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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**THERMAL AND FLUID STUDY IN LIQUID DROPLET
EVAPORATION**

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SCHOOL OF MECHANICAL AND AEROSPACE

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Abstract

Evaporation is related to many engineering applications, and the further understanding of the mechanism of evaporation could be benefited from the studies of droplet evaporation.

The statistical rate theory (SRT) approach has been applied to predict the thermodynamic properties for Deuterium Oxide (D_2O) by using the previously documented experimental data of D_2O evaporation. By comparing the prediction derived from SRT near the triple point with the published data, good agreements are found on saturation pressure, latent heat and specific heat at constant pressure.

An experimental rig has been set up to conduct experiments of evaporation of a pendant droplet at the vacuum conditions. In order to maintain a controllable environment, a vacuum chamber equipped with a three-dimensional manipulation stage which is mounted with a moveable thermocouple has been installed. Inside the chamber, a droplet feeding system and the heated substrate have been used to generate an evaporating pendant droplet under steady state. The degassed

anhydrous ethanol and the deionized water have been used as evaporation liquids in these experiments. The temperature distribution of the pendant droplet along the interface has been measured. When the evaporation rate is high, the temperature at the interface decreases from the periphery to the centerline, and such temperature gradient could generate thermocapillary convection. Thermocapillary convection has been captured by the Particle Tracking Velocimetry (PTV) method as well, and the maximum convection velocity could reach 1 mm/s.

For a droplet measured by Particle Image Velocimetry (PIV) or PTV, the curved shape of the droplet and the differences of the refractive indices between the vapor and liquid phases would act as a convex lens which distorts the image captured by the camera. An image recovery method has been developed to recover the measured images of the droplet. A tilt-angle imaging method has been proved to be able to obtain the full flow field inside the droplet. By tilting the camera upwards between 10 and 20° in angle, about 95% of the full internal flow field in a pendant droplet, especially near the interface, can be recovered to the real positions for further analysis.

A direct velocity recovery method has been proposed to recover the vector field generated by the PIV analysis software to obtain genuine flow results. From the comparison with the image recovery scheme, the direct velocity recovery method demonstrates a good accuracy on the final results. Such method has been applied to recover the flow measurements of a pendant silicone oil droplet during steady

state evaporation. It is found that a higher temperature difference between the apex and the periphery would generate a higher convection velocity, and a higher kinematic viscosity with a relative lower temperature variation would hinder the thermocapillary flow inside the droplet.

The temperature measurements of a heated flat surface have demonstrated the thermocapillary flow could enhance evaporation. The results qualitatively agree with the thermodynamic analysis on which an interfacial flow from a high-temperature position to a low-temperature position can supply sufficient energy for evaporation by overtaking negative thermal conduction to the interface from the liquid and gas phases, or the possible interfacial viscous dissipation.

Last but not least, the conclusions and the future recommendation are drawn.

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Nomenclature

Latin Letters

K_e	the molecular exchange rate between liquid and vapor phases under equilibrium conditions	
K	the evaporation constant	
R	gas constant	
$\bar{j}$	the average evaporation flux	kg/(m ² ·s)
Bo	the Bond number	
g	gravitational acceleration	m/s ²
H	the height of the droplet	m
J	the evaporation rate	kg/s
j	the evaporation flux	kg/(m ² ·s)
l	the local thickness of the film	m
L_{lv}	the latent heat	J

M	molecular mass	
Ma	the Marangoni number	
P	pressure	Pa
P_s	the saturation pressures	Pa
Pr	the Prandtl number	
r	the liquid droplet curvature radius	m
Ra	the Rayleigh number	
Re	the Reynolds number	
T	thermodynamic temperature	K
t_f	the drying time	s
v_θ	the thermocapillary flow velocity	m/s
$\bar{A}$	the dispersion constant	
C	the curvature of the droplet	1/m
c_0	the vapor concentration at the liquid surface	
c_∞	the vapor concentration in the atmosphere	
c_σ	the surface-thermal capacity	kJ/(m ² K)
Ca	the Capillary number	
D	the diffusion coefficient of the surrounding gas at the droplet surface	

Gr	the Grashof number	
Kn	the Knudsen number	
We	the Weber number	
S	the surface area	m^2

Greek Letters

ΔS	the entropy change	J/K
α_L	the thermal diffusivity	m^2/s
β_T	the expansion coefficient	$1/\text{K}$
η	dynamic viscosity of the liquid	$\text{kg}/(\text{s}\cdot\text{m})$
γ	surface tension	N/m
κ_L	thermal conductivities of the liquid	$\text{W}/(\text{m}\cdot\text{K})$
κ_S	thermal conductivities of the substrate	$\text{W}/(\text{m}\cdot\text{K})$
ν	kinematic viscosity of the liquid	m^2/s
ρ	density	kg/m^3
η_i	refractive index of the incident matter	
η_r	refractive index of the refraction matter	
σ_c	the condensation coefficient	
σ_e	the evaporation coefficient	

Superscripts

L the liquid phase

V the vapor phase

Subscripts

$pred$ value from prediction

m value from measurement

Chapter 1

Introduction

Liquid evaporation is a common phenomenon in nature. It is also related to many engineering issues, such as refrigeration [2], printing [3], self-assembly [4] and even the new material fabrication [5], etc.

The evaporation of the liquid is a complex process, and as early as 1820, Dalton began the research on the mechanism of evaporation [6]. The evaporation is related to the thermocapillary effect, the hydrodynamic effect, the temperature distribution, etc. Many prior researchers have performed theories and experiments to explain this phenomenon. However, the understanding of evaporation is still limited for its complexity. It requires us to explore the factors on evaporation further.

1.1 The mechanism of evaporation

1.1.1 The classical approach

Consider a one component evaporation situation with pressure of P_V , and temperature of T_V . From the kinetic theory of gas, the evaporation flux can be calculated from the difference between the rate of molecular moving from liquid phase to vapor phase, j_{LV} , and the molecular moving from vapor phase to liquid phase, j_{VL} . Under the equilibrium conditions, j_{LV} would equal to j_{VL} . That is the number of molecules evaporated from the liquid phase must be equal to those condensed from the vapor phase. It also considers the temperatures of vapor and liquid phases to be the same under the equilibrium condition. If the molecular velocity distribution in the vapor phase follows the Maxwell distribution, for an ideal gas, the rate of molecular cross a unit area at unit time can be expressed as

$$j_{VL} = P_V \sqrt{\frac{M}{2\pi RT_V}} \quad (1.1)$$

where M is the molecular mass and R is the gas constant. Similarly, if the reflection of molecular impact on the interface during the process is not considered, the rate of the molecular leaves the liquid phase at the unit time and unit area is

$$j_{LV} = P_{sat}(T_L) \sqrt{\frac{M}{2\pi RT_L}} \quad (1.2)$$

where T_L is the temperature of the liquid phase and P_{sat} is the saturation pressure. If the condensation and evaporation are treated as two independent processes, the

difference between these two rates can be used to represent the net evaporation rate or condensation rate under the non-equilibrium condition, which is written as

$$j = j_{LV} - j_{VL} = \sqrt{\frac{M}{2\pi k_b}} \left(\frac{P_{sat}(T^L)}{\sqrt{T^L}} - \frac{P^L}{\sqrt{T^V}} \right) \quad (1.3)$$

Under non-equilibrium conditions, there would be a difference between the number of molecules evaporating out of the liquid and condensing from the vapor. Therefore, the evaporation rate or the uni-direction rate of evaporation is only a fraction of the maximum evaporation under the equilibrium. Assuming that the unidirection rate of evaporation under the non-equilibrium condition is also following the Maxwell diffusion theory that the diffusion of the molecules depend on the state of the liquid near the surface. By applying a non-equilibrium liquid-vapor boundary condition, the Hertz-Knudsen formula for the net evaporation rate can be expressed as the difference between the unidirection rate of evaporation and condensation [7]. The equation can be written as

$$j = j_{LV} - j_{VL} = \sqrt{\frac{M}{2\pi k_b}} \left(\sigma_e \frac{P_{sat}(T^L)}{\sqrt{T^L}} - \sigma_c \frac{P^L}{\sqrt{T^V}} \right) \quad (1.4)$$

where j is the net rate of evaporation, σ_e and σ_c are the evaporation coefficient and the condensation coefficient, while superscripts L and V indicate the liquid and the vapor phase. At the equilibrium condition, the two coefficients of evaporation and condensation should be the same, but at the non-equilibrium condition, the two coefficients might not be equal [8,9]. Barrett and Clement [7] also found that

the evaporation coefficient depended only on the properties of the liquid surface, while the condensation coefficient was a function of the properties of both the liquid and vapor.

Schrage [10] assumed the distribution of oncoming molecules in the vapor phase was affected by a net bulk velocity, and he gave the modified expression for a small velocity of the bulk vapor. The Schrage's expression for the net rate of evaporation is written as

$$J = \frac{1}{\sqrt{2\pi Mk}} \left(\frac{\sigma_e}{1 - 0.5\sigma_c} \frac{P_{sat}(T^L)}{\sqrt{T^L}} - \frac{\sigma_c}{1 - 0.5\sigma_c} \frac{P^V}{\sqrt{T^V}} \right) \quad (1.5)$$

Many researchers provided σ_c and σ_e from the results of their own experiments [11, 12]. The most common ways to measure these values were free evaporation and quasi-steady evaporation [6], the former is to let the liquid evaporate into a vacuum, which Knudsen number is far more than 1. The maximum evaporation rate can be achieved, but the vacuum condition could be hard to sustain during the process. The maximum can be written as

$$j_{VL} = \sigma_e P_L \sqrt{\frac{M}{2\pi RT_L}} \quad (1.6)$$

The latter one is to keep a certain pressure difference as a driven force and measure the relevant parameters such as vapor pressure, temperatures at the liquid and vapor phases and evaporation rate during evaporation to calculate these coefficients by assuming a steady condition. However, the quasi-steady state might be tricky to control and the temperature gradient caused by evaporation

might also introduce error. Consequently, Koffman [13], Cercignani [14] and Marek [15] found that these coefficients varied with the conditions from individual to individual and appeared without a proper pattern. The values from different sources could differ from thousands of times, and only the results from one source could be in the same magnitude with the data for other substances. Therefore, the definitions of these coefficients and experimental methods may be imperfect.

1.1.2 The kinetic theory approach

In 1970, Pao [16, 17] found out that there was a large temperature gradient at the Knudsen layers by using the linearized Boltzmann equation. He assumed two horizontal liquid films with different temperatures. One was evaporating, and the other was condensing. He predicted that the vapor interface temperature would be lower than the liquid temperature at the evaporation film. Some theoretical investigations have been carried out to support this prediction [18–22]. Bedeaux et al. [23] also found that their results under non-equilibrium conditions could support Pao’s finding. Shankar and Deshpand [24] and Hisatake et al. [25] have provided their data from experiments, but their thermocouple were too bulky to get accurate data at such subtle experiments. In 1999, Ward et al. [26–28] used a thermocouple with a diameter of $25\text{ }\mu\text{m}$ to study the droplet of water and the other liquids on a funnel. They approached the thermocouple tip to approximately one mean-free-path from the interface, where the molecules could

hit the thermocouple just as they were evaporated. The results proved that the vapor temperature was higher than the liquid phase, and there could be a temperature discontinuity as large as 20 °C for water. Therefore, the assumption of the temperature continuation is problematic.

Ward and Fang [28] proposed the statistical rate theory (SRT), which was derived from the first order Schrödinger equation and Boltzmann definition of entropy, to describe the evaporation phenomenon. It assumed that the evaporation rate in the small volume equaled to that in the steady-state system, the vapour can be treated as ideal gas, and the liquid is incompressible. The SRT can be used to predict the rate of molecular transport across the boundary between two macroscopic phases. The SRT expression for net mass flux, j , could be written as

$$j = 2K_e \sinh\left(\frac{\Delta S}{k_b}\right) \quad (1.7)$$

where ΔS is the entropy change of one molecule crossing the liquid phase to the vapor phase during evaporation, K_e is the molecular exchange rate between liquid and vapor phases under equilibrium conditions.

The SRT expression for net mass flux is in terms of the material thermal properties (i.e., v_{sat}^L , $P_{sat}(T)$, and γ), molecular properties (i.e., molecular vibrational frequencies), and the instantaneous local interfacial properties of liquid and vapor phases (i.e., T_I^V , T_I^L and P_I^V). Moreover, several experiments of water evaporation had proved that the SRT theory can be used to predict the evaporation rate

precisely [27, 29, 30].

1.2 The evaporation of droplet

1.2.1 The process of a sessile droplet evaporation

When a droplet is formed on a substrate, as shown in Fig.1.1, the droplet surface forms a curvature. There would be a three phases contact line of the solid, vapor and liquid phases [31]. The shape of the contact line would be a circle theoretically. A contact angle would be formed between the liquid and solid edge. The area closes to the pipe wall was described in three sub areas [32]: absorbed film, where the van der Waals force dominates the interaction of liquid and solid surfaces. The thickness of this film for water is about 100 nm [31]; micro-region, where the van der Waals force and capillary force are in the same order, and it only takes up 0.5% of the whole extended meniscus [33]; macro-region, where the capillary force dominates. The results of the experiments showed that most of the evaporation was contributed by the micro-region [33–37]. In the macro-region, the rate of evaporation continuously reduced when approaching the droplet tip.

During evaporation, the contact angle of a sessile droplet could experience the following three patterns: a constant contact area at solid-liquid interface; a constant contact angle; and a mix situation of the first two models [38–42].

When the droplet formed on the perfect smooth surface, its radius first ex-

Figure 1.1: Schematic of the extended meniscus.

tended to a maximum value and began to shrink due to evaporation, and the droplet contact angle almost kept at a same value [43], especially if the flow inside the droplet could be ignored on the smooth isothermal silicon surface [44, 45]. Therefore, the movement of the contact line would be related to the properties of the substrate. For a hydrophobic substrate, the evaporation process could also differ from the normal droplet that the contact angle could decrease and the droplet diameter could increase at the initial stage [46–48].

However, since there is always surfactant effect on the nonideal substrate, the evaporation process of the droplet in the real world is usually accompanied by the pinned contact line. During droplet evaporation, the contact line is pinned and the contact angle decreases until it reached a critical value, then the contact line begins to recede with an almost unaltered contact angle [49, 50]. The reasons for the pin and unpin processes were claimed to be caused by the surface tension gradient from the temperature gradient and the concentration gradient within the solution [51] and the roughness of the substrate [52]. The potential

energy barrier generated from the chemical heterogeneities, and roughness on the substrate would keep the contact line pinned [53, 54], since the least surface free energy was achieved when the contact angle of the droplet stayed at the same value. Therefore, when the volume of the droplet was shrinking, the pinned contact line would generate extra free energy. Only when the contact line was unpinned, a certain amount of extra free energy could be released after it reached a critical value, so the pin and unpin processes could occur more than once during the droplet evaporation process. In addition, different evaporation rates led to two scenarios of the unpinning process: at a high evaporation rate, the radius of the unpinned droplet would suddenly reduce to a small value, and contact angle would increase in the meantime. Nevertheless, for a low evaporation rate, the radius of the unpinned droplet would shrink steadily with the constant contact angle. Consequently, impurities in the droplet with their the leftover product, deposition, on the substrate could become the internal factors for pinned contact line during evaporation, and the life of a pinned contact line of an evaporating droplet in the open air is also related to atmosphere pressure, temperature and evaporation rate [55]. At the condition of a rough surface, a high temperature and a high surfactant concentration condition, the unpin process would not happen.

1.3 The temperature distribution of a droplet

During the process of evaporation, the vaporization would decrease the interfacial temperature of the liquid. The difference of temperatures between the interface and the liquid can be compensated by heat conduction inside the liquid. A long heat conduction length could increase the heat resistance and require more efforts for the energy to transfer. There are two common theories about the temperature distribution of the droplet: heat conduction determines the temperature distribution [52, 56]. The tip of the droplet clearly is the longest conduction route, so the temperature would be the lowest. The temperature would increase from the tip to the contact line. Nevertheless, if the uneven evaporation flux is the dominant effect [57, 58], since most of the evaporation happened at the contact line, the interface temperature should rise from the contact line to the top tip.

Hohmann and Stephan [59] measured the temperature distribution of water in a capillary. They found out that there was a temperature drop of 0.08-0.2 K at the micro-region. They believed the intensive evaporation in this region led to such scenario. Steinchen and Sefiane [58] estimated that the tip temperature would be 0.4 K higher than that at the contact line for water in a capillary, if the diameter was $600\text{ }\mu\text{m}$, and the environment temperature was at 298 K. Savino and Fico [60] investigated the temperature distribution of a hanging droplet with respect to time, which showed the temperature distribution variation during the whole

evaporation process, and the temperature of the droplet tip gradually became the hottest point.

Buffone and Sefiane [57,61,62] had detected the temperature distribution during volatile liquids (acetone, methanol, ethanol and pentane) within the capillary by using an infrared camera. Pure evaporation caused the temperature increasing from the borderline to some middle place, and then decreasing until reaching the center. However, they believed that the coldest point in the center was purely from the technical problem of the infrared camera, since it could not focus on both the edge and the center. The exact temperature field should rise from the border to the center continuously, and it was the volatile evaporation at the periphery causing such results.

Hu and Larson [63] conducted a simulation of surface temperature distribution of a water droplet during the evaporation process. Their results showed that the surface temperature was connected with the droplet contact angle. If the contact angle was above the critical angle (14° for water), heat conduction would determine the temperature distribution, which reducing from the contact line to the tip. On the other hand, if it was below the critical angle, evaporation would be the dominated factor, so the temperature would fall from the tip to the contact line. Girard et al. [64,65] had recorded the entire evaporation process of a sessile water droplet, and they found out that the temperature at the center was the lowest. The thermocapillary effect could also cause hydrothermal waves, which

were verified by Sefiane et al. as well [66].

1.4 The flow in the droplet

The flow inside the droplet is the complex results of multiple factors, including the surface tension, gravity, capillary effect, etc.

1.4.1 The flow pattern of convection

If the effects of surface tension gradient and gravity are not considered, the flow towards the contact line inside a droplet during evaporation can be explained [67,68]. When the contact line is pinned, and the contact angle is not equal to 0° , there would be flow from the other part of the droplet to compensate the intensive evaporation at the contact line. In the analysis of Deegan et al., the mean flow velocity at the contact line satisfied the law, $\bar{u} \sim (r - l)^{-\lambda}$, where $\lambda = \frac{(\pi - 2\theta)}{(2\pi - 2\theta)}$, θ is the contact angle, r is the droplet radius and t is the time. When the contact angle approached 0° , $\bar{u} \sim (r - l)^{-0.5}$. At the final stage of evaporation, which was the time t is approaching the drying time t_f , the height of the droplet h would decrease to 0. If the evaporation flux was constant, then the outward flow $h(r)\bar{u}(r)$ would stay the same, then $\bar{u}$ would increase with respect to time, and all of the fluid would be carried to the perimeter before drying time. Some experimental results supported this theory [37,67–69], especially if the evaporation was in an

open atmosphere or its evaporation flux of the surface was evenly distributed.

