.

The initial depinning behavior, emerged in the pure surfactant solution droplets, was expected to be different in nanofluid droplets on the same type of silicon wafers. Nanoparticles have been reported to enhance the contact line pinning, the initial

spreading, and the evaporation rate of a sessile droplet [12, 163]. The interaction between nanoparticles and surfactant, known to reduce the particle-particle sticking force, may exert influence on the dynamics of the droplet as well. Therefore, nanofluids were prepared with the intermediate nanoparticle concentrations C_{nano} to investigate the dependence of the initial depinning behavior on nanoparticles. Fig. 4.14 (a, b) shows the evolution of the contact angle for nanofluid droplets at a C_{surf} (0.28 mM and 0.56 mM). Strikingly, the initial depinning is greatly enhanced with the presence of nanoparticles, reflected by the greater enlargement of the contact angle at a higher C_{nano} . It contradicts to either the frequently observed role of nanoparticles in enhancing the pinning effect or the transient initial spreading of the droplet observed in our previous study [12]. The promoted initial depinning could be attributed to two mechanisms. As explicated in Chapter 3, it has been shown that the graphite nanofluid droplet has a larger initial contact angle than that of the pure water droplet. Graphite nanoparticles reduced the wettability of the sessile droplets through possible trapping at the liquid-vapor and the liquid-solid interfaces. Besides, the consumption of surfactant molecules via decorating particles surfaces leads to fewer surfactant capable of attaching to the solid-liquid and the liquid-vapor interfaces of the droplet. Therefore, the resulting decreases in the corresponding surface tensions were attenuated. According to Young equation $\gamma_{SV} = \gamma_{LV}\cos\theta + \gamma_{LS}$, the horizontal component of the tension directing towards the droplet center is larger as compared to the droplet free of nanoparticles. It contracts and even dominates over the decrease in γ_{SV} owing to the reduced C_{surf} , resulting in an enlargement of the overall force directing inwards at the contact line.

To systematically quantify the effect of nanoparticles on the depinning behavior, the contact angle increment of the water and the nanofluid droplets over C_{surf} from 0 mM to 1.96 mM is illustrated in Fig. 4.15 (a, b). Since the contact angle increment varies highly similarly for different values of C_{nano} , I make fitting curves to describe the relations between $\Delta\theta$ and C_{surf} ranging from 0.14 mM to 1.96 mM

Table 4.2: The value of the parameters in Equation 4.2 at different nanoparticle concentration C_{nano} .

C_{nano}	$\Delta\theta_0$	n	C_0
0.0 g/L	23.861°	0.015	0.012
0.5 g/L	19.418°	0.018	0.012
1.0 g/L	21.138°	0.018	0.012
1.5 g/L	27.080°*	0.022	0.011

Note* At 1.5 g/L of the nanofluid droplet, the addition of surfactant at 0.14 mM induced such a strong depinning that the droplet could not maintain a spherical shape as shown in Figure 4.15 (c), so the contact angle varies with the measured location rather than showing a sole value. Therefore it cannot have a single value to stand for the contact angle of the droplet. For this droplet, $\Delta\theta_0$ is replaced by the value of 27.080 in the fitting Equation 4.2, which could be the $\Delta\theta_0$ when C_{surf} is at 0.14 mM.

at each C_{nano} ranging from 0.0 g/L to 1.5 g/L, as shown by the dashed lines in Fig. 4.15 (a). The corresponding fitting equation can be written as,

$$\Delta\theta = \frac{\Delta\theta_0}{1 + 10^{\frac{(C_{surf}/cmc - n)}{C_0}}} \quad (4.2)$$

where $\Delta\theta_0$ is the contact angle increment at 0.14 mM of C_{surf} , and n and C_0 are the constants for a certain C_{nano} , which are listed in Table 4.2.

Based on Equation 4.2, the contact angle increment $\Delta\theta$ is negatively dependent on C_{surf} , and its value does not exceed $\Delta\theta_0$. The varied $\Delta\theta_0$ and n with C_{nano} as listed in Table 4.2 imply that they are correlated with C_{nano} . Noted that C_0 is almost the same for different C_{nano} , so it can be simply treated irrespective to C_{nano} .

The contact angle increment basically increases with the raised nanoparticle concentration C_{nano} , especially at 1.5 g/L. Noted herein the droplet with 1.5 g/L nanoparticles and 0.14 mM surfactant experienced an intense retraction that the droplet could not maintain a circular shape from the top view (Fig. 4.15 (c)). Therefore, the contact angle of the asymmetric droplet could not be measured as the tensiometer works on the basis of two dimensional image approaches. It is conjectured that such a droplet had a fairly large contact angle increasing,

Figure 4.15: (a) The relation between the contact angle increment and surfactant concentration for 0.0 g/L, 0.5 g/L, 1.0 g/L, and 1.5 g/L nanofluid droplets. The range of initial surfactant concentration, C_{surf} , is from 0 mM to 1.96 mM. The dashed lines are the fitting curves over the range of C_{surf} from 0.14 mM to 1.96 mM. (b) The relation between the contact angle increment and nanoparticle concentration for droplets with 0.14 mM, 0.28 mM, 0.42 mM, 0.56 mM, 0.84 mM and 1.4 mM surfactant. The range of nanoparticle concentration is from 0.0 g/L to 1.5 g/L. (c) The droplet with 0.14 mM surfactant and 1.5 g/L nanoparticle retracts so intense and rapid that it cannot maintain a circular shape from the top view. The two images are captured at 0 s and 100 s.

fulfilling the ascending trend of the contact angle enlargement in Fig. 4.15(b). The mechanisms lying behind, as simply discussed above, was a combination of the reduction in droplet wettability due to nanoparticles adsorption, and the decrease of the free surfactant molecules capable of attaching to the liquid-solid and liquid-vapor interface because an amount of surfactants were bonded with the graphite particles surface. The phenomenon demonstrates that nanoparticles do not always enhance the pinning effect of the droplet, but instead, the particles could be employed to intensify the depinning behavior with appropriate recipe of the liquid solution and substrate.

The consumption of the surfactant attracted to the graphite nanoparticles has been reported to increase with the surfactant concentration [153]. In 1 mM KCL with the pH value at 5.3-5.8, the zeta-potential of a planar graphite surface covered by CTAB hemi-cylindrical micelles was around 40 mV with C_{surf} at 0.1cmc; while

it increased over 70 mV as C_{surf} reached 1.0cmc. It was also found that the zeta-potential for the planar graphite surfaces was slightly smaller than that for the graphite particles [153], indicating a larger amount of CTAB molecules attracted to the particulate graphite. The conspicuous growth of the hemi-cylindrical micelles at the graphite nanoparticle surface could also influence the available amount of surfactant molecules having access to the solid-vapor and the solid-liquid interface. One thing can be sure is that the enhancement in the initial droplet depinning is even greater at a relatively higher C_{nano} , although the resulting larger area of the nanoparticle deposition can cost more surfactant which could have a chance to transport to the solid-vapor interface. At 1.5 g/L of C_{nano} , as shown in Fig. 4.15 (a), the initial depinning behavior which disappears in the pure droplet as C_{surf} is above 1.0cmc emerges even when C_{surf} reaches 1.5cmc. In other words, the presence of the nanoparticles could raise the upper limit of the C_{surf} range over cmc for the initial retraction of the sessile droplet to occur. Therefore, with proper recipes of the solutions, autophobing still can occur at a C_{surf} higher than cmc.

4.4 Summary

In this chapter it is stressed on the base solution of a sessile droplet system via employing water-ethanol solutions and surfactant aqueous solutions to examine their influences in flow paradigms, droplet dynamics, and the deposited patterns if the droplets contain nanoparticles.

In section 4.2 it is showed that the binary mixture droplet had three distinct flow regimes, and the relative weighting of each regime and flow intensity affected by the ethanol concentration determined the movement of the nanoparticles inside the droplet and the final deposition profile of nanoparticles. Regime I featuring vortices and furious flows brought particles to the liquid-vapor interface and made them collide to form aggregates. In Regime II, the initially forming aggregates could be triggered inwards by the Marangoni flow along the liquid-vapor interface.

In the second regime, the aggregates staying at the interior region were increased at a higher ethanol concentration. Once the inward movement stopped, the droplet entered into Regime III and the evaporation-induced decrease of the droplet height made the aggregates deposit onto the substrate ultimately. Regimes I and II were found to be prolonged upon increasing the ethanol concentration in the solvent, which offered a longer time for particles aggregation, promoting aggregates detach from the droplet perimeter, and intensifying the inward motion of the aggregates.

In section 4.3, the autophobic effect was studied in both pure and nanofluid droplets with a wide range of surfactant concentration. For the pure surfactant solution droplets, the depinning of the sessile droplets due to autophobic varies nonmonotonously with the surfactant concentration. It is primarily examined the utmost spreading of the droplet, the contact line motion during the initial depinning stage which showed two distinct phases, and the maximum dewetting the droplet could reach. A transition emerged in the averaged velocity for the rapid depinning phase, while such transition was disappeared in the subsequent slower depinning phase. The transition manifested as well in the maximum contact angle with a higher loading of surfactant. The unique relation between the droplet shrinkage and surfactant concentration can enrich the understanding of autophobic in wettability control of droplet and promote its intersection with the emerging field of the colloidal droplet evaporation.