However, the relationships among the flow, the flux distribution and the contact angle were not demonstrated [37, 56]. If the evaporation rate at droplet tip was maximum, the flow would head to the droplet center [69]. For a droplet with evenly distributed flux, if the contact angle was less than $\pi/2$: when the contact line was pinned, the flow would move toward the contact line; and when the contact line was unpinned with a constant contact angle, the flow would go to the center of the droplet. If the contact angle was larger than $\pi/2$, the flow would always head to the contact line [70–72]. The flow pattern was directly affected by the contact angle, and there was a critical angle for the inside flow to generate a circulation like convection. As the contact angle was above the critical angle 14° [56, 63], there would be violent convection; and as the contact angle was lower than the critical angle, the circular convection inside the droplet would disappear, and the whole liquid would flow to the edge of the droplet.

A higher roughness and thermal diffusivity of the substrates would cause a larger instability and ripples on the free surface of the droplet [73], and the direction of the flow depended on the thermal conductivities of the liquid κ_L and substrate κ_S . Such effects were verified by the deposition pattern between different liquids which experiencing different $\kappa_R = \frac{\kappa_S}{\kappa_L}$ [74], and the reason may be from the temperature gradients within the droplet causing the secondary thermocapillary surface flow.

As a direct and none intrusion method, Particle Image Velocimetry (PIV) technology had been applied to record the flow inside the droplet for decades. Hegseth et al. [75] first visualized the natural convection in the organic droplet during evaporation. By using a laser source with appropriate illuminates, they illustrated the interior convection inside an acetone droplet during evaporation in a sealed chamber. Xu and Luo [76] first measured the thermocapillary flow inside a water droplet by using single frame multiple exposure PIV. Christy et al. has used a micro PIV system to visualize the velocity profile of a droplet of water [77] or water/ethanol mixture [78, 79] along its radius direction, which shows dramatically increasing of velocity at the final drying stage. Moreover recently, with the advance technology of 3D PIV, Ueno and Kochiya [80] traced the travel path of a single particle inside the droplet by the Particle tracking velocimetry with three dimensional components, and even the whole 3D-3C flow field measurements had been achieved with more advance tomography measurement by Kim et al. [81].

For a droplet measured by PIV, the differences of the refractive indices between the vapor and liquid phases would distort the light direction emitted from the illuminated particles inside the droplet. The images captured by the camera can not reflect the genuine flow field. Therefore, all the raw results of such visual measurements should be properly corrected before submitted for PIV analysis. However, only countable studies have implemented image recovery methods [82–84]. An analytical solution for a sessile droplet in hemispherical shape

has been derived by Kang et al. [82]. Although there were some debates on the derivation of the solution from Minor et al. [83], the recovered results of a hemispherical lens were not shown in their paper for validation. In addition, approximately 20% of the flow information near the interface of the drop has been lost [82], where the most important processes of evaporation and thermocapillary flow happen to take place. Furthermore, the correction method only applied to a hemispherical shape, while such assumption would introduce large errors to most of the droplets in the final results.

1.4.2 The thermocapillary effect

The thermocapillary effect is caused by the surface tension gradient along the surface [85]. The surface tension gradient generates a flow from low surface tension to high surface tension. For a droplet, the uneven evaporation rate at the surface would result in a temperature gradient, thus it leads to convection inside the liquid, and the thermocapillary flow is also called Marangoni flow.

The thermocapillary effect was first identified as “tears of wine” by Thomson in 1855 [86]. The surface tension driven convection is indicated by the Marangoni number, Ma , which is a non-dimensional parameter, and it is defined by the ratio of surface tension to viscous force, shown as

$$Ma = \left(-\frac{\partial\gamma}{\partial T}\right)\left(\frac{\partial T}{\partial D}\right)\frac{D^2}{\eta\alpha_L} \quad (1.8)$$

where $\frac{\partial T}{\partial D}$ is the temperature gradient in the liquid, α_L is the thermal diffusivity, γ is the surface tension, η is the dynamic viscosity and D is the thickness of the layer from the interface to the bottom. The critical Ma number for a thermocapillary flow is about 80 for a droplet of silicone oil evaporating on the constant temperature solid plate substrate [87,88]. More precisely, 83.6 ± 0.5 , and an accuracy of ± 11 due to uncertainty of the silicone oil thermal properties [89].

However, the thermocapillary flow in the water is too weak to be noticed, and the surfactant contamination has always been considered as a main factor to restrain the thermocapillary effect in the water even when its concentration is very low (300 molecular per μm) [56]. Xu and Luo [76] claimed that they have observed the thermocapillary flow in the evaporating water droplet, and the suppression of thermocapillary flow in water could not be just explained as caused by surfactant in the liquid and on the substrate, it depended not only on the thermal conductivities of the substrate and the liquid, but also on the ratio of the substrate thickness to the contact-line radius of the droplet.

1.5 The model for droplet evaporation

The evaporation problem has been studied extensively [20, 90, 91], and many researchers have built their own models to explain this phenomenon. The experiments proved that the diameter of the droplet was related to the rate of

evaporation. The evaporation rate of the pinned water droplet on a smooth solid surface was proportional to the water droplet diameter [92], while the rate of evaporation of a constant volume water droplet was not linear but parabolic to its diameter [93].

Assuming in the continuum regime of a spherical droplet ($Kn \ll 0.1$), the temperature is homogeneous and below the critical temperature, the liquid and vapor phases are quasi-steady, and if the convection factor is neglected the famous D^2 law can be developed from hydrodynamic theory [94]. In this model, the rate of change of the droplet-squared diameter is constant,

$$\frac{dD^2}{dt} = -K \quad (1.9)$$

where t is time and K is the evaporation constant. However, the D^2 law corresponds to a homogeneous temperature field, and only reflects a tiny part of the droplet drying period [54].

For all the mentioned models, if only considering a slow evaporation droplet, according to Murisic and Kondic [95], there are mainly two kinds of models: one is the so-called Lens model, and the other is the non-equilibrium on one side model (NEOS).

The simplest Lens model is only considering a spherical cap and isothermal droplet, and its evaporation is controlled by diffusion of the vapor in the gas phase. Therefore, its interface is at equilibrium and the vapor diffusion is quasi-stationary. Then an analogy with a conductor at constant potential can be ap-

plied to solve the local evaporation rate [67]. If assuming the temperature changes are small and their impact on evaporation flux is limited, the Lens model can also be used for non-isothermal situation. However, the Lens model is not aimed to solve the problem with a heated substrate, since the imposed temperature differences are much larger and the interface will not be at equilibrium any more.

Assuming in the vapor would be transported only by diffusion. An analogy model by comparing the electric field with the evaporative flux has been proposed, and it assumed that the rate of droplet evaporation was related to the vapor diffusivity under the steady state [67,68]. The rate of evaporation concentration was like the electrostatic potential, and thus the flux j was similar as solving an equivalent electrostatic problem. The evaporation flux near the contact angle can be expressed as

$$j(r, t) \sim (r - l)^{-\lambda} \quad (1.10)$$

where l is the distance from the droplet center, and $\lambda = \frac{(\pi-2\theta)}{(2\pi-2\theta)}$, θ is the contact angle, r is the droplet radius and t is the time. When the contact angle was close to 0, $\lambda = 0.5$. The evaporation flux became drastically large in the vicinity of the contact line. They explained that there could be more chances for a molecule from the liquid phase to escape to the vapor phase than at the top cap part of a droplet.

On the contrary, the NEOS model means the interface is not at equilibrium [95,96]. It assumes the vapor concentration at the gas phase uniformly equals to

that at infinity. It considers the transfer rate of the molecules which cross the interface as the evaporation rate, and the thermal diffusivities of the liquid and substrate are the main factors of evaporation. Therefore, in the NEOS model, the heated boundary of the substrates can be properly built. The local evaporation flux is

$$j \propto \frac{1}{h + \kappa_L + \kappa_S} \quad (1.11)$$

where h is the film sickness, κ_L corresponds to the heat transfer through the liquid and κ_S through the solid.

From the comparison of Murisic and Kondic [95], the trend of the most of the results from evaporation of deionized water from these two models were almost the same, except at the contact line of the droplet. The NEOS model predicted the heat conducts from the substrate was larger than the loss from evaporation, while the Lens model suggested that the drastic evaporation flux at the contact line leading to a sharp drop of the temperature there. Nonetheless, for isopropyl alcohol, the results can be dramatic large: the Lens model predicted an initial outward drag due to the thermocapillary force and sharply decreasing temperature at the contact line. Sefiane et al. [97] commented the Lens model may be corrected: since the Biot number was large, and evaporating was much volatility. The evaporation should proceed in the vapor diffusion-limited regime, which didn't agree with the experimental data. However, all of these two models have some experimental results to support them. The experiments of Hu

and Larson [63] and Girard et al. [64,65] showed that the increasing tendency of temperature from center to the contact line, which was supported by the NEOS model. While the Lens model predicted a stagnation point, which was the point that the temperature gradient changed its sign. Ristenpart et al. [74] and Xu and Luo [76] had recorded this stagnation point, and it should be a necessary part of the ring shape deposition [52].

Besides, there were also some models from the new approach, for example, Maruyama et al. proposed explaining the phenomenon of evaporation through the model of molecular dynamics method [98], in which they assumed the droplet and the surrounding vapor were Lennard-Jones molecules. From their simulation results, the contact angle in both evaporation and condensation processes was almost the same as in the equilibrium condition.

1.6 The numerical model of interior flow

Several models for droplet evaporation have been proposed to calculate the interior flow and temperature distribution in order to predict the deposition pattern, and most of them were using the lens model to build the evaporation boundary. The most popular model was from the Lens model, which considering a diffusion limited evaporation process and the equilibrium was at both vapor and liquid phases. For a small, flat droplet or surface, the lubrication approxima-

tion [45, 99–102] can be applied to model the droplet evaporation process. The lubrication equation can be written as

$$\frac{\partial l}{\partial t} + \frac{\partial}{\partial x}(lU) = -j \quad (1.12)$$

$$U = \frac{l^2}{3\eta} \frac{\partial}{\partial x} \left[\gamma \frac{\partial^2 l}{\partial x^2} - \rho g l + \Pi(l) \right] + \frac{l}{2\eta} \frac{\partial \gamma}{\partial x} \quad (1.13)$$

where l is the local thickness of the film, ρ is the density of the liquid film, U is the local velocity, γ is the surface tension, and η is the viscosity of the liquid. Therefore, the total film pressure in the hydrodynamic flux hU is from the Laplace pressure $\gamma \frac{\partial^2 l}{\partial x^2}$, the hydrostatic pressure $\rho g h$ and the disjoining pressure $\Pi(l)$, and $\frac{\partial \gamma}{\partial x}$ is the thermocapillary velocity.

Marzo et al. [103, 104] believed that heat conduction was the dominant mechanism in the water droplet. Park and Lee [33] considered the evaporation in the extended meniscus region of a micro-capillary channel as laminar, incompressible flow of both liquid and vapor with constant properties, and they neglected the convective term in the momentum equation in their model. Fischer applied the lubrication theory to predict the particle deposition patterns, while its evaporation flux distribution on the droplet surface was not accurate enough to provide a correct pattern [69]. Hu and Larson [37, 56, 63, 99] conducted an experiment to verify their simulation on evaporation of a sessile droplet with a pinned contact line on a substrate in an open condition. They assumed the evaporation could

be considered as a quasi-steady process, and they verified their model with their results from the experiments [37]. In the meantime, an analytical solution basing on the lubrication theory had been compared with the numerical solution to show good accuracy, and both of these models had been used to solve the micro flow with the thermocapillary effect inside the droplet [63, 99]. In addition, in their theory, the thermocapillary effect would also affect the deposition pattern after the evaporation, and the deposition would be more likely to concentrate in the center with the thermocapillary effect [56]. Petsi et al. [71] also proved that the lubrication theory could be used to solve the evaporation of a thin droplet with fair accuracy, but only limited to a small contact angle.

Petsi et al. developed their analytic solution for droplet evaporation [70–72]. They also compared the difference of flow inside the droplet between pinned and unpinned contact lines and between hydrophilic and hydrophobic substrates. For a pinned contact line, the flow would always move to the contact line. Even the local flux was uniform along the surface. However, for an unpinned contact line with contact angel smaller than $\pi/2$, an inward flow would occur.

Savino et al. suggested their model by considering the Boussinesq assumption [60, 105, 106]. After numerical solution, their results were close to the infrared results on a hanging organic droplet, and they also found that thermocapillary convection contributed to large energy transport in the droplet, which should not be ignored, by comparing the simulation results with the experimental data. From

the same approach, Dunn et al. also suggested a model for a sessile droplet under quasi-steady diffusion-limited evaporation [107]. In this model, the effect of heat conduction in the substrate was considered, thus the temperature of the substrate would not be assumed as uniform. Their continuous work [108–110] provided an experimental proof of such consideration. Dunn and Sefiane et al. [108] had built another model by considering the effect of the atmospheric pressure, and they tested water droplet evaporation under different gases or mixture (air, helium, nitrogen and carbon dioxide) at various pressures. This model gets a satisfactory agreement with the results of their experiments.

1.7 Objectives

As the droplet evaporating, the heat conduction length along the curved drop interface to the substrate varies. Hence, the temperature distribution and evaporation flux of the interface during the evaporation process are not uniform [111–114]. Such temperature differences would cause surface tension gradient, and thus a convection flow can be generated in the liquid. As there is not flow at the liquid surface, it is believed that the energy required at the interface for evaporation is provided merely by the heat condition. Duan et al. [112–114] found that for a water droplet evaporating inside a carefully controlled vacuum chamber, if the temperature variation was high between the centerline and edge of the droplet,

the flow inside the droplet was presented. To show the surface flow, Ward et al. [111–113] used a $12.7\text{ }\mu\text{m}$ in diameter cylindrical probe to detect the velocity of the thermocapillary convection from the vibration of the probe. However, it would be difficult to acquire accurate and steady results as an extra error was introduced by such intrusion way of measuring, especially when the flow was turbulent.

The evaporation of the organic liquids in a self-designed vacuum chamber is investigated and applied in the statistical rate theory for a further understanding of evaporation. The thermocapillary convection of the organic droplets under the vacuum condition needs to be studied by carefully conducted experiments, and as a non-intrusion method, the PIV experiment can be conducted to measure the flow inside the droplet to obtain precise data. In addition, a flow recovery method should be developed to correct the measurements of PIV for a droplet due to the lens effects that distorted the captured images. To eliminate the curvature effects, a small portion of water inside a cube can be treated as a droplet with a flat surface, and the energy transportation at the interface of the droplet during evaporation can be studied.

1.8 Scopes of the report

In this report, several aspects of droplet evaporation with the thermal and fluid analysis have been conducted.

In Chapter 2, the SRT is applied to predict the saturation pressure of D_2O near the triple point by using the interfacial liquid-phase temperature, the interfacial vapor-phase temperature, the droplet radius and the local evaporation flux from 102 local measures under a series of non-equilibrium steady-state evaporation experiments [1]. The predictions have shown good agreements with those independent measurements, which indicate that the SRT could accurately predict the thermal properties of D_2O near the triple point.

In Chapter 3, the steady-state evaporation experiments of a pendant ethanol droplet at vacuum conditions have been measured. A U-shaped $25\text{ }\mu\text{m}$ thermocouple has not only measured the temperature change from vapor phase to liquid phase at the centerline of the evaporating droplet, but it would travel horizontally from the centerline outward to the points of 0.0 mm, 1 mm, 2 mm and 3 mm to measure the temperature profile from vapor phase to liquid phase at each point. In the meantime, the Particle Tracking Method (PTV) experiments have captured the thermocapillary convection which proved the existing of the convection flow during the evaporation.

In Chapter 4, a numerical solution to recover the distorted PIV images of

a droplet has been developed for accurate and trustable flow analysis. After creating a 3D surface model of an axisymmetric droplet from its outline profile, the program can be adopted to recover the distortion PIV images by recording the coordinate of the intersection points of the rays on the light sheet plane.

In Chapter 5, the PIV technique has also been adopted to measure the velocity field of various pendant droplets due to the thermocapillary convection in the ambient condition under different substrate temperatures. A direct velocity recovery method has also been employed to obtain a genuine flow field for massive experimental data.

In Chapter 6, the importance of interfacial flow energy transport at a flat evaporating surface with the global negative thermal conduction to the interface from both liquid and gas phases has been studied.

In Chapter 7, the conclusions and the future recommendation are made.

Chapter 2

Thermal Properties from Deuterium Oxide Droplet Evaporation

In this chapter¹, the statistical rate theory approach is applied to predict the saturation pressure of Deuterium Oxide (D_2O) near the triple point by using the interfacial liquid-phase temperature, since no organic liquid data can be used now. The interfacial vapor-phase temperature, and the local evaporation flux are from 102 local measurements under a series of non-equilibrium steady-state droplet evaporation experiments [1]. The results of these predictions show a good

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agreement with those independent measurements , which indicates that the SRT could accurately predict the thermal properties of D_2O near the triple point.

2.1 Introduction

The data used for validation of the statistical rate theory are taken from published results [1]. In general, the results are coming from several experiments which maintained a steady state evaporating D_2O droplet and acquired its vapor and liquid phase temperature values at various locations under the different evaporation flux in the reduced pressure environment. The apparatus used in the experiments are quite similar to which will be described in chapter 3. The conditions of the experiments are listed in Table 2.1 [1],

The data recorded included the vapor and liquid phase temperature in horizontal directions at 0.0 mm, 0.7 mm, 1.4 mm, 2.1 mm, 2.8 mm, and 3.15 mm from the centerline of the evaporation droplet. As illustrated in Fig. 2.1 [1], for the experiments of EVD3 and EVD11, the interfacial vapor temperature is higher than the interfacial liquid temperature at each position. Although the interfacial temperatures at liquid and vapor phases are roughly uniform if there is no transition of thermocapillary convection [115], the interfacial temperatures show a gradually increasing pattern from the centerline to the periphery of the droplet after the transition. The local evaporation flux, the interfacial temperatures in

Table 2.1: Experimental conditions measured in steady-state evaporation of D₂O [1].

Exp.:	Global	Intf. Rad.	Local Evap Flux (g m ⁻² s ⁻¹)					
	Vap-Ph	R_0	0.0	0.7	1.4	2.1	2.8	3.15
	Press(Pa)	(mm)	mm	mm	mm	mm	mm	mm
EVD1	651.9	6.625	0.059	0.059	0.059	0.059	0.059	0.059
EVD2	654.6	6.740	0.074	0.074	0.074	0.074	0.074	0.074
EVD3	649.3	6.740	0.081	0.081	0.081	0.081	0.081 ^a	0.081
EVD4	642.6	6.740	0.087	0.087	0.087	0.087	0.088	0.090
EVD5	625.3	6.625	0.098	0.110	0.141	0.179	0.234	0.291
EVD6	591.9	6.625	0.111	0.148	0.225	0.284	0.414	0.664
EVD7	549.3	6.625	0.199	0.286	0.492	0.697	0.864	1.026
EVD8	450.6	6.625	0.408	0.589	1.067	1.646	2.032	2.093
EVD9	350.6	6.515	0.667	0.966	1.721	2.530	2.828	2.630
EVD10	308.0	6.625	0.764	1.479	2.867	3.350	2.344	1.897
EVD11	253.3	6.569	0.945	1.736	3.281	3.857	2.839	2.455

^a At 2.7 mm

Figure 2.1: Interfacial liquid and vapor temperature measures across the interface of the droplet of D_2O under steady-state conditions, the insert is a sketch of the droplet which has a spherical interface with a radius of R_0 if the maximum height of the droplet was maintained at 1.0 mm. [1]

the liquid and vapor phases, and the thermal and molecular properties will be substituted into the SRT to predict the saturation pressure at each measured position of the steady-state evaporation experiments of D_2O and compare them with the third party results for validation.