Nanoparticles addition into the surfactant solution droplets were shown to produce various deposition patterns with the change of the surfactant concentration. Surfactant adsorption to the particles surfaces and the liquid-solid interface are attributed to the behaviors of nanoparticles, whether trapping at the liquid-vapor interface, attracted to the solid-liquid interface or driven toward the droplet rim. The initial depinning of pure surfactant solution droplets was found to also occur in the droplets containing nanoparticles. The initial depinning behavior was more intense in the nanofluid droplet especially with a relatively high nanoparticle concentration. Unlike the pure surfactant-water droplet, the initial

depinning behavior still occurred at a surfactant concentration higher than cmc in the 1.5 g/L nanofluid droplet. Therefore, the nanoparticles could increase the upper limit of the surfactant concentration range for the initial retraction to occur. The enhanced depinning behavior by nanoparticles was due to the decrease in the liquid-solid area available to have a hydrophobic interaction with the bulk solution due to the occupation of the deposition, and a hydrophilic interaction between the bulk liquid and the head-to-head micelles adsorbed at the deposition, as compared with the pure surfactant solution droplet. Therefore, the nanoparticles do not always enhance the pinning effect, or promote the initial spreading of a sessile droplet.

Chapter 5

Substrate Temperature Effects on Nanoparticle Deposition of Sessile Droplets

5.1 Introduction

Substrate temperature plays an important role in inducing fluid flows in a sessile droplet. Upon a natural droplet drying, the concentrated evaporation in the vicinity of the contact line could lead to a non-uniform evaporative cooling over the liquid-vapour interface which likely results in interfacial flows. Cooling and heating solid surfaces are anticipated to impose enhanced temperature gradients along a droplet free surface and to produce a distinct deposition profile if the droplet contains suspensions. In this chapter, it is probed the flow paradigms, nanoparticles trajectories and the various deposits formed after droplets evaporation on substrates from cooling to heating conditions.

5.2 Experimental Methods

The nanofluid samples with the nanoparticle concentration at 0.5 g/L were prepared by mixing graphite nanopowders (2-3 nm, SkySpring Nanomaterial Inc., Purity ≥ 99 %) and Milli-Q nano-filtered water with resistivity at 18.2 M Ω -cm obeying the two-step method. The sample was placed in the ultrasonic bath (Fisher Scientific model 500) at first and then underwent magnetic stirring to obtain evenly dispersed suspensions. The freshly prepared sample was employed within 48 hours to avoid particle agglomeration and sedimentation. The evaporation substrates

were brand new silicon wafers (Latech Scientific Supply Pte. Ltd.,) with an average roughness at $0.106\ \mu\text{m}$. The wafers were ultrasonically cleaned in water for 1 hour and then dried by compressed dry nitrogen prior to each test.

The experimental configuration is shown in Fig. 5.1. Nanofluid droplets with an initial volume at around $0.2\ \mu\text{L}$ controlled by the micropipette (Thermo-Fisher) was deposited inside a shielding plastic cylinder with two open sides on a silicon wafer to avoid external air disturbance. The wafer was attached to the lower aluminum heating module by a thin layer of conductive silica-gel. The heat/cooling bath (F25-EH, JULABO) connected to the heating module controlled its temperature and so was that of the silicon wafer. The silicon wafer temperature is adjusted to $10\ ^\circ\text{C}$, $12\ ^\circ\text{C}$, $15\ ^\circ\text{C}$, $16\ ^\circ\text{C}$, $22\ ^\circ\text{C}$ (room temperature) and 50°C . Two K-type thermocouples with the accuracy at $0.1\ \text{K}$ were adhered to the surface of the silicon wafer with one at the edge and the other at the center to monitor the temperature uniformity by a Data Acquisition (Agilent, 34972A). The substrate temperature difference from the two thermocouples was less than $0.2\ \text{K}$ during the entire droplet lifetime thanks to the high conductivity of the silicon wafer.

We employed an optical microscopy (LV100D-U from Nikon Inc.) with bright-field (BF) and dark-field (DF) schemas to obtain particles motion during droplet evaporation and the resulting nanoparticles profiles from a top view. The time $0\ \text{s}$ is defined as the moment when the droplet touches the substrate. In order to probe nanoparticle motion along the cross-section of the droplet, the microscope was adjusted to focus at either the solid-liquid or the liquid-air interfaces. Whether a particle or an aggregate is at focus suggests us its approximate vertical position. After droplet evaporation completed, the “three-dimensional light intensity analysis” and the “inverted grayscale intensity analysis” of the microscope were utilized to present the spatial and the radial stain distribution for the droplets respectively. At least three batches of tests were conducted for each substrate temperature to guarantee experimental repeatability. The experiments were conducted under the ambient condition with the temperature and the relative

Figure 5.1: Schematic diagram of the experimental configuration consists of an optical microscope visualizing the droplet placed on the silicon wafer substrate which is adhered to the heating alumina module below. The module temperature is controlled by the heat bath. Two thermal-couples are attached to the silicon wafer with one at the center and the other at the edge to monitor the substrate temperature by a Data Acquisition (DAQ). After droplet evaporation, a deposition pattern is left on the substrate as shown by the image at the right side. The scale bar indicates 400 μm .

humidity fixed to 22 °C and 40 %~50 %.

5.3 Results and Discussion

5.3.1 Deposited Profiles Formed at Various Substrate Temperatures

The particle deposition profiles are shown in Figure 5.2 at each substrate temperature. The pattern is displayed from a top view together with its “three-dimensional light intensity profile” and the “normalized inverted grayscale intensity profile” reflecting the spacial and radial nanoparticles distributions. At 10 °C, a disk-like deposition is produced with nanoparticles uniformly covering the interior region enclosed by an exterior coffee ring, except for a fairly narrow annular gap

adjacent to the edge where the nanoparticles are more sparsely distributed. At 12 °C and 15 °C, the coverage of the nanoparticles at the annular gap is further reduced, and at 16 °C there barely has nanoparticles. Meanwhile, contrary to the uniform central region at 10 °C, the interior deposit becomes hollow with the increase of the substrate temperature. The vacancy detectable at 12 °C and 15 °C becomes evident at 16 °C. As the temperature reaches 22 °C and 50 °C, the interior deposition has entirely alters to a secondary ring.

Fig. 5.2 reveals that the deposited profile transfers from a homogeneous pattern to a dual ring with an increase of the substrate temperature, and the transit point seems to occur at around 15 °C to 16 °C when the secondary ring begins to take shape while the central region is still uniformly covered with nanoparticles. After carefully examining the nanoparticles motion upon droplet evaporation, it is strikingly found that the flow paradigm is distinctly different for the substrate below and above roughly 16 °C. Therefore, we decompose the phenomena for the two corresponding temperature ranges.

5.3.2 Flow Patterns under Substrate Cooling at 10°C

Droplets placed on the cooler substrates were found to display evolving fluid flow patterns with the proceeding of evaporation instead of a mono-paradigm. The droplet on the 10 °C substrate exhibited three evaporation stages which were distinguished by the distinct nanoparticle trajectories in each stage along the liquid-vapor interface, near the solid surface or in the bulk. The intensity and duration of each stage were greatly affected by the substrate temperature, and the combination of the stages determined nanoparticles locations and the deposit profile as a whole.

At the moment the droplet was placed on the substrate cooler than the surrounding atmosphere, the droplet edge was cooled down firstly, and the surface temperature should increase as going away from the perimeter. Therefore, the surface tension near the droplet perimeter is higher, so the nanoparticles at the liquid-vapor interface are carried towards the contact line. It was evidenced by the

Figure 5.2: (I) The deposition patterns, (II) the corresponding three-dimensional light intensity profiles and (III) the normalized inverted grayscale intensity profiles along the diameter of the 0.5 g/L graphite nanofluid droplets on the silicon wafer substrates with the surface temperature at 10 °C, 12 °C, 15 °C, 16 °C, 22 °C and 50 °C. The scale bar indicates 400 μm .

Figure 5.3: The entire evaporation of the droplet placed on the 10 °C substrate is divided into (a) Stage I, (b) Stage II and (c) Stage III with the corresponding schematic diagram at the left. For Stage I, the snapshots taken at 8.2 s, 57.1 s and 151 s indicate the outward transports of two nanoparticle aggregates along the liquid-vapor interface enclosed by the dashed circles denoted by “a” and “b”, and the descendance of the four aggregates onto the solid surface denoted by the number “1”, “2”, “3” or “4”. The arrows denote an annular gap with sparsely-distributed nanoparticles next to the contact line. In Stage II, the snapshots taken at 781.8 s, 829.6 s and 899.2 s at the right side show some nanoparticles under Brownian motion at the liquid-vapor interface without palpable orientations. In Stage III, the snapshots at 1469.5 s, 1530 s and 1618.2 s indicate the filling of the annular gap adjacent to the contact line by outward transported nanoparticles. The scale bar indicates 100 μm .

outward motion of the nanoparticle aggregates shown in the frames of Figure 5.3 (a). The aggregates denoted by the yellow and the red circles are vaguely observed at time 8.2 s as the microscope focuses at the solid-vapor interface, suggesting that they are nearer to the liquid-vapor interface. At 151 s the aggregates carried to approach the contact line region are clearly visualized by the microscope. The enhancement in the clarity of these aggregates confirms their trajectories along the droplet free surface. Meanwhile, at the liquid-vapor interface far away from the contact line, nanoparticles were observed to fluctuate erratically around their original positions, implying the domination of Brownian motion. Simultaneously,

a few nanoparticles close to the solid surface are shown to directly rest on the substrate without evident horizontal displacements. It suggests that there has no advective flow or that such the flow is too weak to induce massive transports of nanoparticles no matter inwards or outwards. The aggregates denoted by the number “1”, “2”, “3” or “4” at time 8.2 s are away from the solid surface according to their blurring outlines. While at 57.1 s, the four aggregates can be observed clearly, implying that they have descended onto the substrate. Besides, it is found that the four aggregates barely change their horizontal locations before and after the sedimentation.