2.2 Methodology

The vapor phase pressure predicted from SRT [28] can be obtained by

$$P_{pred}^V = f_{SRT}(T^V, T^L, C_0, j_{ev}, P_s, \gamma, v_s) \quad (2.1)$$

where f_{SRT} is a function for a droplet. The evaporation flux, j_{ev} could be expressed in SRT as

$$j_{ev} = 2K_e \sinh\left(\frac{\Delta S_{sv}}{k_b}\right) \quad (2.2)$$

$$K_e = \frac{\eta P_s(T_I^L)}{\sqrt{2\pi M k_b T_I^L}} \quad (2.3)$$

where T_I^L is the temperature at the liquid phase, T_I^V is the temperature at the vapor phase, and

$$\eta = \exp\left[\frac{v(T_I^L)}{k_b T_I^L} (P_e^L - P_s(T_I^L))\right] \quad (2.4)$$

$$\begin{aligned} \Delta S = k_b \{ & 4(1 - \frac{T^V}{T^L}) + (\frac{1}{T^V} - \frac{1}{T^L}) \sum_{l=1}^{15} [\frac{\theta_l}{2} + \frac{\theta_l}{\exp(\frac{\theta_l}{T^V}) - 1}] + \\ & \frac{v_s^L}{k_b T^L} [P^V + \frac{2\gamma}{r} - P_s(T^L)] + \\ & \ln[(\frac{T^V}{T^L})^4 \frac{P_s(T^L)}{P^V}] + \ln[\frac{q_{vib}(T^V)}{q_{vib}(T^L)}] \} \end{aligned} \quad (2.5)$$

$$\theta_l = (\hbar \omega_l) / k_b \quad (2.6)$$

$$q_{vib}(T) = \sum_{i=1}^3 e^{-\theta_i/2T} / (1 - e^{-\theta_i/T}) \quad (2.7)$$

and P_e^L must satisfy

$$P_e^L - \gamma^{LV}(T)(C_1 + C_2) = \eta P_s(T_I^V) \quad (2.8)$$

where k_b is the Boltzman constant, $\hbar$ is the reduced Planck constant, M is the mass of a molecule undergoing evaporation, ω_l is the vibration frequencies in wavenumber, for heavy water (D_2O) is 1178.38, 2669.4, and 2787.92 cm^{-1} ; v_s is

the specific volume of the liquid at saturation, γ^{LV} is the surface tension at the liquid-vapor interface, P_s is the saturated pressure of vapor and P_e^L is the liquid pressure that would exist at equilibrium. C_1 and C_2 are the curvatures of the interface, which can be obtained from the droplet profiles. At the centerline, the curvatures would reduce to $C_0 = C_1 = C_2$.

The correlation between the local vapor-phase pressure, P_I^V , and the saturation pressure, $P_s(T_I^L)$, are given in Eq. 2.5, and the interfacial liquid and vapor temperatures, the local evaporation flux, the radius of droplet, and the molecular and thermal properties are known at each measured position. Since recent studies [115] claimed that the value of the local vapor-phase pressure was different from that of the measured global vapor-phase pressure, if a thermocapillary flow occurred at the interface of the evaporating droplet. Consequently, an iteration process may be applied to find the from the preset values of the local vapor-phase pressure as shown in Fig. 2.3.

As is shown in Fig. 2.2, an initial local vapor-phase pressure would be substituted into Eq. 2.5 to calculate the saturation pressure for each measured point, and each result will compare with the results from the equation of Pupezin et al. [116] P_{sP} and the fitting relation from the data of Kraus and Greer [117] P_{sKG}^7 . The predicted saturation pressure $P_s(T_I^L)$ should be between the values of P_{sP} and P_{sKG}^7 , or an increasing step of the initial local vapor-phase pressure would be calculated. During iteration, the local vapor-phase pressure could also

be acquired.

2.3 Results and Discussion

2.3.1 Saturation pressure prediction from the evaporation experiments

As illustrated in Fig. 2.3(a), the uniform local vapor phase pressures are equal to the measured global vapor phase pressures since there is no thermocapillary convection present at the interface in EVD3. On the contrary, the local vapor phase pressure becomes parabolic increasing from centerline to its edge when the thermocapillary convection transition occurs in the experiments of EVD11, and the variation of the local vapor phase pressure could be over 38.4 Pa from the centerline to 3.15 mm away from the centerline. However, the value of the measured global vapor phase and the average of the predicted vapor phase pressures still agree with each other.

As is shown in Fig. 2.3(b), the predicted saturation pressure is uniform in the experiment of EVD3 as there is no thermocapillary convection at the interface, while the saturation pressure increases from the centerline to the periphery of the droplet after the thermocapillary convection transition in EVD11.

Then, the local liquid phase pressure P_I^L could be obtained at the designated position of the droplet by the Laplace equation, when the local vapor-phase pres-

Figure 2.2: The iteration process to obtain the local vapor-phase pressure and saturated pressure.

Figure 2.3: The local predicted pressure as a function of position from the centerline to the periphery of the evaporating droplet. The predicted vapor-phase values from SRT are compared with the global measured vapor-phase pressure in (a). The saturated pressure is computed numerically to satisfy the saturation pressure from the formulas in (b).

sure P_I^V is determined.

The results of the local vapor phase pressure and the local liquid phase pressure with respect to their phase temperature are drawn in Fig. 2.4. The liquid phase pressure and the vapor phase pressure are located on the either side of the extrapolated saturation pressure curve from Pupezin et al. equation [116] at the same measured position. The liquid phase pressure is higher than the extrapolated saturated pressure at the same interfacial liquid temperature, and the vapor

Figure 2.4: Comparison of the non-equilibrium pressures measured in the liquid and vapor phases during steady-state evaporation with the extrapolated saturation pressure below the triple point at 3.82°C .

phase pressure is the lowest value at the same interfacial vapor temperature. The reason of these results may come from the curvature effect and the interfacial temperature discontinuity under the various local evaporation fluxes.

As seen in Fig. 2.5, the SRT predicted saturation pressures are plotted as a function of the interfacial liquid temperature. The fitting curve of the predicted saturation pressures is expressed in Eq. 2.9 with a mean derivation within 0.18%.

$$\begin{aligned}
P_s(T) = & 659.3 \exp[368.046 - 12146.9/T + 0.322999T \\
& - 4.11204 \times 10^{-4}T^2 + 3.48776 \times 10^{-7}T^3 \\
& - 1.32759 \times 10^{-10}T^4 - 69.1219 \ln T], \quad (2.9)
\end{aligned}$$

where P_s is in Pa, and T is in K.

The insert of Fig. 2.5 demonstrates the relative variation between the fitting expression of the saturation pressure from SRT and the existing formulas proposed by Jones [118], Pupezin et al. [116], Bottomley [119], Hill MacMillan [120], Kraus and Greer [117], Matsunaga and Nagashima [121] and Harvey and Lemmon [122]. The extension of the expression of Jones [118] below the triple point and the fitting equation of Bottomley [119] and Kraus and Greer [117] are away from the fitting curve from SRT for more than 2%, so only the part are shown in the insert. The SRT curve is extended from 250 to 283 K shows small deviation of less than 0.4% in the insert of Fig. 2.5 comparing with others. The latent heat $L_{LV}(T)$ of the heavy water will be calculated to express the slopes of these curves of the pressure to further visualize the difference in the expression of $P_s(T)$.

2.3.2 Calculation of the latent heat of D₂O

Gibbs-Duham equation [123] gives,

$$-s^L(T)dT + v^L dP_s = -s^V(T)dT + v^V dP_s, \quad (2.10)$$

Figure 2.5: The predicted saturation pressure of D_2O from SRT is compared with the fitting curve. The comparison of SRT fitting curve with the other analytical expressions is shown in the insert.

where v^L or v^V is the specific volume in the liquid or vapor phase, and s^L or s^V is the specific entropy in the liquid or vapor phase. After simplified, the equation can be expressed as,

$$L_{LV} = T(v^V - v^L) \frac{dP_s}{dT}, \quad (2.11)$$

where the latent heat, $L_{LV} = h^V - h^L$.

The specific volume of D₂O vapor could be as 10^5 times as that of liquid at the triple point, so the latent heat of D₂O could be expressed as,

$$L_{LV} = RT^2 \frac{d \ln P_s}{dT}, \quad (2.12)$$

where R is the gas constant. The expression of $L_{LV}(T)$ could be obtained by substituting the equations for $P_s(T)$ are substituted into Eq. 2.12, and its results are plotted in Fig. 2.6. As is in the plot, only the latent heat values of $L_{LV}(T)$ calculated from the expressions proposed by Pupezin et al [116], Hill and MacMillan [120], Matsunaga and Nagashima [121] and Harvey and Lemmon [122] differ from the reported data [124,125] by less than 1%. The rests [117–119] are in disagreement with the measurements [124,125]. Nevertheless, the SRT expression of the latent heat shows good consistency with the measures close to the triple point at 3.82°C [124,125].

Figure 2.6: Comparison of the latent heat of D_2O with the saturation pressure expressions and the measured values close to the triple point.

2.3.3 Calculation of the constant pressure specific heat of D₂O in the liquid phase

After taking the further partial differential of the latent heat, $L_{LV}(T)$ with respect to T , one finds [123]

$$C_p^L = C_p^V - 2RT \frac{d \ln P_s}{dT} - RT^2 \frac{d^2 \ln P_s}{dT^2}, \quad (2.13)$$

where C_p^V can be fitted from the data of Friedman and Haar [126], and expressed as,

$$\begin{aligned} C_p^V = & 1.59376 + 1.52952 \times 10^{-3}T + 1.18615 \times 10^{-5}T^2 \\ & + 3.65264 \times 10^{-8}T^3 + 3.02103 \times 10^{-11}T^4, \end{aligned} \quad (2.14)$$

where T in K.

The values of C_p^L calculated from the expressions of $P_s(T)$ given by Kraus and Greer [117], Jones [118], Pupezin et al. [116], Bottomley [119], Hill and MacMillan [120], Matsunaga and Nagashima [121], Harvey and Lemmon [122] and the SRT expression are compared with the data measured by John et al., Braibanti et al., Smirnova et al., Rivkin and Egorov, and Angell et al. [127–131], as illustrated in Fig. 2.7. The curves of C_p^L from Jones [118], Bottomley [117] together with the expression from Kraus and Greer [117] are out of range in the plot, and the variation of curves of Pupezin et al. [116] could reach 5% from the SRT curve and measured values. Although equations of the saturation pressure

Figure 2.7: Comparison of the specific heat at constant pressure of D_2O in the liquid phase.

of Jones [118], Pupezin et al. [116], Hill and MacMillan [120], Matsunaga and Nagashima [121], and Harvey and Lemmon [122] are all for the temperature range above the tripe point, their calculated values of C_p^L do not agree with the measurements by Rivkin and Egorov [127], John et al. [128], Braibanti et al. [130], and Smirnova et al. [131] in the range from the triple point to 335 K. Nevertheless, the SRT analytical expression is agreeable with the measured values which have less than 1% variation as indicated in Fig. 2.7. In the range that below the triple point, two groups of measurements of $C_p^L(T)$ were reported by Angell et al. [129], from bulk samples and emulsion samples separately, which reflect no measurable difference with the SRT curve. Only less than 2% of difference in the temperature range above 260 K is between the SRT calculated values and the emulsion data. However, the disagreement of values of C_p^L between the emulsion samples and the SRT equation could go up to above 4% from 250 to 260 K. In the temperature range, the SRT calculation is shown in a dashed line in Fig. 2.7. And while the temperature extends down to 250 K, there is also significant disagreement between the measures of C_p^L and calculated values from the equations of saturation pressure of Pupezin et al. [116], Jones [118], Hill and MacMillan [120], Harvey and Lemmon [122], or Matsunaga and Nagashima [121] in the temperature range below the tripe point.

2.4 Summary

The expression for saturated pressure, $P_s(T)$, obtained from the SRT approach from 102 local evaporation experiments of D_2O in a non-equilibrium process shows consistent in accurate predicting the values of $L_{LV}(T)$ and C_p^L than the other existing ones. In addition, only the SRT expression for $L_{LV}(T)$ and C_p^L is almost in a complete agreement with the reported data. It suggests that the SRT approach could be applied to predict the saturation pressure, P_s , the latent heat, L_{LV} , and the liquid-phase constant-pressure specific heat, C_p^L , for D_2O near the triple point at a non-equilibrium interface. Therefore, the SRT approach is valid in predicting thermodynamic properties of D_2O , and it is a useful tool for evaporation studies. The evaporation studies of organic liquids, such as ethanol, can benefit from the SRT approach. The evaporation of a pendant droplet under vacuum condition will be studied in the next chapter with the help of the SRT approach.

Chapter 3

Evaporation of a Pendant Ethanol and Water Droplet

An experimental apparatus has been built to analyse the evaporation of the pendant droplet under the steady state conditions, and the experiments have been achieved to obtain the temperature distribution along the droplet interface. The SRT approach has been applied to predict the vapor phase pressure. Meanwhile, convection inside the droplet has been measured through the PTV method as well.

3.1 Introduction

As a droplet evaporates, the temperature distribution and evaporation flux of the interface during the evaporation process are not uniform [111–114]. Such temperature differences would cause surface tension gradient, and thus convection flows can be generated in the liquid. Duan and Ward [112–114] found that for a water droplet evaporating inside a well controlled vacuum chamber, if the Marangoni number was between 100 to 22000, the flow inside the droplet was presented. A 12.7 μm in diameter cylindrical probe is used to detect the velocity of the thermocapillary convection of a sessile droplet from the vibration of the probe [111–113]. However, an extra error was introduced by such an intrusion way of measuring, especially when the flow was turbulent. The temperature distribution of a pendant droplet along the interface during evaporation has not been thoroughly investigated, and there was no direct measurement of the thermocapillary convection of a pendant droplet evaporating under steady state conditions. Therefore, the experiments of a pendant ethanol droplet would pave the way to further study the thermocapillary convection.

3.2 Experimental setup

3.2.1 Experimental apparatus

As illustrated in Fig.3.1, a vacuum system has been designed and assembled. A cubic vacuum chamber with four viewports has been connected with a 3D-positioner on the bottom and a liquid supply system on top. The 3D-positioner can move horizontally with an accuracy of $5\text{ }\mu\text{m}$ and vertically with an accuracy of $10\text{ }\mu\text{m}$. A U-shaped $25\text{ }\mu\text{m}$ K-type thermocouple (Omega CHAL-001), as shown in Fig.3.3, has been mounted on the 3D-positioner, and the temperature was acquired by a readout (Fluke 1560-2565). The readout has been characterized by a series of coefficients for the thermocouple, which was calibrated by a Standard Platinum Resistance Thermometers (SPRT) (Fluke 5681) with system uncertainty of $0.05\text{ }^{\circ}\text{C}$. The liquid supply system was equipped with a heat exchanger circuit that connected to a heat bath. The pendant droplet can be generated on the top of the copper substrate by carefully controlling the syringe pump on the other end of the liquid supply system. The copper substrate was treated with a ring-shaped Polytetrafluoroethene coating, so that the bottom diameter of the droplet is pinned at 8 mm . The pressure was monitored by a pressure transducer (Inficon CDG045D (0-1000 Pa) with measuring uncertainty of 0.1% of the reading) and a full range gauge (Omega PX304-050A5V) with an uncertainty of 0.1% . A high speed camera (Fastec HiSpec 1) which was synchronized with a dual

head Nd-YAG pulse laser (Litron nano L120) was adopted to measure the flow inside the droplet by PTV method. The camera was used to examine the size of the droplet as well.

Figure 3.1: Schematic of the evaporation experiment.

3.2.2 The fuzzy feedback control system

3.2.2.1 Introduction of the fuzzy control system

Unlike previously introduced apparatus for a sessile droplet evaporating under the vacuum condition by Popov et al. [132], the pendant droplet was very difficult to control its size while maintain stability under vacuum condition. If the

Figure 3.2: A photo of the evaporation experimental apparatus.

Figure 3.3: The 25 μm Omega U-shaped thermocouple

evacuation rate of the vacuum pump changed too fast, or the size of the droplet was too large, the droplet would boil or fall down suddenly. To ensure the droplet evaporating steadily, it is necessary to control the evacuation rate of the vacuum pump with respect to the actual evaporation rate of the droplet. However, it is very coarse to adjust the dosing valve to control the pumping rate by hand, and the convergence time to the steady state mainly depends on the experience. In order to precisely control the evaporation process, an auto control system is desirable. Generally, the feedback control scheme is one of the approaches to control the system automatically. By filling in proper feedback parameters, the system can adjust its output against any possible interferences. The mathematical model and the experimental method are two major ways to obtain the feedback parameters. To build a mathematical model, some assumptions have to be made to simplify the system. For a nonlinear and time variant system, there is no universal solution which could make the problem quite tricky. On the contrary, the experimental method achieves those parameters by carrying experiments from discrete input points, and the process is often costly and time consuming. The interpolation of results from the discrete points would introduce errors as well. Although Inficon has provided a Proportional-Integral-Derivative (PID) control system (Inficon controller VCC500 with dosing valve VDE016), to tune a set of PID parameters is often toilsome and each group of PID parameters can only be used in one specific condition. Additionally, the PID control system can only

monitor the pressure, so the size of the droplet is not guaranteed. Furthermore, the pumping rate of this system is often changing too vigorously to be applicable. Therefore, a heuristics method such as fuzzy control can be adopted basing on the previous understanding of the system. Comparing with the PID control system, the fuzzy control system is known for its advantages of robust and self-adaptation control, it is especially suitable to operate under an unsteady and nonlinear system. A series of control strategies can be promoted to form a fuzzy control system. As long as the rules are reasonable, the fuzzy control system can function properly. Therefore, a fuzzy feedback control system is proposed to maintain a steady pressure for experiments. After configuring the fuzzy control table for the specific control purpose, the control system will adapt to different working conditions and try to preserve a stable experimental condition.

3.2.2.2 Schematic of the fuzzy control system

A fuzzy control system follows several steps to control a system, as shown is Fig. 3.4. The input signals were fuzzification to a few control sets basing on the range of input signals. From our previous manual controlled experiments, the pressure of the system and the rate of change of the pressure were chosen as the input. For better describing of the input signals, seven levels of the control condition were chosen. The strategies of fuzzy control can be described in linguistic implements as: *If the pressure of the system is high, then turn the dosing valve*

Figure 3.4: Fuzzy controller block diagram.

to large; and vice versa.

A complete control table is listed in Table 3.1 [133], in which e_h is the error between nominated pressure and measured pressure, and ce_h is the error change at unit time, N denotes negative, P denotes positive and B, M and S are short for big, median and small respectively.