We noticed that nanoparticles were seem to be repelled from reaching the annular region neighboring the contact line in this stage despite that there had no perceptible inward motion of nanoparticles observed in my experiment. It differs from the flow pattern proposed by Kim, et al. [112] that the temperature gradient induced outward Marangoni flow along the liquid-vapor interface triggered an inward flow near the solid surface which brought dissolved polymers to the central area, evidenced by the evolution of the light absorbance there. The discrepancy between the study from Kim, et al. and ours could be attributed to the weaker droplet wettability in their study such that the larger droplet thickness and contact angle were likely to enhance the temperature gradient and thus the accompanied inward flow near the substrate. This could also account for the more central-concentrated deposit profile even at a smaller temperature difference between the atmosphere and the substrate in their study. The absence of an outward radial flow should be partially accountable to the annual vacant gap adjacent to the coffee ring shown in Fig. 5.3 (a).

Stage I lasted for roughly a short 15% of the droplet lifetime for the 10 °C substrate. Its ending is characterized by an increase of the nanoparticles in the bulk driven radially outward so the coffee ring is gradually pronounced, as indicated by the snapshots in panel (b) of Fig. 5.3. Besides, the outward transport of nanoparticles along the liquid-vapor interface is remarkably attenuated and instead

they randomly oscillate without a palpable trend. The snapshots in panel (b) of Fig. 5.3 demonstrate some nanoparticles at the droplet free surface between the two dashed lines fluctuating locally over even 100 s. The absence of the outward transport of nanoparticles along the liquid-vapor interface was attributed to the homogenized temperature profile of the droplet due to a longer time of cooling. In addition, the nanoparticles at the central region near the solid surface were less affected by the enhanced radial flow, and they still descended toward the solid surface directly. The behaviors of the nanoparticles at the liquid-vapor, the liquid-solid interfaces and in the bulk are schematized at the left side of Fig. 5.3 (b). The droplet kept pinned during Stage II so the height decreased due to by evaporation. The associated evaporation flux and the radial advective flow were enhanced, carrying plenty of nanoparticles to contribute to the coffee ring. Even though the outward transports of the nanoparticles in the bulk solution were enhanced, the annular gap next to the contact line still remained sparsely-covered. The low temperature at 10 °C of the substrate allowed a relatively slow evaporation, so the outward flow with an intermediate velocity enabled the nanoparticles to arrive at the contact line region and freely assembled with the coffee ring, rather than being flushed to hit the annular vacant area before reaching the droplet edge.

Stage III represents the instantaneous dry-up of the droplet at the latest moment. The annular region confined by the coffee ring and the dashed curve has few nanoparticles as shown by the image taken at 1469.5 s in panel (c) of Fig. 5.3. But as the radial capillary flow increases greatly at the ultimate stage, nanoparticles and their congregates are flushed outwards to fill the vacant annular region, as shown by the frames at 1530 s and 1618.2 s in Fig. 5.3 (c). In Stages I and II, along with the downward liquid-vapor interface, some nanoparticles deposited onto the substrate due to the lack of evident flows in the bulk. Therefore, before the droplet dried out, the central region had been already covered with plenty nanoparticles. They could block the free pathes of those close to the substrate, and allow them to transport only by a short distance before immobilized. It explains

Figure 5.4: The snapshots taken at around 50 % of the lifetime of the 0.5 g/L graphite nanofluid droplet on the (a) 10 °C, (b) 12 °C, (c) 15 °C and (d) 16 °C substrates. The region confined by the dashed curve and the contact line is sparsely covered at the 10 °C and 12 °C substrates, while it is densely covered at the 15 °C and 16 °C substrate. The scale bar indicates 100 μm .

why many nanoparticles ended with touching the previous vacant annular area near the perimeter, resulting in a homogenized morphology for the entire droplet region.

5.3.3 Flow Patterns for the Substrate Temperature from 10 °C to 16 °C

The pattern evolving from a homogenous profile to a blurring dual ring from 10 °C to 16 °C of the substrate was determined by the combination of the three stages. The duration, intensity and even nanoparticles transport for each stage were sensitive to the substrate temperature. It is worth mentioning herein that as the substrate temperature increased, the transition from Stage I to II was difficult to distinguish since even at an early moment a few nanoparticles were noticed to be carried outward in the bulk, particularly at 15 °C and 16 °C. One thing can be seen is that Stage I was conspicuously shortened and the onset of Stage II was brought in advance with a raise of the substrate temperature. Although at the very

beginning the particles directly resting on the solid surface were still observable, the amount of which was substantially reduced. Most nanoparticles in the bulk were dominated by the enhanced outward flow owing to the intensified evaporation at a higher substrate temperature. Their relatively high velocity resulted in a greater chance of their impact on the annular region. The snapshots taken at the same time of 50% of each droplet lifetime in Fig. 5.4 present that from 10 °C to 16 °C, the region confined by the contact line and the dashed curve is more densely distributed at a higher temperature. The massive outward transport of the nanoparticles was expected to reduce the amount of them remaining in the central bulk, which thinned the central deposit and thus the hollowing there was enhanced upon increasing the substrate temperature.

Another essential reason for the deposit variation is the reversal of the nanoparticle aggregates trapped at the liquid-vapor interface at the latest stage of evaporation. At 10 °C of the substrate, the nanoparticles are monotonously driven outward to fill the annular gap right before drying out, as shown by the snapshots in Fig. 5.3 (c). Such a phenomenon manifests itself as well in the droplet at the 12 °C substrate (see Fig. 5.5(a)). The annular vacancy at time 845 s is partially covered by the outward swept nanoparticles despite of a thin region remaining uncovered in affinity with the coffee ring. At 15 °C the gap shown at time 315 s is slightly extended until the end of evaporation (Fig. 5.5 (b)). For the droplet at 16 °C, however, the aggregates at the liquid-vapor reverse their orientations distinctly to depart away from the contact line (Fig. 5.5 (c)). Consequently, the gap is widened and it further enhances the secondary ring. Therefore, it can be concluded that lowering the substrate temperature actually suppressed the inward transports of nanoparticles at the liquid-vapor interface. Additionally, right before droplet drying out, the thin droplet thickness comparable to the size of nanoparticle aggregate made the secondary ring block the free pathes of the nanoparticles travelling outward from the center, which in turn intensified the secondary ring from its inside.

Figure 5.5: Snapshots of the ultimate drying of the 0.5 g/L graphite nanofluid droplet on the (a) 12 °C, (b) 15 °C and (c) 16 °C substrates. The nanoparticles in the region confined by the dashed curve and the contact line become denser at 12 °C while they are evacuated at 15 °C and 16 °C. The scale bar indicates 100 μm .

5.3.4 Transition of the Flow Patterns and the Deposition

The flow pattern of the droplet altered greatly as the substrate temperature increased to 16 °C, rather than the room temperature of 22 °C as anticipated. The transition of the flow pattern was mainly embodied in the remarkably intensified outward radial flow, and most importantly the reversal of the surface flow at the latter drying stage. The reversal of the nanoparticle aggregates occurs at the latest moment of droplet drying at the 16 °C substrate (Fig. 5.5(c)), and it gives rise to a discernable inner ring. Such inward nanoparticle transport is brought forward to approximately 57% of the droplet lifetime when the substrate temperature is increased to 20 °C. Despite that the substrate at 16 °C and 20 °C was maintained cooler than the room temperature, the corresponding flow patterns resembled the one at the room temperature and even higher temperatures of the substrate. The water-based droplet evaporating on a silicon substrate at the room

temperature was warmest at its edge while coolest at its apex, as reported by Parsa, et al. [19]. Evaporative cooling was greatest at the droplet apex due to the highest resistance to heat conduction from the solid surface. The high relative thermal conductivities of the silicon substrate and the water-based solution enabled energy to be readily supplied to the contact line region, so evaporative cooling would not be produced there [84]. Substrate cooling could counteract the evaporative cooling induced temperature gradient, and even reverse it if the substrate is cooled down to relatively low temperatures. It explained why the inward transport of nanoparticles at the liquid-vapor interface was still in presence at the 20 °C and 16 °C substrates, while it basically disappeared as the substrate temperature was further lowered.

Figure 5.6: (a) Sketch of the flow pattern of the co-existing of a Marangoni flow and a radial flow as the substrate temperature is higher than 16 °C, with a stagnation point at a distance from the contact line. (b) Snapshots indicate a reversal motion of an aggregate denoted by the circle subject to the Marangoni flow of the droplet on the 50 °C substrate. The dashed curves indicate the position the stagnation point. The scale bar indicates 100 μm .