Table 3.1: Rule of fuzzy control

ce_h/e_h	NB	NM	NS	0	PS	PM	PB
NB	PB	PB	PB	PB	PM	0	0
NM	PB	PB	PB	PB	PM	0	0
NS	PM	PM	PM	PM	0	NS	NS
0	PM	PM	PS	0	NS	NM	NM
PS	PS	PS	0	NM	NM	NM	NM
PM	0	0	NM	NB	NB	NB	NB
PB	0	0	NM	NB	NB	NB	NB

The defuzzification of the control scheme is the centroid method, and the output signals would be sent to the dosing valve for the system to comply. The output signal is the evacuation rate of the vacuum pump, which is controlled by the dosing valve. The described control scheme has been programmed by Matlab, and the pressure gauge, the dosing valve have been connected to the computer by RS232.

3.2.2.3 Experiments of the fuzzy control system

An ethanol droplet was formed by manual control initially, and the fuzzy control system was applied for steady state control under designated pressures. Three kinds of control scheme (manually control, automatic dosing system control and fuzzy control) were adopted to control the droplet experiments respectively, and the recorded pressure of the system with respect to time were drawn in Fig. 3.5. The manual control was achieved by a self-developed RS232 connection software to send control variable directly to the dosing valve. The automatic control scheme is provided with the dosing system by setting up an automatic feedback loop (the scheme was not described in its manual) with the controller, pressure gauge and the dosing valve. The solid line depicts the set point for the automatic control method, and the lines with symbols are recorded values. The instability error could not be eliminated by the manual and automatic dosing system control, and the experiment of the automatic control failed with the droplet falling down

Figure 3.5: Comparison of different control methods. The dot line demonstrated the fuzzy control can achieve better experimental condition than the manual control.

after about 300 seconds. The fuzzy control reached stable in about half of the time comparing with the manual control method. In general, despite several seconds of convergence time at the beginning, the pressure in the fuzzy control method approached the steady state with less than 1 % of the variation, and the instability error was significantly reduced. The final pressure at the steady state is not necessary the same as the nominated pressure in the fuzzy control program, as long as the pressure is stable, the measurements can be conducted. It is also need to mention that due to the computational speed of the computer, and the limitation of the dosing valve, the control frequency is only 1 Hz, for liquids like ethanol and acetone, higher control frequency is suggested.

3.3 Experiments of the pendant droplet

3.3.1 Temperature measurements at the centerline of the droplet

3.3.1.1 The experimental procedure

The system was evacuated by a turbomolecular pump to 10^{-4} Pa, then the reagent A.C.S. grade, anhydrous ethanol and deionized water were be degassed in a flask before transferring to the syringe pump through a tube. The system was pumped with nitrogen to 10^4 Pa for 6 hours to prevent the bubble formation. After that, about 0.5 ml of the liquid was flushed out, and the mechanical pump began to vacuum the system. When the chamber was dry, a mechanical pump controlled by the gas dosing system (Inficon VCC500 with VDE016) can be activated for experiments, and the syringe pump was set to pump the liquid to the evaporation substrate. During this process, the pumping rate of the syringe pump would gradually decrease as the droplet reached the substrate. When the droplet was formed, the syringe pump would be set to the evaporation rate of the specific point. There was a cold trap of -20 °C to capture the evaporated vapor between the chamber and the vacuum pump. Another vacuum pump was connected to the back end of the syringe to prevent air leak through the piston of the syringe to the liquid feeding system. The thermocouple began its measurements at about

1 mm away from the interface of the droplet in the vapour phase at the centre line of the droplet, and the temperature was recorded with 0.5 mm step into the liquid phase until the topmost of the droplet to record the top temperature.

3.3.1.2 Results and discussion

Water and ethanol were used in the system initially with SRT calculation for validation. The thermocouple has been used to record the T^V and T^L at the centre line of the droplet. Meanwhile, the pressure of the system has been recorded as well, and all the data are averaged with standard deviation.

Five different sets of experiments under steady state conditions have been conducted for water and ethanol, and the measured results with standard deviation are listed in Table 3.2.

Table 3.2: The measured data of the evaporation experiments, and the experiments of water and ethanol were listed in the table.

Exp No.	T^L °C	T^V °C	P_m^V Pa	h mm	J $\mu\text{l} / \text{h}$
WATERC1	3.4 ± 0.03	7.8 ± 0.07	786 ± 8	2.6 ± 0.04	70
WATERC2	3.6 ± 0.08	6.0 ± 0.10	797 ± 8	2.4 ± 0.05	70
WATERC3	4.1 ± 0.07	6.5 ± 0.10	821 ± 8	2.7 ± 0.02	60
WATERC4	4.6 ± 0.09	7.5 ± 0.10	854 ± 9	2.5 ± 0.04	55
WATERC5	5.0 ± 0.07	6.5 ± 0.07	875 ± 9	2.5 ± 0.05	40
ETHANOLC1	2.3 ± 0.07	4.5 ± 0.09	1899 ± 19	3.8 ± 0.03	3100
ETHANOLC2	3.7 ± 0.03	4.8 ± 0.08	2095 ± 21	3.5 ± 0.02	2850
ETHANOLC3	6.2 ± 0.08	8.1 ± 0.07	2421 ± 24	4.2 ± 0.02	2550
ETHANOLC4	7.3 ± 0.05	8.0 ± 0.08	2579 ± 26	3.6 ± 0.02	2100
ETHANOLC5	9.4 ± 0.03	8.8 ± 0.08	2988 ± 30	3.8 ± 0.04	1900

The SRT has been described in Chapter 2, and the vibration frequencies in wavenumber, for water are 1591, 3651, 3756 cm^{-1} , and for ethanol are: 2989, 3689, 1456, 1391, 1242, 801, 1320, 1270, 1067, 877, 427, 1040, 1104, 267, 350 cm^{-1} ; The surface area of the droplet was calculated by numerical integral of the droplet profile. The profile of the droplet was achieved by the least square fitting the droplet edge curve from the Canny edge detector with the Young-Laplace equation to minimize undesirable noises. The differential Young-Laplace equation for the droplet profile could be written as [134]

$$\begin{cases} \frac{dx}{ds} = \cos \sigma \\ \frac{dz}{ds} = \sin \sigma \\ \frac{d\sigma}{ds} = 2b + z\Delta\rho g/\gamma - \frac{\sin\sigma}{x} \end{cases} \quad (3.1)$$

where b is the curvature at the apex of the droplet, ρ is density, σ is the tangential angle, and γ is the surface tension of the droplet. Then by using numerical integration, the surface area of the pendant droplet can be expressed as

$$S = \sum_{i=1}^N C_i = \pi \sum_{i=1}^N l_i (r_i + r_{i+1}) \quad (3.2)$$

where r is the radius of each point on the profile to the rotation axis, and

$$l_i = \sqrt{(r_i - r_{i+1})^2 + dH^2} \quad (3.3)$$

where dH is the minimum integration distance, and the volume of the droplet is

$$V = \sum_{i=1}^N A_i = \pi \sum_{i=1}^N r_i^2 dH \quad (3.4)$$

The evaporation flux can be obtained by assuming an even distribution of evaporation along the droplet interface. By applying the SRT approach to the measured data, the predicted pressures can be calculated, and the results are listed in Table 3.3. The comparison of the measured and predicted pressures of these two liquids are shown in Fig. 3.6 as well. The uncertainties of the equipments together with the standard deviation of the measurements were shown as the error bar. As seen in Fig. 3.6, the differences between the measured and predicted pressure in the system are only within 3 % for water and 6 % for ethanol, which demonstrated a good accuracy of the experimental apparatus.

Figure 3.6: Measured vapour-phase pressure comparing with the predicted pressure from SRT approach. The measured vapour-phase pressure and the predicted vapour-phase pressure from the SRT approach in each group of the measurement was in good agreement with each other, and a 45° line was drawn to demonstrate the agreement.

Table 3.3: The results of vapour-phase pressure prediction at the centerline during steady state evaporation, and the experiments of water and ethanol were listed in the table.

Exp No.	P_m^V	P_{pred}^V	S	j
	Pa	Pa	m^2	kg/m ² .s
WATERC1	786 ± 8	780 ± 2	4.03×10 ⁻⁵	4.8×10 ⁻⁴
WATERC2	797 ± 8	791 ± 6	4.08×10 ⁻⁵	4.8×10 ⁻⁴
WATERC3	821 ± 8	819 ± 9	4.60×10 ⁻⁵	3.6×10 ⁻⁴
WATERC4	854 ± 9	848 ± 6	4.13×10 ⁻⁵	3.7×10 ⁻⁴
WATERC5	875 ± 9	873 ± 9	3.91×10 ⁻⁵	2.8×10 ⁻⁴
ETHANOLC1	1890 ± 19	1874 ± 15	1.30×10 ⁻⁴	5.3×10 ⁻³
ETHANOLC2	2090 ± 21	2065 ± 11	1.22×10 ⁻⁴	5.2×10 ⁻³
ETHANOLC3	2420 ± 24	2447 ± 16	1.04×10 ⁻⁴	5.5×10 ⁻³
ETHANOLC4	2570 ± 26	2634 ± 24	1.18×10 ⁻⁴	4.0×10 ⁻³
ETHANOLC5	2980 ± 30	3025 ± 16	1.32×10 ⁻⁴	3.2×10 ⁻³

3.3.2 The measurements of the temperature distribution along the droplet surface

3.3.2.1 The experimental procedure

To measure the temperature distribution, the Reagent A.C.S. grade, anhydrous ethanol was degassed in a flask before transferring to the syringe pump through a tube. In order not to contaminate the entire evaporation system, only 0.1 % wt. of the tracing particle (Lavision, hollow glass, mean diameter $10\ \mu\text{ m}$, density $0.8\ \text{kg/m}^3$) was added to the ethanol. From the image analysis by the axisymmetric droplet shape analysis (ADSA), the change of the surface tension due to the seeding particle is less than 2 %. When the chamber was dry, a mechanical pump controlled by a gas dosing system (Inficon VCC500 with VDE016) was activated for experiments, and the syringe pump was set to pump the liquid to the evaporation substrate. During this process, the pumping rate of the syringe pump would gradually decrease as the droplet reached the substrate. When the droplet was formed, the syringe pump would be set to the evaporation rate of the specific point. Another vacuum pump was connected to the back end of the syringe to prevent air leak through the piston of the syringe to the liquid feeding system. The thermocouple began its measurements at about 1 mm away from the interface of the droplet in the vapour phase at the centreline of the droplet, and the temperature was recorded with 0.5 mm step into the liquid phase until the

topmost of the droplet to record the top temperature. The same procedures were taken in the horizontal direction at horizontal distances of 1, 2, and 3 mm from the centre line, as demonstrated in Fig. 3.7. If the difference in temperature between the centerline and the periphery was larger than $0.5\text{ }^{\circ}\text{C}$, and the temperature of the center line was lower than the periphery, the buoyancy driven convection can be eliminated, therefore the surface tension gradient caused by the temperature gradient would induce the thermocapillary flow. Then, the PTV measurements would be conducted in order to capture the thermocapillary flow directly, and the results would be processed by Lavision Davis 8 to trace the movements of the seeding particles. The particle size range is between 8 and 15 pixel, and the software could trace the movement of each seeding particle by assuming the movement of the particles can represent the flow inside the droplet.

3.3.2.2 Results and discussion

Sixteen different sets of experiments under steady state conditions have been conducted for ethanol, and the interfacial data of these measurements are listed in Tables 3.4 and 3.5. The predicted pressure in the table was calculated at the centerline. The evaporation flux can be calculated from the rate of the syringe pump and the surface area of the droplet measured by the camera. The results of the interfacial temperature at different horizontal distance were shown in Figs. 3.8, 3.9 and 3.10. The temperature profiles close to interface demonstrated

Figure 3.7: Temperature measured across the interface of the droplet: (a) a photo of the pendant droplet; (b) an illustration of the temperature measurements at designated locations by using a U-shaped thermocouple.

the temperature distribution along the vertical centerline of the droplet was from higher temperature in the vapor phase to lower temperature at the liquid phase. The sharp temperature jump at the interface was documented ranging from 1 to 3 °C. The same patterns of the temperature distribution were noticed in the measurements along the droplet interface as well. As shown in Fig 3.11, when the vapor pressure of the system was relatively high, a nearly uniform interfacial temperature appeared since the rates of evaporation were low for Ethanol2 and Ethanol9. However, the temperature of the centerline was about 0.8 °C lower than the periphery in Ethanol16 with a higher rate of evaporation, and a thermocapillary flow could be generated because of the temperature gradient. From the results of the PTV measurements, the velocity perpendicular to the interface was around 30 $\mu\text{m/s}$, which was negligible when comparing with the thermocapillary flow ranging from 100 to 1700 $\mu\text{m/s}$ in the measurements, as shown in Table 3.5. The PTV result of Ethanol16 is shown in Fig. 3.13, and the vectors demonstrated a flow toward the center of the droplet near the edge. The strong thermocapillary flow would generate a return flow below the interface of the droplet toward the periphery, and the convective heat transfer should have a contribution on the energy transportation during evaporation. It is necessary to mention that the diameter of the tube of the liquid feeding system is 1.59 mm, therefore the maximum inward velocity (Ethanol16), V_{in} , is 442 $\mu\text{m/s}$, which is less than 25% of the tangential velocity near the edge. This inward flow could hinder the thermo-

capillary flow with lower temperature gradient. With the strong counter flow at the centerline of the droplet, a strong mixing process should happen. As shown in Fig. 3.10, the liquid temperature gradient at the centerline ($1507\text{ }^{\circ}\text{C/m}$) was also smaller than at the periphery ($2741\text{ }^{\circ}\text{C/m}$).

Figure 3.8: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol2 under steady state condition. The temperature distribution along the droplet at the liquid interface was almost uniform. $\Delta T_{max}^L = \pm 0.03^{\circ}\text{C}$ and $\Delta T_{max}^V = \pm 0.03^{\circ}\text{C}$.

Figure 3.9: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol9 under steady state condition. The temperature distribution along the droplet at the liquid interface was almost uniform.

$$\Delta T_{max}^L = \pm 0.03^\circ\text{C} \text{ and } \Delta T_{max}^V = \pm 0.03^\circ\text{C}.$$

Figure 3.10: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol16 under steady state condition. The temperature at the liquid interface at the centerline was about 0.8 °C higher than at the 3 mm away from the centerline, and a thermocapillary flow was expected to take place. $\Delta T_{max}^L = \pm 0.04^\circ\text{C}$ and $\Delta T_{max}^V = \pm 0.09^\circ\text{C}$.

Table 3.4: The measured data of the evaporation of an ethanol droplet in liquid and vapor phases during steady state evaporation, and only the centerline data are shown.

Exp No.	Ethanol1	Ethanol2	Ethanol3	Ethanol4	Ethanol5	Ethanol6	Ethanol7	Ethanol8
P^V (Pa)	2909 $\pm$ 19	2766 $\pm$ 18	2788 $\pm$ 12	2535 $\pm$ 9	2488 $\pm$ 15	2393 $\pm$ 13	2371 $\pm$ 16	2227 $\pm$ 18
H	3.97	3.66	3.73	3.81	3.58	4.09	3.75	3.92
(mm)	$\pm$ 0.03	$\pm$ 0.03	$\pm$ 0.02	$\pm$ 0.02	$\pm$ 0.02	$\pm$ 0.02	$\pm$ 0.02	$\pm$ 0.02
S (m^2)	1.19×10^{-4}	1.13×10^{-4}	1.19×10^{-4}	1.05×10^{-4}	9.69×10^{-5}	9.80×10^{-5}	1.19×10^{-4}	1.18×10^{-4}
J (μ l/h)	1900	2000	1970	2150	2500	2600	2630	2700
throat temp	9.0	9.4	8.4	8.4	7.8	7.7	7.8	5.8
($^{\circ}$ C)	$\pm$ 0.03	$\pm$ 0.03	$\pm$ 0.02	$\pm$ 0.03	$\pm$ 0.08	$\pm$ 0.02	$\pm$ 0.04	$\pm$ 0.03
T^V	8.8	8.6	8.9	7.2	7.0	6.9	6.7	5.7
($^{\circ}$ C)	$\pm$ 0.03	$\pm$ 0.02	$\pm$ 0.05	$\pm$ 0.10	$\pm$ 0.10	$\pm$ 0.03	$\pm$ 0.04	$\pm$ 0.03
T^L	8.5	8.3	7.7	6.9	6.6	6.0	6.3	4.7
($^{\circ}$ C)	$\pm$ 0.03	$\pm$ 0.03	$\pm$ 0.03	$\pm$ 0.03	$\pm$ 0.05	$\pm$ 0.05	$\pm$ 0.03	$\pm$ 0.03
Ma	120	110	130	150	80	110	100	130

Table 3.5: The measured data of the evaporation of an ethanol droplet in liquid and vapor phases during steady state evaporation, and only the centerline data are shown. The PTV experiments were conducted for these group as well.

Exp No.	Ethanol9	Ethanol10	Ethanol11	Ethanol12	Ethanol13	Ethanol14	Ethanol15	Ethanol16
P_m^V (Pa)	2151±17	2205±19	2128±8	2073±16	2018±19	1996±7	1985±18	1864±18
H	4.12	3.88	3.84	4.16	4.03	4.03	4.46	3.96
(mm)	±0.03	±0.03	±0.04	±0.03	±0.02	±0.04	±0.01	±0.04
S (m^2)	1.01×10^{-4}	1.07×10^{-4}	1.06×10^{-4}	1.13×10^{-4}	1.10×10^{-4}	1.20×10^{-4}	1.18×10^{-4}	1.16×10^{-4}
J ($\mu\text{l/h}$)	2800	2730	2850	2900	3000	3100	3150	3200
throat temp	5.3	5.9	6.0	5.4	4.8	4.1	4.2	3.7
(°C)	±0.03	±0.02	±0.03	±0.03	±0.02	±0.03	±0.02	±0.02
T^V	5.7	5.3	4.8	5.2	5.1	4.3	4.3	4.8
(°C)	±0.03	±0.06	±0.08	±0.06	±0.07	±0.06	±0.07	±0.08
T^L	4.4	4.4	3.6	3.3	3.0	2.4	2.2	1.7
(°C)	±0.03	±0.03	±0.02	±0.02	±0.03	±0.03	±0.02	±0.03
V_{tan} ($\mu\text{m/s}$)	0	0	212±28	333±30	400±49	919±73	1310±143	1745±168
V_{in} ($\mu\text{m/s}$)	387	377	394	401	415	428	435	442
Ma	110	100	310	440	530	1050	1390	1620

Since the evaporation is under steady state condition, the syringe pumping flow rate would equal to the evaporation rate. Therefore, the average evaporation flux could be calculated by assuming an evenly distributed local evaporation flux. By applying the T^L , T^V and evaporation flux at each measuring position to the SRT, the predicted vapor pressure P_{pred}^V was calculated for comparison. The results are shown in Fig. 3.12 as the predicted vapor pressure with respect to the distance from the centerline of the droplet. It is found that the distribution of the predicted pressure for Ethanol2 and Ethanol9 are all within the error bar of the prediction at the centerline. For the Ethanol16, the predicted value at 3 mm is about 5 % higher from the others, which is consistent with the temperature distribution. The reason is that the present assumption of the evaporation flux is even, while a higher prediction of the pressure demonstrated a higher evaporation flux at the periphery than at the centerline.

Table 3.6: The vapour-phase pressure prediction from SRT approach in liquid and vapor phases during steady state evaporation, and only the centerline data are shown. The results of the predicted vapour-phase pressure from SRT agreed with the measured vapour-phase pressure.

Exp No.	Ethanol1	Ethanol2	Ethanol3	Ethanol4	Ethanol5	Ethanol6	Ethanol7	Ethanol8
$\bar{j}$ (kg/m ² s)	3.5×10^{-3}	3.9×10^{-3}	3.7×10^{-3}	4.6×10^{-3}	5.7×10^{-3}	5.9×10^{-3}	4.9×10^{-3}	5.1×10^{-3}
P_{pred}^V (Pa)	2853±29	2816±31	2704±35	2565±42	2514±48	2415±32	2464±35	2212±33
Exp No.	Ethanol9	Ethanol10	Ethanol11	Ethanol12	Ethanol13	Ethanol14	Ethanol15	Ethanol16
$\bar{j}$ (kg/m ² s)	6.2×10^{-3}	5.7×10^{-3}	6.0×10^{-3}	5.7×10^{-3}	6.1×10^{-3}	5.8×10^{-3}	6.0×10^{-3}	6.2×10^{-3}
P_{pred}^V (Pa)	2167±33	2167±41	2051±45	2007±45	1966±48	1887±41	1861±45	1797±46

Figure 3.11: The interfacial liquid temperature with respect to the distance from the centerline of the droplet in three experiments. The interfacial liquid temperature of Ethanol2 and Ethanol9 were almost uniform, while there was a temperature difference of 0.8 °C in the Ethanol16.

3.3.3 Summary

The temperature distribution along the interface of the pendant droplet has been measured, and the convection inside the droplet has been captured in PTV. The SRT approach demonstrated good agreements with the experiment results. The convective heat transfer should have a contribution on energy transportation during evaporation, and it is necessary to conduct further studies on the flow pattern.

Figure 3.12: The predicted vapour-phase pressure with respect to the distance from the centerline in three experiments. The predicted vapour-phase pressure along the droplet interface of Ethanol2 and Ethanol9 were almost uniform, and the vapour-phase predicted pressure of Ethanol16 at 3 mm was about 80 Pa higher than at the other locations.

Figure 3.13: The PTV measurements of the thermocapillary flow of Ethanol9 Ethanol14 and Ethanol16. A tangential flow near the edge of the droplet towards the centerline was found, and it demonstrated the thermocapillary convection caused by the temperature gradient, which was discovered by the measurements of the temperature distribution along the droplet interface.

However, all the visual measurements of the flow inside droplet, including PIV and PTV, should be properly corrected before further analysis. An image recovery method will be provided to solve this problem in the next chapter.

Chapter 4

Convection Flow Recovery in a Pendant Droplet

The PIV technique has been used for measuring the convection inside the droplet for decades. However, when the light beam passing the liquid-air interface, it can be distorted as the droplet acts as a convex lens. All the visual measurements for the flow inside a droplet should be corrected before further analysis. In this chapter, an image recovery method is provided¹.

4.1 Introduction

For a droplet measured by PIV, the differences of the refractive index between the vapor and liquid phase would distort the light direction emitted from the illu-

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minated particles inside the droplet. The images captured by the camera cannot reflect the genuine flow field, especially when the ratio of the refractive index of the two phases and the droplet curvature are high. Therefore, all the raw results of such visual measurements should be properly corrected before submitted for PIV analysis. However, only countable studies [82–84] have implemented image recovery methods. An analytical solution for sessile droplet with hemispherical shape has been derived by Kang et al. [82]. Although there were some debates on the derivation of the solution from Minor et al. [83], the recovered results of a hemispherical lens were not shown in their paper for validation. In addition, approximately 20% of the flow information near the interface of the drop has been lost [82], whereas the most important processes of evaporation and thermocapillary flow happen to take place. Furthermore, the correction method merely applied to a hemispherical shape, while most droplets studied are not in reality, such assumption would introduce large errors to the final results. Therefore, an universal and reliable method of image recovery is essential.

4.2 Methodology of ray tracing recovery

A numerical program to solve the problem of recovery has been developed based on the assumptions that the diffraction effect is ignored since the wave length of the illuminated laser is far smaller than the droplet size; the image deformation

Figure 4.1: Illustration of the ray tracing theory: the ray has been refracted to P_s after hitting P_r .

due to perspective view has been ignored, since the magnification ratio of the lens is 1:1; the droplet is considered to be axisymmetric, by rotating the outline extracted from droplet profile analysis algorithm [135] around its symmetric axis, a surface model of the droplet can be generated. The outline is achieved by the least square fitting the droplet edge curve from the Canny edge detector with the Young-Laplace equation described in Eq.3.1 to minimize undesirable noises. Hereafter, the droplet surface model will be meshed with triangles for the ray tracer to process. To simplify the problem, the Cartesian coordinate of the ray tracing system is built. As seen in Fig. 4.1, the light sheet will be on the XY plane, and the image will be located at the plane of $z = 1$.

The concept of ray tracing is to trace each ray from where it has been recorded,

the pixel on the image, reversely to where it emitted, the light sheet plane. By carrying the tracing, the route of each ray will be calculated, including refraction and reflection that could alter the direction of the ray. When firing a ray, $\mathbf{p} = \mathbf{o} + t\mathbf{d}$, from the image, the intersection can be checked by traversing all the triangles whether they satisfy [136]

$$\mathbf{o} + t\mathbf{d} = \mathbf{a} + j(\mathbf{b} - \mathbf{a}) + k(\mathbf{c} - \mathbf{a}) \quad (4.1)$$

$$at \left\{ \begin{array}{l} 0 < j < 1 \\ 0 < k < 1 \\ 0 < j + k < 1 \end{array} \right. \quad (4.2)$$

where $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ are vectors that define a triangle, $\mathbf{o}$ is the original point of the ray, $\mathbf{d}$ is the direction of the ray, and t , j and k can be solved by Cramer's rule. If t , j and k are valid values, the intersection point can be calculated by $\mathbf{p} = \mathbf{o} + t\mathbf{d}$. Then, according to Snell's law, from this intersection point, and the refracted ray will be diverted to

$$\left\{ \begin{array}{l} \mathbf{d}_r = \frac{\eta_i}{\eta_r} \mathbf{i} + (\frac{\eta_i}{\eta_r} \cos \theta_i - \sqrt{1 - (\frac{\eta_i}{\eta_r})^2 (1 - \cos^2 \theta_i)}) \mathbf{n} \\ \cos \theta_i = -\mathbf{n} \cdot \mathbf{i} \end{array} \right. \quad (4.3)$$

where $\mathbf{i}$ is the incident vector, $\mathbf{n}$ is the normal vector of the intersection plane, η_i and η_r are refer to the refractive index of the incident and refraction matters, and θ_i and θ_r are the incident and refraction angles respectively. Finally, the intersection of the refracted ray and the light sheet plane can be determined by the same procedure. If the refracted ray hits the light sheet plane, which is the

original point the light released, the coordinate of collision and the color of the ray will be recorded. A recovered image can be generated after all the pixels in the image have been traced. Generally, although a higher triangle mesh density means better accuracy during intersection calculation, excessive triangle density also leads to extraordinary slow performance during traversal. Additionally, it is suggested to apply Octree or k -d tree on the triangle mesh to accelerate the detection of the intersection as well [137]. It is necessary to mention that for an axisymmetric object such as droplet, the ray tracing scheme can be accelerated by substituting the triangle mesh with the cone-shaped mesh, which could reduce the time of recovery significantly. The intersection of the tracing ray with a small cone ($y_i < y < y_{i+1}$) can be checked by finding whether the ray of $\mathbf{p} = \mathbf{o} + t\mathbf{d}$ could satisfy $x^2 + z^2 = y^2$ within $y_i < y < y_{i+1}$.

4.3 Program description

The program for the recovery is based on C++ with openCV library to handle the image process, and the diagram of the core ray tracing program is shown in Fig. 4.2. The program can generate simulation results based on ray tracing method as well. The tilted angle to the model can be modified in the program before the ray tracing begin. The image and the model of the droplet will be processed and normalized after submitting to the program, and the ray tracing

engine will be initialed and prepared to generate rays. A plane marked as target will be put into the model as the light sheet plane. The origin of the ray is at the position of each pixel on the image, and the ray with the color information of the pixel will be fired parallelly to the z axis to the droplet model. An intersection detection will traverse with all the triangles and target plane: if the ray hits one of the triangles, a new ray will be fired from the point of intersection to the direction calculated by Snell's law, and the new ray will traverse with all the objects for intersection again until such iteration reach a global limitation; if the ray hits the target plane, the ray tracing will terminate, and the final point of intersection and color of the ray will be recorded. When all the pixels have been traced, the program will draw the recovered image according to the recorded. The program has the capacity to handle the recover model with 10 million triangles, and the process time for one image with 1 million triangles is about 30 minutes.

4.4 Tilted angle method

A simulation was conducted for a droplet-shaped lens to show the recovered results under different α of 0° , 10° , 15° and 20° respectively. Figures 4.3 and 4.4 list the results of simulation and the recovery of a droplet with $350 \times 350 \times 2$ triangles at different tilted angles. The droplet model was obtained from the PIV measurement, and the mesh precision was equal to 1 pixel on the image.

Figure 4.2: Diagram of the ray tracing program

The refractive index is 1.33 as same as pure water used in the experiments. To demonstrate the distortion, the light sheet was rendered in a chess grid. By comparing the results of images, it is found that the distorted shape in Figs.4.3 (a-d) at the edge of the pendant droplet can be reserved by the tilted angle method, as shown in Figs.4.4 (a-d). With the tilted angle at 0° , the droplet information near the droplet surface cannot be resumed with black spots. At $\alpha = 10^\circ$, the edge has not been fully recovered, and some lines near the edge are not straight, as illustrated in Fig.4.4 (a). While $\alpha = 15$ or 20° , the tip of the pendant droplet is fully recovered in Figs. 4.4 (c,d). However, an inevitable blank area, which is less than 0.2% of the droplet size, appeared on the top part of the image. The unrecovered top edge section (see Fig. 4.4 (d)) becomes larger if the tilted angle is too large. Therefore, it is suggested to adopt a balance angle between $\alpha = 15^\circ$ and 20° to retain the most information of an image or choose a proper angle depending on the experiments.

4.5 Experiments of pendant droplet

To examine the effects of the recovery program, a tiltable Nikon D7000 camera with a calibrated Nikkor 105 mm micro lens with the distortion rate of 0.2 % to the reference grid was used to capture the images. As shown in Fig. 4.5, a water droplet of 3.86 ± 0.02 mm in diameter and 1.73 ± 0.02 mm height was

Figure 4.3: Simulation results of a droplet with a chess plane in the middle, (a), (b), (c) and (d) are the simulation images of tilted angles of 0° , 10° , 15° and 20° respectively; only left part of each image is shown.

Figure 4.4: Simulation results of a droplet with a chess plane in the middle, (a), (b), (c) and (d) are the recovered results of tilted angles of 0° , 10° , 15° and 20° respectively, only left part of each image is shown.

placed on a grid paper for the validation. The lower part of the droplet can be treated as a demonstration of the side view of a pendant droplet, and the light sheet plane is represented by the calibration grid behind the droplet. Since the depth of field is limited for the micro lens, only the tilted angles of 0° and 5° were recorded for the validation as in the Figs. 4.5(a,c). The droplet was modeled by $405 \times 190 \times 2$ triangles with the mesh precision of 1 pixel. The recovered images are displayed in Figs.4.5 (b,d), and the curved lines of the grid in the middle of the lens were recovered to their original positions. A Matlab program has been used to calculate the distortion rate of the recovery according to ISO 9039-2008. It is found that 61.5 % and 71.0 % of the bottom half of the recovered droplet areas in Figs.4.5 (b,d) were corrected with an accuracy of average -1.3 ± 0.7 % (barrel distortion) and -1.5 ± 0.8 %. The recovered area of the bottom half of the droplet has increased for about 10 % by tilting the camera for merely 5° .

The promising method can be applied in the PIV experiments. The PIV experiments were conducted to investigate the recovery in flow analysis, and the schematic drawing of the experiment setup is illustrated in Fig.4.6. A pendant droplet evaporating in the open air was illuminated by a dual head Nd-YAG pulse laser (Litron nano L120) with a light sheet optic. A high speed camera (Phantom V711) with a pixel resolution of 1280×800 was used to capture the side view of the droplet. The camera was mounted on a translator stage that could be tilted with the desired angles. The camera was equipped with a Nikkor 105 mm

Figure 4.5: Schematic drawing of the PIV system (a) and the Scheimpflug principle (b) when using the tilted camera to focus on the light sheet.

micro lens and a Scheimpflug adapter (Lavision). The Scheimpflug adapter was used to focus on the whole viewed light sheet as the camera was tilted with a predefined angle. The extend lines of the light sheet (subject plane), the lens plane and the image plane must be intersected for the Scheimpflug principle to work [138]. A calibration plate with a dot grid of $30 \times 30 \text{ mm}^2$ was used to check the focus of the lens with the adapter. Another camera (Fastec Hi-spec1) was mounted perpendicularly to the light sheet to capture the profile of the droplet when the high speed camera was tilted. The high speed camera and laser were connected to a synchronizer to work simultaneously. The droplet was infused onto the substrate with a syringe until the same size during each measurement. The images had been processed by the recovery software, and then the corrected images were analyzed in Davis 8 PIV software. A two-pass iteration with grid size of 32×32 and 16×16 was chosen for PIV vector calculation.

4.6 Results and discussion

In the PIV experiments, the results at $\alpha = 0^\circ$ (normal to the light sheet) and $\alpha = 15^\circ$ are shown in Fig. 4.7. Figures 4.7 (a, c) show the vector fields without image restoration, while Figs.4.7 (b,d) demonstrate the corrected images by using the two different tilted angles. The droplet in Fig.4.7 (c) became flat because of the tilted view. In Fig.4.7 (b), the missing pattern can be observed near the edge of

Figure 4.6: Schematic drawing of the PIV system and the Scheimpflug principle when using the tilted camera to focus on the light sheet. The extend lines of the light sheet (subject plane), the lens plane and the image plane must be intersected for the Scheimpflug principle to work.

the pendant droplet, although the images show centripetal vortex flows, i.e. the information at the droplet edge cannot be obtained from the camera without the tilting angle. In Fig.4.7 (c), the vector field is shown with the tilted angle at 15° . The velocity field is different from which in Fig.4.7 (a) due to the effects of the tilted angle and the unsteady open evaporation conditions. Figure 4.7 (d) clearly shows flow pattern both in the middle and at the edge of the pendant droplet, and more than 95 % of the flow inside the droplet has been restored. The vortex in the middle of image without the tilted angle in Fig.4.7 (b) can also be observed in Fig.4.7 (d). The strong upward flow in the middle domain and the downward flow near the interface induced by evaporation can be observed. The asymmetric flow pattern is a result of the unsteady evaporation in the open conditions.

The PIV images were taken in the relative same volume droplet at the same evaporation conditions for both 0° and 15° in the tilted angle. Note that the time interval should be shorted to eliminate the possible flow change in the droplet in the open conditions. In addition, one may notice the loss of the information on the top left and top right corner of the flow field might be resulted from the limitation of the tilted correction method. Adding another high speed camera perpendicular to the light sheet to capture the images without the tilted angle and with the tilted angle simultaneously can reduce the loss of flow vectors in a droplet.

Figure 4.7: The results of PIV processed vectors: (a) normal PIV processed vectors from the original image, (b) normal PIV processed vectors with recovered image, (c) tilted angle of 15° PIV processed vectors without recovered image, (d) tilted angle of 15° PIV processed vectors with recovered image.

Figure 4.8: The deviation of the ray from mesh approximation. The solid line demonstrates the actual route of the ray, and the dot line shows the deviation of ray due to mesh approximation.

4.7 Error analysis

According to Kajiya [139], there is a limitation of tessellation, so the fraction of the surface can only be an approximation of the original surface. If the profile extracted by the ADSA is accurate, such approximation leads to two sources of errors in the ray tracing [140]: the error of the intersection point and the deviation of the normal vector of the refraction plane. A 2-dimension (2D) demonstration of the origin of errors are shown in Fig. 4.8, and one ray should intersect with the original curved surface, while it hits on the triangular mesh, and the refracted ray has been mixed with errors.

The error of the mesh approximation can be estimated if the parametric function of the surface has known [141]. However, for a droplet model fitted from

Young-laplace equation, a universal equation for error estimation is not achievable. Even so, it is believed that the error can be minimized by finer mesh. By comparing the results from different mesh precision (the longest edge of a triangle), a reasonable mesh precision can be obtained. Different mesh precisions of 10, 5, 2, 1, and 0.5 pixels per point were chosen to investigate their effects on the results of the velocity vectors, and their results are listed in Fig. 4.9. In Figs. 4.9.(b) and (c), the mesh precisions of 10 and 5 pixels can keep the rough flow pattern in the middle part of the droplet, but vectors near the surface are barely visible, and both the magnitude and direction of all the vectors are in doubt. In the meantime, Fig. 4.9.(d) with the mesh precision of 2 pixels shows an improvement on the vectors in the middle part, yet the vectors near the surface are not ameliorated. When comparing Fig. 4.9.(e) with the mesh precision of 1 pixel with Fig. 4.9.(f) with 0.5 pixel, there are no significant differences between the vector fields of the two for the most part. The velocity deviation at the middle of the droplet, where the maximum velocity exists, is only 1.1 %. Generally, although high triangle mesh density means better accuracy during intersection calculation, excessive triangle density also leads to extraordinary slow performance during traversal. If the mesh precision increases to 0.5 pixel, the time consuming for the recovery increases 10 to 100 times, which is almost meaningless for practical use.

Additionally, the tilted angle recovery stretches the original image, if the tilted angle is too large, the recovered image would be fragmented vertically.

Figure 4.9: The results of PIV processed vectors with different mesh precision: (a) Processed vectors from the original image; (b) to (f) are the processed vectors from recovered images with mesh precision of (b) 10 pixels, (c) 5 pixels, (d) 2 pixels, (e) 1 pixel and (f) 0.5 pixel. The results of the recovered flow become better with a high mesh precision.

Figure 4.10: Fragmented recovered image when the tilted angle is too large, and the gray horizontal lines were the results of the vertical stretching.

The fragmented image is demonstrated in Fig. 4.10 from simulation, and the gray horizontal lines reveal the fragments from the recovery. During the ray tracing process, the original tilted image was stretched with an aspect ratio in the vertical direction to the recovered image on the light sheet plane. Since the recovered image was drawn from the coordinate of the intersection point of each ray with the light sheet plane, the pixel gaps were left on the image. Although such fragments are barely to be noticed when $\alpha < 20^\circ$, the recovered images can be shrunk to eliminate the blank pixels, or use another camera perpendicularly to the light sheet to capture the images and combine the images together for an accurate vector generation.