As the substrate is under natural and heating conditions, the inward motion of nanoparticles along the liquid-vapor interface emerged at the very beginning of

Figure 5.7: The evaporation process of the 0.5 g/L graphite nanofluid droplet evaporating on the (a) 10 °C and (b) 22 °C substrate. For the droplet on the (a) 10 °C substrate, nanoparticles are central-concentrated with an annular gap next to the contact line during Stages I and II; afterward the gap is filled in Stage III. For the droplet on the 22 °C substrate, nanoparticles are edge-concentrated and lead to a central hollow profile in Stage I; in Stage II the hollow is further enhanced, while the nanoparticle aggregates are transported away from the contact line and form the secondary ring. The scale bar indicates 400 μm .

evaporation. Fig. 5.6 (a) shows a schematic drawing of the flow pattern with the co-existing radial flow due to the greater evaporation at the droplet edge and the Marangoni flow induced by a temperature gradient for the substrate temperature equaling and higher than 16 °C in my experiments. The capillary flow leads to the exterior coffee ring while the Marangoni flow brings nanoparticles backwards to accumulate as the inner ring with a certain distance from the contact line. Besides, the stagnation point is found close to the droplet edge, reflected by the reversal of an aggregate firstly carried outwards until arriving at the stagnation point at 1.8 s and then brought back along the liquid-vapor interface as the substrate is heated to 50 °C (Fig. 5.6 (b)). Many other nanoparticles behave similarly that they reverse the orientations at the stagnation point. It can be seen that the region is free of any nanoparticles beyond the stagnation point indicated by the dashed curve in Fig. 5.6 (b) to the contact line.

Under natural and heating conditions, at the early period nanoparticles were

driven radially outward firstly and then were carried to the liquid-vapor interface near the droplet rim by Marangoni flows. Afterward, the gathered nanoparticles there began to move inwards, forming a distinct secondary ring. Therefore, I decomposed the entire process into two stages, with Stage I featuring the radially outward traveling and the assembling of nanoparticles at the liquid-vapor interface, and Stage II characterized by the detachment of the annular agglomeration from the contact line to be the inner ring. As a comparison, snapshots demonstrating the entire evolutions of the droplets from a top view on the substrates at 10 °C and the room temperature are shown in the panels (a) and (b) of Figure 5.7 respectively. When the droplet is evaporated on the cooler substrate, the nanoparticles stay in the interior region with an annular gap next to the contact line over Stages I and II. At Stage III, the gap is rapidly filled due to a sudden enhanced outward transport of nanoparticles (Figure 5.7 (a)). Contrarily, at the room temperature substrate, nanoparticles in the bulk in Stage I are driven outward, emptying the interior region of the droplet. Meanwhile, nanoparticles arrival at the liquid-vapor interface by Marangoni flows leads to a dense gathering as shown by the frame at 152 s in Figure 5.7 (b). The dense accumulation of nanoparticle is pulled inside during Stage III and the central hollow is further pronounced, producing a distinct secondary ring at the end of drying. Therefore, it was the combination of the temperature-dependent distinct stages decided nanoparticles transport both at the interfaces and in the bulk, and the last stage was vital for the deposit transition as the substrate was varied from cooling to heating.

5.4 Summary

In this chapter, it is experimentally investigated the effect of the substrate temperature from cooling to heating on the flow patterns and the deposited profiles of nanoparticles from the evaporating sessile nanofluid droplets. The deposited patterns transferred from a disk profile to a dual ring with an increase of the

substrate temperature. The associated transition of the flow pattern occurred when the substrate was still cooled owing to the counteractive evaporative cooling at the droplet apex. The droplet on the substrate with relatively low temperatures experienced three main stages. In the former two stages most nanoparticles either stayed at the interior region or contributed to the exterior coffee ring, leaving an annular gap between them. And in the last one the pattern was homogenized by filling of the gap by the nanoparticles transported from the interior area. Above the transition temperature of the substrate, the occurrence of the inward Marangoni flow was brought in advance for a higher substrate temperature such that an increasing amount of nanoparticles were carried to the liquid-vapor interface. Together with the greatly enhanced radial flow which drove the nanoparticles to the contact line, a dual ring pattern was produced after the droplet dried out. This study highlights the role of substrate temperature in tuning the deposit profiles from suspension droplets, and provides potential for enhancing the deposit uniformity by substrate cooling.

Chapter 6

Conclusions and Future Recommendation

6.1 Conclusions

Sessile droplet evaporation in respect to the effects of suspended mono-species, dual-sized and dual-species of solutes, the base solution of ethanol-water mixtures and aqueous surfactant liquids, and the substrate temperature from cooling to heating conditions were experimentally investigated on the evaporation dynamics, the flow paradigms, nanoparticles behaviors and the resulting deposited morphologies in this study. The major contributions during my PhD study are listed as follows:

1. Effects of Mono-Species, Dual-size and Dual-Species of Nanoparticles Suspended in Sessile Droplets

The mono graphite nanoparticles added in the sessile droplets were found to intensify and then attenuate the initial spreading with an increase of the nanoparticle concentration. Nanoparticles enhanced the pinning effect and increased the contact angle as compared to the pure water droplet. Evaporation rate was shown to be enhanced with the loading of nanoparticles, while its increasing trend was terminated as the nanoparticle concentration further was increased owing to particles agglomerations.

For the dual-sized nanoparticle mixtures, the pattern of either the pure 5 nm or the 40 nm Al_2O_3 nanoparticles was non-uniform. But such a non-uniformity disappeared in the pattern formed by a mixture of them with specific ratios.