4.8 Summary

A numerical solution to recover the distorted PIV images of a droplet has been developed for accurate and trustable flow analysis. This method is a purely physical process, and no additional assumption is involved during ray tracing calculation. It is also suggested to add another PIV camera that is perpendicular to the light sheet, if the whole flow measurement inside a droplet is desired. Once the recovery process is accomplished, further studies on the thermocapillary convection can be achieved. It is necessary to mention that there is no axisymmetric requirement in the ray tracing methodology. If a proper mesh can be provided, the image recovery for any abnormality transparent objects is possible. The ray tracing recovery provided a powerful tool for the evaporation studies, and the further investigations of the thermocapillary flow can be conducted. The evaporation of a pendant droplet under ambient condition will be studied in the next chapter with the help of ray tracing recovery.

Chapter 5

Evaporation of a Heated Droplet at Different Temperatures

When the droplet is heated from the substrate, the uneven evaporation flux would cause temperature gradient along the droplet interface, such temperature gradient would cause surface tension gradient and a convection flow could be generated, which is called the thermocapillary flow. For a heated pendant droplet, the thermocapillary convection generated by the temperature gradient would play an important role in energy transportation. The thermocapillary convection under different temperature was not well studied, and the study the flow in a pendant droplet would increase the understanding of evaporation.

5.1 Introduction

As the droplet evaporating, the heat conduction length along the drop interface to the substrate varies. Hence the temperature distribution and evaporation flux of the interface during the evaporation process are not uniform. Such temperature differences would cause surface tension gradient, and thus a convection flow can be generated in the liquid. After Deegan et al. [67] pointed out that the outward flow inside the droplet caused the coffee ring deposition; extensive researches have focused on the convection inside the droplet. Marangoni flow caused by the surface tension gradient from temperature or concentration difference was proved to contribute to the energy distribution inside the evaporating droplet. Ristenpart et al. [74] found that the flow direction was related to the ratio of conduction coefficient between the substrate and the fluid. Xu et al. [76] showed that the flow direction was also connected with the thickness of the substrate. Dunn et al. [108] built a model to simulate the effects of the heating substrate on the sessile droplet evaporation. However, most of the researches were concerned about a sessile droplet. During heating, the convection inside the droplet consists of not only Marangoni flow but buoyancy flow. Studies of a heated pendant droplet could minimize the buoyancy effect with a higher density liquid on the top, and the open condition provide flexibilities to conduct and measure the experiments. However, the rate of evaporation of ethanol is so high under the

open conditions that the flow inside the droplet is always complex and turbulent even with the minimum heating. In addition, water is easy to be contaminated, and the thermocapillary convection is often too fragile to be captured. Therefore, the silicone oils have been chosen since their relative low evaporation rate and various ranges of viscosity, and the flow could keep laminar flow even heated at 80°C. The velocity normal to the edge due to evaporation and the inward flow can be negligible, so the investigation could focus more on the thermocapillary flow, and how the convection would behave under different heating temperatures.

5.2 Experimental apparatus

A schematic drawing of the experiment apparatus is illustrated in Fig. 5.1. A syringe pump (KDS 210) was pumping liquid through a heat exchanger connected with a heat bath to orifice at the middle of the evaporation substrate. The heat exchanger is 30 cm long, and the substrate is made of copper to make the temperature distribute evenly. The liquid has been mixed with 4% wt. of seeding particles (Lavision, hologlass) by ultrasonic bath for 30 minutes, and rest for 4 hours. Only the middle section of the liquid in the flask will be using in the experiments. The PIV has been adopted to record the velocity field inside the droplet. A dual head Nd-YAG pulse laser (Litron nano L120) with light sheet optic illuminated a slice of the droplet so that the movement of the seeding parti-

cles inside the droplet can be recorded by a high speed camera (Phantom V711). The images were analyzed in Davis 8 PIV software, and a two-pass iteration with grid size of 32×32 and 16×16 was chosen for PIV vector calculation. In the meantime, a k-type $25 \mu\text{m}$ U-shaped thermocouple mounted to a XYZ translate stage had been used to record the temperature at the apex, the periphery and the orifice of the droplet, and the thermocouple is connected with a DAQ (NI-6251 with SCC-T with an accuracy of 0.1°C) recording at 10 Hz. A humidity meter with an accuracy of $\pm 5\%$ was also used to monitor the humidity inside the room. The droplet was evaporated in the lab at room temperature of $24 \pm 1^\circ\text{C}$ with a relative humidity of $55 \pm 5\%$. A 50 by 50 cm^2 semi-opened transparent chamber (without cap) surrounded the droplet to prevent any disturbances from the side. We selected two types of the silicone oils from Dow Corning with the viscosity at $10 \times 10^{-6} \text{ m}^2/\text{s}$) for a series of experiments of SO10 and $50 \times 10^{-6} \text{ m}^2/\text{s}$ for a series of experiments of SO50.

5.2.1 The experimental procedure

During the experiment, the temperatures of the heat bath were set to 30, 40, 50, 60, 70 and 80°C respectively. The droplet was formed by setting the syringe pump at 1 ml/min until the droplet reaching at about same size. Then the steady state was reached by adjusting the syringe pumping rate to keep the droplet size unchanged. The steady state flow rate was obtained by recording the image of the

Figure 5.1: Schematic of the experimental setup

droplet for 1 hour under each condition, the value was recorded if the shape of the droplet did not change during the period. Since the minimum resolution of the high speed camera is 1 pixel, it is expected a uncertainty of $2 - 3 \mu\text{l/h}$ depending on the size of the droplet. At the time, the evaporation rate, J , was equivalent to the syringe pumping rate. The surface area can be calculated by the image analysis from the droplet shape profile. Then average evaporation flux, j , can be computed by dividing the evaporation rate with the surface area. Since the rate of evaporation of the silicone oil in the air is negligible, the effects of the liquid feeding on the flow inside the droplet can be ignored. The recorded temperatures for 1 minute at the apex and the periphery were then calculated with the mean

value and standard deviation, listed in Table 5.1. The recorded images were processed by Lavision Davis 8, and a two-pass iteration with a window size of 32×32 and 16×16 was chosen for vector calculation.

5.2.2 Direct velocity recovery method for flow recovery

As mentioned in the previous chapter, the PIV measurements of the velocity of a droplet should be corrected for appropriate results, and the image recovery scheme by ray tracing could accomplish such job properly. For a trustworthy measurement, an average result of numerous measurements of a single droplet under the steady state condition is necessary to minimize measurement error. However, for the image recovery method, the processing time for a single image is about 20 minutes currently, so the recovery of a large amount of data is a tedious work. Therefore, a direct velocity recovery method is proposed for a faster generation of the recovered results. If the flow inside the droplet is without turbulent flow, the vectors of the flow can be processed directly for recovery.

Instead of submitting to the recovery software, the captured images were firstly sent to the PIV analysis software (Lavision Davis 8) for vector calculation, and the vectors of thousands of instantaneous measurements can be averaged for a decent result. After that, the vector data can be submitted to the software for direct velocity recovery. After establishing a proper model for the measured droplet, the recovery could commence just like the image recovery by tracing each

vector from the image plane to the light sheet plane. Theoretically, the velocity vectors from the PIV analysis is calculated from the particle displacement within a certain time, $\Delta t = t_2 - t_1$,

$$\begin{cases} V_x = \frac{X_{t2} - X_{t1}}{\Delta t} \\ V_y = \frac{Y_{t2} - Y_{t1}}{\Delta t} \end{cases} \quad (5.1)$$

where V_x and V_y are the velocity component at x and y direction, and X and Y are the position of the particles at time t_1 or t_2 . Assuming the vectors from the PIV analysis is correct, and then the velocity mapping method can be achieved by tracing the positions of the particles at time t_1 and t_2 respectively. The position of the particle at t_2 is

$$\begin{cases} X_{t2} = X_{t1} + V_x \cdot \Delta t \\ Y_{t2} = Y_{t1} + V_y \cdot \Delta t \end{cases} \quad (5.2)$$

By tracing the two positions separately and regenerating the velocity from the corrected location through Eq. 5.2, the recovered position (X_{t1}' , Y_{t1}') and velocity (V_x' , V_y') can be generated. A velocity mapping method can be achieved when all the vectors in the PIV analysis results have been traced.

After tracing all the vectors of the velocity field, the recovered results can be generated. A comparison of the image recovery method with the direct velocity recovery method is shown in Fig. 5.2. The droplet was meshed with $350 \times 350 \times 2$ triangles, and a two-pass iteration with a grid size of 32×32 and 16×16 was chosen for PIV vector calculation. It can be noticed that there are merely

any differences of the flow pattern between the two methods, while the direct velocity recovery method could keep more vectors in the middle of the droplet. Theoretically, the results from these two methods should be identical, as can be seen in the Fig. 5.2, the velocity mapping method is more similar to condense the vectors in the middle from the vectors of the original image in Fig. 5.2.(a), which could keep more vectors at the center of the droplet. The flow pattern and the velocity magnitude are only with a difference of 5 % between this two methods.

5.3 Results and discussion

Two series of experiments of SO10 and SO50 were conducted, the temperature and average evaporation flux are listed in Table 5.1. It is seen that with an increase of the heating bath temperature, the temperature variation, $\Delta T = T_{peri} - T_{apex}$, increases, the average evaporation flux also increase, but the rise rate in the experiments of SO10 is higher than those of SO50. It is noted that T_{peri} was always higher than T_{apex} . Two effects can be generated: the first one is that as a higher temperature can lead to a lower density in the silicone oil, the lower-density liquid is at the top of the higher-density liquid, so the buoyancy-driven convection can be eliminated; the second one is that the temperature difference cause the lower surface tension liquid at the periphery point and the higher surface tension liquid at the apex. The surface tension difference would drive a flow from

Figure 5.2: Comparison of different recovery method: (a) vectors from the original image, (b) vectors from the direct velocity recovery method and (c) vectors from the image recovery method

a high temperature position to low temperature position at the liquid surface. The results of the PIV measurements demonstrate the convective flow inside the droplet. The flow should be result from the surface tension gradient due to the temperature variation at the liquid-gas interface of the droplet. Once the Marangoni or thermocapillary flow reached the apex of the droplet, the return flow would go upwards for the mass conservation. The dimensionless characteristic numbers [60] were also calculated for reference purposes, including the Capillary number $Ca = \frac{d\gamma}{dT}\Delta T/\gamma$, the Bond number $Bo = \rho g r^2/\gamma$, the Weber number $We = \rho V^2 r/\gamma$, the Reynolds number $Re = \frac{d\gamma}{dT}\Delta T r/\eta\nu$, the Marangoni number $Ma = \frac{d\gamma}{dT}\Delta T r/\eta\alpha_L$, the Prandtl number $Pr = \nu/\alpha_L$, the thermal Grashof number $Gr = (\beta_T\Delta T)r^3g\nu^2$, and the Rayleigh number $Ra = Gr * Pr$. In the present experiments, the orders of magnitude of the Bo and We are less than 10^{-4} and 10^{-5} , and these indicate that surface tension dominates. The order of the Ca is less than 10^{-2} , which demonstrates the droplet interface is undeformable. For the silicone oil of 10 cSt, the Re ranges from 0 to 10^2 , the Ma ranges from 10 to 10^3 , the Gr ranges from 0 to 10, and the Ra ranges from 10 to 10^2 . For the silicone oil of 50 cSt, the Re ranges from 0 to 1, the Ma ranges from 10 to 10^3 , the Gr ranges from 0 to 1, and the Ra ranges from 10 to 10^2 .

Based on the initial positive direct flow recovery results, the flow vectors of the experiments of SO10 and SO50 were recovered. The vectors were generated by averaging of more than 5,000 pairs of images which were taken in about 10 minutes

after the droplet evaporation was in steady state. Due to the severe reflection of the laser at the substrate, about 10 % of the vectors near the substrate was masked off during the vector calculation at the PIV analysis software to eliminate error. The droplet was modeled by $300 \times 300 \times 2$ triangles, and no manipulation of the vectors of the recovered results except discarding some of the obvious errors near the edge of the droplet.

The recovered vector fields are shown in Fig. 5.3. The return upward flow can be observed. The magnitude of the velocity increases as the bath temperature increases for the experiments of SO10 or SO50 respectively. The vortices in Figs. 5.3(a1) to 5.3(a3) and Figs. 5.3(b2) to 5.3(b5) were barely noticeable from these corrected PIV images, since the information near the edge is lost. However, the velocity for a return flow at the center would reflect the strength of the droplet interface from the periphery to the center. From Figs. 5.3(a4) to 5.3(a6), some evidences of the strong interfacial flow can be found with the center of the vortices moving towards inner of the droplet. In addition, the stronger vortices is also shown in Fig. 5.3(b6), but the higher viscous silicone oil indicated a lower velocity in the similar heating temperature at the bath.

In order to express the strength of the returning flow for the experiments, the mean velocity, V_{center} , was calculated in a 0.5 mm by 0.5 mm square region shown in Fig.5.3 at the center of the droplet. The mean velocity and average evaporation fluxes are summarized and plotted as a function of the surface tem-

perature differences, ΔT , in Figs.5.4 and 5.5. As the difference in temperature between the periphery and the apex of the droplet increases, the magnitude of the mean velocity increases. It is also suggested that a higher temperature variation induces a stronger thermocapillary flow for the each type of the silicone oil. But the rise slope of SO10 is higher than that of SO50 due to the different viscosity. It is believed that a smaller viscosity could generate a higher convection flow at the same temperature gradient at the liquid surface.

Table 5.1: The measured results of the silicone oil droplets evaporated under difference heating temperature, and the standard deviation of the measurements was shown. The velocity V_{center} shown in the table is the mean velocity of a 0.5 mm by 0.5 mm square calculated at the center of the droplet

Exp.	T_{bath} °C	T_{throat} °C	T_{apex} °C	$T_{periphery}$ °C	V_{center} m/s	J $\mu\text{l/h}$	S m^2	h mm	r mm
SO10-1	30	30.0 ± 0.03	29.7 ± 0.04	29.8 ± 0.02	$2.2 \times 10^{-4} \pm 2.5 \times 10^{-5}$	1 + 2	$1.14 \times 10^{-4} \pm 2 \times 10^{-6}$	1.3	1.8
SO10-2	40	40.0 ± 0.04	37.3 ± 0.11	39.2 ± 0.08	$7.3 \times 10^{-4} \pm 3.2 \times 10^{-5}$	2 ± 3	$1.27 \times 10^{-4} \pm 2 \times 10^{-6}$	1.4	1.9
SO10-3	50	48.8 ± 0.06	44.7 ± 0.22	48.7 ± 0.21	$1.1 \times 10^{-3} \pm 6.5 \times 10^{-5}$	10 ± 2	$1.23 \times 10^{-4} \pm 2 \times 10^{-6}$	1.2	1.9
SO10-4	60	57.8 ± 0.06	52.0 ± 0.27	57.8 ± 0.21	$1.3 \times 10^{-3} \pm 7.3 \times 10^{-5}$	20 ± 2	$1.24 \times 10^{-4} \pm 2 \times 10^{-6}$	1.2	1.9
SO10-5	70	67.2 ± 0.09	60.0 ± 0.22	67.1 ± 0.15	$1.7 \times 10^{-3} \pm 7.8 \times 10^{-5}$	25 ± 2	$1.08 \times 10^{-4} \pm 2 \times 10^{-6}$	1.2	1.8
SO10-6	80	76.3 ± 0.09	67.3 ± 0.36	76.1 ± 0.36	$1.8 \times 10^{-3} \pm 1.4 \times 10^{-4}$	30 ± 2	$1.11 \times 10^{-4} \pm 2 \times 10^{-6}$	1.2	1.8
SO50-1	30	30.8 ± 0.03	29.6 ± 0.05	30.1 ± 0.03	$9.5 \times 10^{-5} \pm 9.5 \times 10^{-6}$	1 + 2	$1.20 \times 10^{-4} \pm 2 \times 10^{-6}$	1.2	1.9
SO50-2	40	39.0 ± 0.04	34.9 ± 0.13	38.3 ± 0.09	$1.3 \times 10^{-4} \pm 1.5 \times 10^{-5}$	5 ± 2	$1.25 \times 10^{-4} \pm 2 \times 10^{-6}$	1.3	1.9
SO50-3	50	47.1 ± 0.05	41.5 ± 0.12	47.0 ± 0.12	$2.5 \times 10^{-4} \pm 1.9 \times 10^{-5}$	10 ± 2	$1.26 \times 10^{-4} \pm 2 \times 10^{-6}$	1.2	1.8
SO50-4	60	58.2 ± 0.06	48.5 ± 0.21	57.9 ± 0.16	$3.2 \times 10^{-4} \pm 6.8 \times 10^{-5}$	11 ± 2	$1.25 \times 10^{-4} \pm 2 \times 10^{-6}$	1.1	1.9
SO50-5	70	67.3 ± 0.05	55.7 ± 0.29	66.4 ± 0.27	$3.6 \times 10^{-4} \pm 7.5 \times 10^{-5}$	12 ± 2	$1.26 \times 10^{-4} \pm 2 \times 10^{-6}$	1.2	1.8
SO50-6	80	75.6 ± 0.11	62.7 ± 0.23	75.3 ± 0.18	$7.2 \times 10^{-4} \pm 1.7 \times 10^{-4}$	13 ± 2	$1.27 \times 10^{-4} \pm 2 \times 10^{-6}$	1.2	1.9

Table 5.1, Figs.5.4 and 5.5 show that the average evaporation flux increases with an increase of the temperature variation between the apex and the periphery of the droplet surface. A higher average evaporation flux is found at a higher heating bath temperature, a larger ΔT , and a higher mean velocity in the droplets of SO10 or SO50. Although the flow information near the edge is lost, and there is no direct measurement of the thermocapillary flow, there should be a relation between ΔT , the intensity of the surface flow, or the evaporation flux.

5.4 Summary

The experiments of heated pendant silicone oil droplets were conducted with different bath temperature from 30 °C to 80 °C under the open conditions. A direct velocity recovery method was proposed to recover the vector field generated by the PIV analysis software to obtain genuine flow results. From the recovered results, it was found that a higher temperature difference between the apex and the periphery would generate a high convection velocity, and a higher kinematic viscosity would hinder the thermocapillary flow inside the droplet. The details of the energy transportation, and the effects of the convective heat transfer during evaporation encourages more studies. A small flat surface, which can be treated as a small flat droplet, could simplify the study of evaporation, and it will be investigated in the next chapter.

Figure 5.3: The recovered velocity of PIV measurement of silicone oil in the experiments of silicone oil of 10 cSt (a1-a6) and silicone oil of 50 cSt (b1-b6).

Table 5.2: The comparison of temperature difference with the average evaporation flux, and the average evaporation flux was calculated by assuming a even evaporation flux along the droplet interface.

Exp.	T_{bath}	ΔT	$\bar{j}$	Ma	Ra	Gr
	$^{\circ}C$	$^{\circ}C$	$kg/m^2 \cdot s$			
SO10-1	30	0.1 ± 0.05	$2.3 \times 10^{-6} \pm 4.6 \times 10^{-6}$	3.0×10	6.0	10^{-1}
SO10-2	40	2.0 ± 0.05	$4.1 \times 10^{-6} \pm 6.3 \times 10^{-6}$	3.1×10^2	8.0×10^1	1
SO10-3	50	4.0 ± 0.09	$2.1 \times 10^{-5} \pm 4.1 \times 10^{-6}$	5.3×10^2	1.2×10^2	2
SO10-4	60	5.8 ± 0.29	$4.3 \times 10^{-5} \pm 4.2 \times 10^{-6}$	1.2×10^3	2.6×10^2	4
SO10-5	70	7.1 ± 0.22	$6.0 \times 10^{-5} \pm 4.8 \times 10^{-6}$	1.4×10^3	3.0×10^2	7
SO10-6	80	8.9 ± 0.41	$7.0 \times 10^{-5} \pm 4.7 \times 10^{-6}$	2.1×10^3	4.7×10^2	12
SO50-1	30	0.6 ± 0.04	$2.2 \times 10^{-6} \pm 4.0 \times 10^{-6}$	5.0×10	1.0×10	10^{-2}
SO50-2	40	3.5 ± 0.06	$1.1 \times 10^{-5} \pm 3.8 \times 10^{-6}$	1.9×10^2	5.0×10	10^{-1}
SO50-3	50	5.5 ± 0.07	$2.1 \times 10^{-5} \pm 4.3 \times 10^{-6}$	3.0×10^2	7.0×10	10^{-1}
SO50-4	60	9.4 ± 0.16	$2.4 \times 10^{-5} \pm 4.0 \times 10^{-6}$	5.3×10^2	1.1×10^2	10^{-1}
SO50-5	70	10.7 ± 0.20	$2.5 \times 10^{-5} \pm 4.3 \times 10^{-6}$	7.7×10^2	1.7×10^2	10^{-1}
SO50-6	80	12.6 ± 0.28	$2.7 \times 10^{-5} \pm 4.1 \times 10^{-6}$	1.1×10^3	2.6×10^2	1

Figure 5.4: The comparisons of the temperature differences with the velocity at the center of the droplet at different conditions, and a higher temperature difference between the apex and the periphery of the droplet would cause a larger velocity inside the droplet.

Figure 5.5: The comparisons of the temperature differences with the average evaporation flux at the middle of the droplet at different conditions, and a higher temperature difference between the apex and the periphery of the droplet would cause a larger average evaporation flux at the interface of the droplet.

Chapter 6

Evaporation of Liquid Heated at Interface

The thermocapillary convection flow could transport energy during evaporation at the interface. The interesting point is how the energy transport at the evaporating interface with by convection from the high-temperature edge to the low-temperature position. In this chapter¹, the importance of interfacial flow energy transport at a flat evaporating surface with the global negative thermal conduction to the interface from both liquid and gas phases has been studied.

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6.1 Introduction

Marek and Straub pointed out that the evaporation coefficients differed by several orders in magnitude under the similar experimental conditions [15]. The significant variation might come from the experimental uncertainty affected by contact line motion, thermal conduction, temperature discontinuity across the interface, or hydrodynamic instabilities including buoyancy-driven convection, thermocapillary convection, and vapor-liquid interface moving [15]. Among them, thermocapillary convection at the interface and positive thermal conduction to the interface were found to improve the evaporation in the recent steady-state experiments at the spherical and cylindrical interfaces [113, 114] if the other factors, including vapor-liquid interface moving, buoyancy-driven convection, and contact line motion, were eliminated in the confined containers under the steady-state evaporation conditions. A measurable temperature gradient was found at the evaporating interface after the thermocapillary convection transition. The thermocapillary convection flow transported up to 40% energy for evaporation at the vapor-water interface [113]. The interesting point was how the energy transport at the evaporating interface with almost zero cross-section area by the convection from the high-temperature edge to the low-temperature position. Therefore, a rig has been designed for global negative thermal condition to the interface from both liquid and gas phases in order to explain the importance of interfacial flow

energy transport at a flat evaporating surface.

6.2 Experimental apparatus

The overall experimental apparatus is illustrated in Fig.6.1. The equal-length heating wires with a diameter of 0.125 mm were installed in a pair at both the top and 5 mm lower than the top position in parallel at a Poly(methyl methacrylate) evaporation chamber (15 mm in length, 10 mm in width, and 15 mm in height). The deionized water was supplied in the evaporation chamber by a syringe mounted on a syringe pump at room temperature. Simultaneously, the heating wires were electrified at Level 0 (top) or Level 1 (5 mm below). The heat from the pair of elements was provided by a power supplier at a predetermined voltage and current listed in Table 6.1. The level of the water surface was regulated at the top edge of the container shown in Fig.6.2 by adjusting the pumping rate of the syringe pump. The experiments were conducted in a laboratory with the temperature at 25 °C and the relative humidity at 40 %. Under steady states, the water surface level monitored by a microscope, the heating wire power supply, and the syringe pump rate were maintained to be constant during the measurement. The three U-shaped calibrated K-type thermocouples (25 μ m in diameter) mounted on a positioner are shown in Fig.6.2. The thermocouples were arranged at the different height. Since the water surface was flat, the junction of

the middle thermocouple was put to be just submerged at the water surface for each experiment. Thus, the top thermocouple (about 2.5 mm above the junction of the middle thermocouple) was in the gas phase, and the bottom thermocouple (about 2.5 mm below the junction of the middle thermocouple) was at the liquid phase.

6.3 The experimental procedure

Two series of steady-state experiments were conducted: (1) the top pair of heating wires at Level 0 were maintained at 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 V respectively, and (2) the pair of heating wires with 5 mm below the water surface at Level 1 were maintained at 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 V respectively during water evaporating. When the evaporation is in the steady state, the thermocouples were moved manually across the water surface. As shown in Fig.6.2, the thermocouples were moved from one side of the container to the other side with approximately 0.3 mm intervals. The readings for each position were recorded for about 10 seconds. The mean temperature was then calculated. In each of the experiments, the water evaporation rate, J , was recorded at the syringe pump with an accuracy at $\pm 0.5\%$. Then the average evaporation flux, $\bar{j} = J/S$, where S is the evaporating flat surface area. The calculated values are listed in Table 6.1.

Figure 6.1: The sketch of evaporation apparatus, two pairs of heating elements were aligned in the evaporation chamber at Level 0 (top) and Level 1 (5 mm lower). The temperatures at the gas phase, interface, and liquid phase were measured with the three calibrated thermocouples.

6.4 Results and discussion

As shown in Table 6.1 for the steady-state experiments from E1 to E12, the average evaporation flux of E1 has a value of $0.133 \text{ g/m}^2\text{s}$ at Level 0, while E7 has $0.100 \text{ g/m}^2\text{s}$ at Level 1 under the same power input from the heating wires. The difference of the average evaporation rate is about 33%. The average evaporation flux in E6 is $1.596 \text{ g/m}^2\text{s}$, but it is $0.399 \text{ g/m}^2\text{s}$ in E12 at similar conditions. The ratio of E6 to E12 is about 4 times. The results indicate an interesting physical

phenomenon: the average evaporation fluxes are higher as the heating is at Level 0 than those at Level 1 at the same power input. The ratio of the evaporation fluxes at the both heating levels increases with an increase of electric power input. The temperature distribution of the pair of experiments of E1 and E7 is illustrated in Fig.6.3 while that of E6 and E12 is in Fig.6.4. As shown in Fig.6.3, the temperatures in the liquid phase, interface, and air phase are approximatively uniform respectively. However, the interfacial temperature, 25.6°C as the heating wires are at Level 0, is higher than that at Level 1 (23.8°C). In Fig.6.4, although the interfacial temperature is relatively uniform at 26.1°C with a deviation of 0.12°C (lower than that in the liquid phase) as the heating is at Level 1, the interfacial temperature with the heating wires at Level 0 is more parabolic. As illustrated in Figs. 6.3 and 6.4, with the heating at Level 0 (the water surface), the interfacial temperature is higher than the liquid temperature, while it is also higher than that in the gas phase. Thus, thermal conduction in both phases would take energy away from the water surface globally when the heating is at the water surface. Thus, in the experiments, buoyancy-driven convection in the liquid phase would be absent because the lighter water at the higher interfacial temperature is on the top of the denser bulk liquid. If the energy transport by the air flow is negligible, the main energy for evaporation should be from convection. In addition, the ratio of the heating elements (0.125 mm in diameter) to the water surface width (10 mm) is almost zero. The cross-section area is almost

zero at the interface for thermal conduction if the temperature variation is at the interface. Therefore, as the kinetic energy and viscous dissipation at the interface (I) are negligible, the local evaporation flux can be calculated from the conventional Stefan condition $j = [(\kappa^V \nabla T^V - \kappa^L \nabla T^L)_I \cdot i_n] / (h^V - h^L)_I$, where i_n is the normal direction to the evaporation interface, $(h^V - h^L)_I$ is the enthalpy change in evaporation with a positive value. Consequentially, the negative value in the right side of the above equation should lead to condensation globally, which is contrary to our observation in the experiments. On the other hand, when the heating is at Level 1, 5 mm below the water surface, the interfacial temperature in Figs. 6.3 and 6.4 is lower than the liquid temperature. Thermal conduction in the liquid phase would improve evaporation by conducting more energy to the surface from the liquid phase in comparison with the conditions heating at Level 0. However, the average evaporation flux at Level 1 is smaller than that at Level 0 at the relative same electric power input. To clarify the contradiction, we have to pay more attention to the interface. The measured interfacial temperature along the water surface shows a significant temperature variation at the water surface in Fig. 6.4. The interfacial temperature at the heating elements is higher than that at the centerline between the two heating elements. The average temperature difference between the periphery and the centerline is about 6.9°C. Subsequently, a large interfacial temperature variation can result in an interfacial flow due to surface tension difference. The interfacial flow should enhance energy transport

from the “hot” heating wires to the “cold” place at the water surface, as seen in the phenomena with higher average evaporation fluxes occurring at Level 0. To describe the process, the mass and energy balances are derived in cartesian coordinates at a flat evaporating surface element as shown Fig.6.2 on the basis of the Gibbs dividing-surface approximation. The system in the analysis includes three phases, liquid phase (L), gas phase (V), and interface (LV or I).

Under steady-state evaporation, no net changes in the number of moles are assumed in the evaporating surface element,

$$\begin{aligned} (n^L v^L)_I \cdot i_z &= (n^V v^V)_I \cdot i_z + \nabla(n^{LV} v^{LV}) \cdot i_x \\ &+ \nabla(n^{LV} v^{LV}) \cdot i_y, \end{aligned} \quad (6.1)$$

where n and v are the density and velocity in each of three phases, i_x and i_y are in x- and y- directions. The steady-state evaporation flux, j , can be expressed as,

$$j = (n^L v^L)_I \cdot i_z = (n^V v^V)_I \cdot i_z. \quad (6.2)$$

The conservation of energy requires the energy being transported into the surface element to equal the sum of those leaving and being dissipated by viscosity at the surface, Φ_I . Thus, we have,

$$\begin{aligned} (n^L h^L v^L - \kappa^L \nabla T^L)_I \cdot i_z &= (n^V h^V v^V - \kappa^V \nabla T^V)_I \cdot i_z \\ &+ [n^{LV} v^{LV} (\nabla u^{LV}) + u^{LV} \nabla(n^{LV} v^{LV})] \cdot i_x \\ &+ [n^{LV} v^{LV} (\nabla u^{LV}) + u^{LV} \nabla(n^{LV} v^{LV})] \cdot i_y + \Phi_I, \end{aligned} \quad (6.3)$$

where u^{LV} is the specific internal energy per mole, and $du^{LV} = T^{LV}ds^{LV} + \gamma^{LV}d\alpha^{LV}$ if the gas phase is assumed not to be dissolved in water, s^{LV} is the intensive surface entropy per mole, γ^{LV} is the surface tension, and α^{LV} is the intensive surface area per mole ($=1/n^{LV}$). A Helmholtz function, $f^{LV} \equiv u^{LV} - T^{LV}s^{LV}$, would have $f^{LV} = f^{LV}(T^{LV}, \alpha^{LV})$. Since s^{LV} also has the same independent variables as f^{LV} , $u^{LV} = u^{LV}(T^{LV}, \alpha^{LV})$.

If any variations in v^{LV} , u^{LV} , and T^{LV} are neglected as a function of the position in x-direction at the evaporating element as shown in Fig.6.2, we have Eq.(6.4) after Eq.(6.3) is simplified,

$$j(h^V - h^L)_I = (\kappa^V \nabla T^V - \kappa^L \nabla T^L)_I \cdot i_z - n^{LV} v_y^{LV} \left(\frac{\partial u^{LV}}{\partial y} \right) - \Phi_I, \quad (6.4)$$

where

$$\left(\frac{\partial u^{LV}}{\partial y} \right) = \left(\frac{\partial u^{LV}}{\partial T^{LV}} \right) \left(\frac{\partial T^{LV}}{\partial y} \right) + \left(\frac{\partial u^{LV}}{\partial \alpha^{LV}} \right) \left(\frac{\partial \alpha^{LV}}{\partial y} \right). \quad (6.5)$$

The changes in α^{LV} as a function of position are negligible at the interface at the steady-state condition, Eq.(6.4) is then expressed as,

$$j(h^V - h^L)_I = (\kappa^V \nabla T^V - \kappa^L \nabla T^L)_I \cdot i_z - c_\sigma v_y^{LV} \left(\frac{\partial T^{LV}}{\partial y} \right) - \Phi_I, \quad (6.6)$$

where $c_\sigma \equiv \frac{\partial u^{LV}}{\partial T^{LV}} \cdot n^{LV}$, the surface-thermal capacity has been determined from the experiments at the spherical and cylindrical interfaces [112, 113] with a value at

30.6±0.8 kJ/m²K for water, and it was not a negligible value for energy transport at the interface once there is a flow.

As indicated in Eq.(6.6), the evaporation flux is determined by the local thermal conduction to the interface from both the liquid and gas phases, the local interfacial viscous dissipation, and the local interfacial flow at v_y^{LV} which can be induced by the surface tension variation due to the interfacial temperature difference. The local velocity at the interface has not been determined yet. However, if the velocity at the interface is assumed to be mainly generated by the surface tension gradient by overcoming the viscosity shear stress, the thermocapillary convection velocity would have a proportional relation to the temperature gradient from the high interfacial temperature (at the heating wires) to the low temperature (at the centerline of the pair of wires) [142]. Since the thermocapillary convection flow is always opposite to the temperature gradient at the evaporating interface, the term, $-c_\sigma v_y^{LV} \left(\frac{\partial T^{LV}}{\partial y} \right)$, would be positive to enhance evaporation. Therefore, we can use the thermodynamic model to analyze the steady-state experiments qualitatively. In the experiments at Level 0, only the interfacial flow supplied energy to increase evaporation, since thermal conduction to interface from both liquid and gas phases were negative, and the possible viscous dissipation would reduce the energy for evaporation at the interface as well. An increase on the interfacial temperature gradients and/or the interfacial flow velocities would increase the evaporation flux. The average interfacial

temperature variation was 0.03°C in E1 and 6.89°C in E6 between the heating wires and the centerline of the two elements. As a result, the average evaporation flux increased from $0.133\text{ g/m}^2\text{s}$ in E1 to $1.596\text{ g/m}^2\text{s}$ in E6. However, in the experiments at Level 1, the average interfacial temperature variation was 0.02°C of E7 and 0.12°C of E12. As shown in Fig.6.4, the average evaporation flux is much lower than the counterpart experiment, e.g. $\bar{j}_{E12} < \bar{j}_{E6}$, even though the energy for evaporation can be supplied more to the interface by thermal conduction from the liquid phase in z-direction with the heating at Level 1. Therefore, thermocapillary convection should transport energy to enhance the evaporation at the interface with the heating at Level 0.

6.5 Summary

In sum, the experimental study demonstrated that a larger interfacial temperature gradient with the heating at a flat water surface can enhance the evaporation. The results qualitatively agreed with the thermodynamic analysis on which an interfacial flow from a high-temperature position to a low-temperature position can supply sufficient energy for evaporation by overtaking negative thermal conduction to the interface from the liquid and gas phases, or the possible interfacial viscous dissipation.

Figure 6.2: Levels 0 and 1 of the heating wires are displayed when the evaporating water surface is maintained at the top edge of the chamber. The temperatures were measured in the gas phase, interface, and liquid phase in the steady-state evaporation. The evaporating surface element in cartesian coordinates for mass and energy analyses. The U-shaped K-type thermocouples are shown in the insert.

Table 6.1: Summarization of the experimental conditions in steady-state evaporation.

Exp:	Heating wire	Heating wire	Heating wire	$\bar{j}$
	level	Voltage /(V)	Current(A)	(g/m ² s)
E1	Level 0	0.5	0.05	0.133±0.007
E2	Level 0	1.0	0.10	0.266±0.013
E3	Level 0	1.5	0.13	0.599±0.030
E4	Level 0	2.0	0.22	0.931±0.047
E5	Level 0	2.5	0.28	1.197±0.060
E6	Level 0	3.0	0.31	1.596±0.080
E7	Level 1	0.5	0.05	0.100±0.005
E8	Level 1	1.0	0.11	0.133±0.007
E9	Level 1	1.5	0.14	0.173±0.009
E10	Level 1	2.0	0.23	0.200±0.010
E11	Level 1	2.5	0.30	0.279±0.014
E12	Level 1	3.0	0.34	0.399±0.020

Figure 6.3: The temperature distribution at the gas phase, interface, and liquid phase as a function of position with the heating at Level 0 and Level 1 for E1 and E7.

Figure 6.4: The temperature distribution at the gas phase, interface, and liquid phase as a function of position with the heating at Level 0 and Level 1 for E6 and E12.

Figure 6.5: The average evaporation flux as a function of the average interfacial temperature variation with the heating at Level 1 and at Level 0.

Chapter 7

Conclusions and Future Work

7.1 Major findings

The major findings of this investigation are listed as follows:

1. SRT can be used to estimate the thermodynamic properties of D_2O near the triple point. It well predicts the saturation pressure, the latent heat and specific heat.
2. The experiments of a pendant ethanol droplet under the steady-state evaporation conditions have been conducted in the chamber designed. The thermocapillary convection has been captured by using the PTV method, with the maximum convection velocity at 1 mm/s.
3. A full flow field recovery method is achieved with 95 % of the genuine flow information of a droplet, especially the flow near the interface.

4. The effects of viscosity on the silicone oil droplet evaporation have been studied. It was found that a higher temperature difference between the apex and the periphery would generate a higher convection velocity.

5. An interfacial flow from a high-temperature position to a low-temperature position can supply energy for evaporation by overtaking negative thermal conduction to the interface from the liquid and gas phases, or the possible interfacial viscous dissipation.

7.2 Conclusions

The thermal and fluid investigations of liquid evaporation have been carried out in this study.

The previous experimental data of D_2O during evaporation are applied in the SRT to estimate the thermodynamic properties of D_2O near the triple point. The comparison of the literature results with the SRT approach shows less than 5 % of difference on not only the saturation pressure prediction, but also the latent heat and specific heat.