Attachments between the small and the large particles limited the central-oriented movements of the small particles. While the pronounced pinning effect prevented the depinning-induced fractal-like structures of the large particles.

The mixture pattern assembled by two species of nanoparticles exhibited the features in both the single species patterns or solely one of them. Each species of nanoparticles tended to behave the same for the single pattern and the mixture pattern, as evidenced by the EDX analysis. The counteractive or the coordinate interplay depending on the two species determined the evaporative regimes and the deposited morphologies.

2. Effects of Base Solutions on Pure/Nanofluid Sessile Droplets Evaporation

In respect to the water-ethanol binary solutions based sessile droplets, three distinct flow regimes were produced across the evaporative lifetime. Regime I featuring vortices and furious flows carried particles to the liquid-vapor interface to form aggregates. In Regime II, those aggregates were driven inwards by the Marangoni flow arising from the uneven distribution of ethanol. Regime III featured the evaporation of the left water, so aggregates deposit onto the substrate ultimately. Regimes I and II were prolonged upon increasing the ethanol fraction, extending the duration for the particles agglomeration, and promoting aggregates detach from the droplet rim.

For the pure surfactant solution droplets, the autophobic effect shrinking the droplets varied non-monotonously with the surfactant concentration. The initial depinning stage showed two distinct phases including a rapid depinning phase firstly and then a slower one. A transition emerged in the averaged velocity of the contact line for the rapid depinning phase, while such a transition disappeared in the subsequent phase. The transition manifested as well in the maximum contact angle with a higher loading of surfactant. The initial depinning of the pure surfactant

solution droplets was found to also occur in the droplets containing nanoparticles. The initial depinning behavior was more intense in the nanofluid droplet especially with a relatively high nanoparticle concentration.

Unlike the pure surfactant-water droplet, the initial depinning behavior still occurred at a surfactant concentration higher than cmc in the droplet with a high nanoparticle concentration. Therefore, nanoparticles increased the upper limit of the surfactant concentration range for the initial retraction to occur. Besides, nanoparticles in the surfactant solution droplets produced various deposition patterns at different surfactant concentrations. Surfactant adsorption at the particles surfaces and the liquid-solid interface accounted for the behaviors of nanoparticles, whether trapping at the liquid-vapor interface, attracted to the solid-liquid interface or flushed toward the droplet rim.

3. Substrate Temperature Effects on Nanoparticle Depositions of Sessile Droplets

Substrate temperature plays an important role in varying the deposited profiles of nanoparticles. The deposited patterns transferred from a disk profile to a dual ring with an increase of the substrate temperature from cooling to heating conditions. The transition of the flow pattern occurred when the substrate was still cooled owing to the counteractive evaporative cooling at the droplet apex. The droplet on the substrate at low temperatures experienced three main stages. In the former two stages most nanoparticles either stayed at the interior region or contributed to the exterior coffee ring, leaving an annular gap between them. In the last stage the pattern was homogenized by filling of the gap by the nanoparticles transported from the interior area. Above the transition substrate temperature, the inward Marangoni flow took place earlier at a higher substrate temperature, such that an increasing amount of nanoparticles were carried to the liquid-vapor interface. Together with the greatly enhanced radial flow driving the nanoparticles to the

contact line, a dual ring pattern was produced.

6.2 Future Recommendation

Based on the presented study, some recommendations are made for future research to improve the understanding of basic physics of droplets evaporation and explore further potential applications in micro/nanofluidics.

1. Effect of dual-sized fluorescent spheres with different size and emission spectrums

The experiment of dual-sized nanoparticles presented in Chapter 2 can be extended to droplets containing dual-sized fluorescent particles with different emission spectrums, so particles motion can be visualized directly during droplet drying, especially the small-large particles interplay and their separate trajectories. It is expected to enrich our understanding about the size effect of solutes and provides potential for controlling deposited profiles.

2. Effect of textured substrates with applied temperature gradient

The substrate employed in this study are planar silicon wafers. In future works, textured surfaces are anticipated to be used to obtain distinctly different droplet dynamics and evaporation modes. If the textured surface is applied with a temperature gradient, a droplet as a whole may exhibit unexpected motion. Engineered substrates are of a great interest due to the distinctly different behaviors of sessile droplets as compared to planar surfaces.

3. Thermal patterns of sessile droplets obtained by infrared thermographic technique

For the study of thermocapillary flow, or thermal Marangoni flow, along a droplet liquid-vapor interface, an infrared thermographic system can detect the temperature profile of the droplet free surface and thus indicate the origin of surface flows led by temperature non-uniformity. For binary mixture droplets, it is likely to distinguish the two components at the droplet surface by an infrared camera due to the different emissivities. Therefore, in future works infrared thermographic technique is strongly recommended to be included for providing information that normal optical techniques fail to do.

Publications

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