A series of experiments of measuring the temperature distribution of a pendant ethanol droplet under the steady-state condition during evaporation have been conducted in the chamber designed. 16 sets of experiments of ethanol droplet evaporation have been conducted. The temperature distribution of the pendant

droplet along the interface has been measured. The results of the predicted pressure from the SRT approach have less than 6 % of the differences with the results of the measured pressure. The temperature of the center line is about 0.8 °C lower than the periphery in Ethanol16 with a higher rate of evaporation, and a thermocapillary flow can be generated because of the temperature gradient. When the evaporation rate is high, the temperature at the interface decreased from the periphery to the centerline, and such temperature gradient can generate the thermocapillary convection. The thermocapillary convection has been captured by using the PTV method, and the maximum convection velocity can reach 1 mm/s.

A numerical solution to recover the distorted PIV images of a droplet has been developed for accurate and trustable flow analysis. After creating a 3D surface model of an axisymmetric droplet from its outline profile, the program can be adopted to recover the distortion PIV images by recording the coordinate of the intersection points of the rays on the light sheet plane. This method is a purely physical process, and no additional assumption is involved during ray tracing calculation. If using one tilted camera, about 95 % of the full internal flow field of a droplet is recovered, especially the flow near the interface. It is also suggested to add another PIV camera that is perpendicular to the light sheet, if the whole flow measurement inside a droplet is desired. Once the recovery process is accomplished, further study on the thermocapillary convection can be

achieved. It is necessary to mention that there is no axisymmetric requirement in ray tracing methodology. If a proper mesh can be provided, the image recovery for any abnormality transparent objects is possible.

For a steady flow, a direct velocity recovery method has been proposed for faster vector recovery for the measurements of the droplet. The experiments of heated pendant silicone oil droplets have been conducted with different bath temperature from 30 °C to 80 °C under ambient condition. The flow measurements of the droplet during steady-state evaporation are recovered through this method. It is found that a higher temperature difference between the apex and the periphery would generate a higher convection velocity, and a higher kinematic viscosity would hinder the thermocapillary flow inside the droplet. For silicone oil of 10 cSt, the maximum velocity was 1.8×10^{-3} m/s at the center of the droplet with a temperature difference of 8.9 °C, while for silicone oil of 50 cSt, the maximum velocity is 7.2×10^{-4} m/s with a temperature difference of 12.6 °C.

The experimental study demonstrates that a larger interfacial temperature gradient with the heating at a flat water surface can enhance evaporation. The average evaporation flux increased from 0.133 g/m²s in E1 to 1.596 g/m²s in E6. On the contrary, in the experiments at Level 1, the average interfacial temperature variation is 0.02°C of E7 and 0.12°C of E12. The results qualitatively agrees with the thermodynamic analysis on which an interfacial flow from a high-temperature position to a low-temperature position can supply sufficient energy

for evaporation by overtaking negative thermal conduction to the interface from the liquid and gas phases, or the possible interfacial viscous dissipation.

7.3 Future recommendations

Due to the safety regulations, the cold trap with liquid nitrogen cooling is not applicable currently for the evaporation experiments in the vacuum chamber, so that the pressure of the experiments of ethanol evaporation in the vacuum chamber could not reach below 2000 Pa. Therefore, the turbulent transition of the flow inside the droplet is not recorded in the experiments. It is suggested to adopt a proper exhaust system to install the cold trap with liquid nitrogen cooling to conduct the experiments further. It is also found that the pendant droplet in the experiments is extremely difficult to maintain, and the droplet kept falling even only minor mistakes are performed. The current fuzzy control system can be combined with the axisymmetric droplet shape analysis (ADSA) scheme to control the size of the droplet simultaneously. Therefore, an automatic liquid feeding system can be developed to facilitate the experiments in the future.

For the flow recovery, although the ray tracing recovery program can bring significant results, the time of the processing takes about 20 minutes on an Intel i7 computer. It is suggested to utilize more computer techniques to improve the calculation, such as Streaming SIMD Extensions (SSE), multi-thread and even graphics processing unit (GPU) computing, and the real-time image recovery is possible.

The direct velocity recovery method can be combined with the tilt-angle imag-

ing method to obtain the full flow field of the droplet, especially the flow near the interface can be captured.

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Appendix A

Uncertainty analysis

A.1 Uncertainty analysis of the evaporation of a pendant droplet under vacuum condition

The expression for the net evaporation rate may be used to determine the variation in this rate that results from a small change in the independent variables [26].

If the changes in the independent variables are sufficiently small, and if one use the linearized approximation to estimate the error of the evaporation flux, then

$$\begin{aligned} \frac{\Delta j}{j} = \frac{1}{j} \left| \left(\frac{\partial j}{\partial P^V} \right) \right| \Delta P^V + \frac{1}{j} \left| \left(\frac{\partial j}{\partial T^L} \right) \right| \Delta T^L + \\ \frac{1}{j} \left| \left(\frac{\partial j}{\partial T^V} \right) \right| \Delta T^V + \frac{1}{j} \left| \left(\frac{\partial j}{\partial r} \right) \right| \Delta r \end{aligned} \quad (\text{A.1})$$

where

$$\frac{1}{j} \left| \frac{\partial j}{\partial r} \Delta r \right| = \left| -2 \frac{v_s^L \gamma}{k_b T^L} \frac{\Delta r}{r^2} \coth \left(\frac{\Delta S}{k} \right) \right| \quad (\text{A.2})$$

$$\frac{1}{j} \left| \frac{\partial j}{\partial P^V} \Delta P^V \right| = \left| \frac{\Delta P^V}{P^V} \left(-1 + \frac{P^V v_s^L}{k_b T^L} \right) \coth \left(\frac{\Delta S}{k_b} \right) \right| \quad (\text{A.3})$$

$$\begin{aligned} & \frac{1}{j} \left| \frac{\partial j}{\partial T^V} \Delta T^V \right| = \\ & \left| \frac{\Delta T^V}{T^V} \left\{ 4 \left(1 - \frac{T^V}{T^L} \right) - \frac{1}{T^V} \sum_{i=1}^{15} \left[\frac{\Theta_i}{2} + \frac{\Theta_i}{\exp(\frac{\Theta_i}{T^V}) - 1} \right] + \right. \right. \\ & \left. \left. \left(\frac{1}{T^{V2}} - \frac{1}{T^V T^L} \right) \sum_{i=1}^{15} \left[\frac{\Theta_i^2 \exp(\frac{\Theta_i}{T^V})}{(\exp(\frac{\Theta_i}{T^V}) - 1)^2} \right] \right\} \coth \left(\frac{\Delta S}{k_b} \right) \right| \end{aligned} \quad (\text{A.4})$$

$$\begin{aligned} & \frac{1}{j} \left| \frac{\partial j}{\partial T^L} \Delta T^L \right| = \\ & \left| \frac{\Delta T^L}{T^L} \left\{ \left[\frac{v_s^L}{k_b T^L} (P_s - P_e) - \frac{1}{2 T^L} \right] + \right. \right. \\ & \left. \left[\frac{4 T^V - P^V \frac{v_s^L}{k_b} + \sum_{i=1}^{15} \left[\frac{\Theta_i}{2} + \frac{\Theta_i}{\exp(\frac{\Theta_i}{T^V}) - 1} \right]}{T^L} - 4 \right] \coth \left(\frac{\Delta S}{k_b} \right) \right\} \right| \end{aligned} \quad (\text{A.5})$$

To estimate the sensitivity of the rate expression to the different parameters, we may consider the experiment with the highest evaporation rate. The quantitative change in the evaporation flux may be calculated from the values of the parameters for the experiments that are listed in Table 3.2,

$$\frac{\Delta j}{j} = \left(\frac{2.3 \times 10^{-3}}{Pa} \right) \Delta P^V + \left(\frac{1.3 \times 10^{-3}}{m} \right) \Delta r + \left(\frac{3.2}{K} \right) \Delta T^L + \left(\frac{3.2}{K} \right) \Delta T^V \quad (\text{A.6})$$

The magnitudes of the coefficients of the $\Delta P^V, \Delta T^L, \Delta T^V$ and r are smaller in the expression of $\Delta j/j$ at the lower rates of evaporation. The accuracy of the

net evaporation flux is 0.5 %, while one of the least accurately measured was the pressure at the interface, with an accuracy of 0.1 %. The thermocouple used in this experiment was calibrated with an accuracy of 0.05 K, and the radius of the droplet was measured with an accuracy of 0.05 %. If the ΔT^L , ΔT^V and r are taken to have been measured exactly, then in order for the value of the net evaporation flux j to be calculated as accurately as it would be measured, the pressure in the vapor would have to be measured to approximately 2.0 Pa. However, it was measured to within only 100.0 Pa for ethanol. If we assume that ΔP^V , ΔT^V and r were measured exactly, then in order for the net evaporation flux to be calculated as accurately as it could be measured, the temperature at the interface in the liquid would have to be measured to within 2.0×10^{-3} K, and it was 0.05 K. The error in the measured value of ΔP^V results in an error in the calculated evaporation rate that is one order of magnitude larger than that from the error in the measured value of ΔT^V or ΔT^L . Therefore, the total system error of calculated flux was 10 %, and near 50 % came from the pressure measurement.

A.2 Uncertainty analysis of the evaporation of a heated pendant droplet

The uncertainties of the thermocouples in the present study are determined from the root mean square of the uncertainties of all the equipment used in the cali-

bration, which is ± 0.1 K. From the error propagation method [143]

$$\delta_f = \sqrt{\left(\frac{\partial f}{\partial x}\delta_x\right)^2 + \left(\frac{\partial f}{\partial y}\delta_y\right)^2 + \left(\frac{\partial f}{\partial z}\delta_z\right)^2 + \dots} \quad (\text{A.7})$$

where δ_f represents the standard deviation of the function f , δ_x represents the standard deviation of x , δ_y represents the standard deviation of y , and so forth. It is found the uncertainties of the Marangoni, Rayleigh and Grashof number is 6.1 %, 8.1 % and 8.9 % respectively. The PIV system is calibrated at 1 pixel, therefore the uncertainty of the whole system is less than 1 %.

A.3 Uncertainty analysis of the evaporation of liquid heated at interface

The error of the distance between the thermocouple is less than 0.1 mm, the error of the distance between each measuring point is less than 0.05 mm, and the accuracy of the net evaporation flux is 0.5 %. The uncertainties of the thermocouples is ± 0.1 K, which is one order of magnitude smaller than the temperature difference recorded in the experiments, and this chapter is based on the qualitative analysis of the experimental results. Therefore, the uncertainty in these experiments will not alter the conclusions.

Appendix B

Thermal Properties of Water and Ethanol

The thermal properties of water are as follows [112]: the saturated liquid density is from IAPWS 1995:

$$\rho = \rho_c(1 + b_1\theta^{1/3} + b_2\theta^{2/3} + b_3\theta^{5/3} + b_4\theta^{16/3} + b_5\theta^{43/3} + b_6\theta^{110/3}) \quad (\text{B.1})$$

where $b_1 = 1.992\,740\,64$, $b_2 = 1.099\,653\,42$, $b_3 = 20.510\,839\,303$, $b_4 = 21.754\,934\,79$, $b_5 = 245.517\,035\,2$, and $b_6 = 26.746\,944\,503\,\text{E}5$, $\theta = 1 - T/T_c$, $T_c = 647.096\,\text{K}$, and $\rho_c = 322\,\text{kg/m}^3$. The saturated vapor pressure is from ASAE standards (1989)

$$\ln(P_s/R) = \frac{A + BT + CT^2 + DT^3 + ET^4}{FT - GT^2} \quad (\text{B.2})$$

where $R = 22105\,649.25$, $A = -27405.526$, $B = 97.5413$, $C = -0.146244$, $D = 0.12558\text{E-}3$, $E = -0.48502\text{E-}7$, $F = 4.34903$ and $G = 0.39381\text{E-}2$. The surface

tension is from IAPWS 1994

$$\gamma = B(1 - T/T_C)^{1.256}(1 + b(1 - T/T_C)) \quad (\text{B.3})$$

where $T_c=647.096$ K, $B = 235.8$ mN/m and $b = -0.625$.

The thermal properties of ethanol are from DIPPR [30] and listed as follows,

The specific volume is

$$v_s^L = (46.0684 \times 1.6288 / 0.27469^{(1+(1-T/514)^{0.23178})})^{-1} \quad (\text{B.4})$$

The saturated vapor pressure is

$$P_s = \exp(73.304 - (7122.3/T) - 7.1424 \times \ln(T) + 2.8853 \times 10^{-6} \times T^2) \quad (\text{B.5})$$

The surface tension is

$$\gamma = 0.03764 - 0.00002157 \times T - 1.025 \times 10^{-7} \times T^2; \quad (\text{B.6})$$

Appendix C

Core Code of SRT for Pressure Prediction

The SRT code for pressure prediction (Matlab 2008) is shown as follows:

```
1  clc
2  clear
3  global c hb k m NA mpm vibfreq;
4  c = 2.99792458*10^10; %(*cm/s*)
5  hb = 1.05457266*10^-34; %(*Js*)
6  k = 1.380658*10^-23; %(*J/K*)
7  NA = 6.023*10^23; %(*1/mol*)
8
9
```

```

10 fluidName = 'water';
11 if strcmpi (fluidName,'ethanol') || strcmpi (fluidName,'
    C2H6O')
12     m = 46.06844/1000; %(*kg/mol*)
13 %     vibfreq = [3689, 2989, 1456, 1391, 1320, 1242, 1067,
    1040, 877, 427,...
14 %         2789, 1456, 1270, 1104, 801] .* 2 * pi * c;
15     vibfreq = [2989 3689 1456 1456 1391 1242 801 1320 1270
    ...
16     1067 877 427 1040 1104 267 350] .* 2 * pi * c;
17 elseif strcmpi (fluidName,'water') || strcmpi (fluidName,'
    H2O')
18     m = 0.018; %(*kg/mol*)
19     vibfreq = [1591, 3651, 3756] .* 2 * pi * c;
20 end
21 mpm = m / NA;
22
23 flux1 = [0.000297905    0.000271002    0.000152873
    0.000248842    0.000259892];%Average Evaporation Flux-
    Kg/m^2S
24 TV = 273.15+ [7.97027    6.16273 6.66008 7.69869 6.66181];%

```

```

25 TL = 273.15+ [3.43544    3.70834  4.2586   4.69771  5.14871];%
26 %zm = [0.98].*1e-3;
27 re = 1e-3*[2.6748        2.1536   2.8245   2.033    2.1995];%(
        zm.^2+(3.5e-3).^2) ./ (2.* zm)%
28 % ds = deltaS(TL, TV, PV, re, fluidName);
29
30 % fprintf('out = %f\n, ou1 = %f\n, ou2 = %f\n, ou3 = %f\n,
        ou4 = %f\n, ou5 = %f\n',out, out1,out2,out3,out4,out5)
        ;
31 % global Ps Vs TL poe Ga
32 Ps = Psat(TL,fluidName);
33 Ga = Gamma(TL,fluidName);
34 Vs = Vsat(TL,fluidName);
35 for i = 1:numel(TV)
36     pet = fsolve(@(Pe)(Pe - Ps(i) .* exp(Vs(i)./(k./
        mpm.*(TL(i))).*(Pe - Ps(i) )) - (2.*Ga(i))./re(
        i)), [1 1000]);
37     pe(i)=pet(1);
38 end
39
40 qvibL = Qvib(TL,fluidName);

```

```

41  qvibV = Qvib(TV,fluidName);

42

43  ke1 = ke(TL, pe, Ps, Vs, fluidName);

44  for i = 1:numel(TV)

45      dst = fsolve (@(ds)(flux1(i) - 2.*ke1(i).* sinh(ds))

                     ,[0.1 10] );

46      ds(i) = dst(1);

47  end

48  % syms ds

49  % ds = solve ((flux1 - 2*ke1* sinh(ds)),ds )

50

51  for i = 1:numel(TV)

52      summ(i) = sum(hb.* vibfreq./(2.*k) + hb.*vibfreq./ (k

                     .*(exp(hb.*vibfreq/(k.*TV(i))) - 1)));

53

54      pvt = fsolve(@(Pv)(-ds(i) + 4.*(1 - TV(i)./TL(i)) +

                     (1./TV(i) - 1./TL(i)) .* summ(i) + ...

55      Vs(i)./(k./mpm .* TL(i)) .* (Pv + (2.*Ga(i)) ./ re

                     (i) - Ps(i)) + ...

56      log((TV(i)./TL(i)).^4 .* Ps(i) ./ Pv) + log(qvibV(

                     i) ./ qvibL(i))), [1 1000]);

```

```

57     PV(i)=pvt(1);

58 end

59

60 SKct = Vs.*(PV + 2.*Ga./re - Ps)./(k./mpm.*TL) + log(Ps./

    PV);

61 SKt = 4*(1 - TV/TL) + log((TV./TL).^4);

62 SKomega = (1./TV - 1./TL).* summ + log(qvibV ./ qvibL);

63

64 SKct = SKct*1e6;

65 SKt = SKt*1e6;

66 SKomega = SKomega*1e6;

67 j2k=flux1./(2.*ke1).*1e6

68

69 FID=fopen('a.txt','w');

70 for i = 1:numel(TV)

71 fprintf(FID, '%f %f %f %f %f %f %f\r\n', PV(i), j2k(i),

    SKct(i), SKt(i), SKomega(i), SKt(i)+SKomega(i), SKct(i)

    +SKt(i)+SKomega(i));

72 end

73 fclose(FID);

74

```

```

75 % put = [PV j2k SKct SKt SKomega SKt+SKomega SKct+SKt+
           SKomega];

76 % dlmwrite('a.txt', put, 'delimiter', ' ', 'precision', 8);

77

78

79 function out = Psat(T, fluidName)

80 % return the saturation pressure of a fluid

81 if strcmpi (fluidName, 'ethanol') || strcmpi (fluidName, '
           C2H6O')

82     out = exp(73.304 - (7122.3 ./ T) - 7.1424.*log(T) +
           2.8853*10.^(-6) .* T.^2);

83 %     out = exp(52.165-6445./T-3.75424.*log(T)
           -3.0053.*10.^(-6).*(T.^2-T));

84 elseif strcmpi (fluidName, 'water') || strcmpi (fluidName,
           'H2O')

85     out = 22105649.25 .* exp((-27405.526 + 97.5413.*T -
           0.146244.*T.^2 + 0.12558.*10.^-3.*T.^3 - ...

86     0.48502.*10^-7.*T.^4) ./ (4.34903.*T - 0.39381*10^-2.*T
           .^2));

87 end

88

```

```

89
90 function out = Qvib(T,fluidName)
91 % return the specific volume of a fluid
92 global c hb k vibfreq;
93 % if strcmpi (fluidName,'ethanol') || strcmpi (fluidName,'
    C2H6O')
94 %     vibfreq = [3689, 2989, 1456, 1391, 1320, 1242, 1067,
        1040, 877, 427,...
95 %         2789, 1456, 1270, 1104, 801] .* 2 .* pi .* c;
96 % elseif strcmpi (fluidName,'water') || strcmpi (fluidName
    , 'H2O')
97 %     vibfreq = [1591, 3651, 3756] .* 2 .* pi .* c;
98 % end
99 % out=1;
100 %     for j = 1:numel(vibfreq)
101 %         each(j) = exp(-hb * vibfreq(j) /(2 * k * T)) / ...
102 %             (1 - exp(-hb * vibfreq(j) /(k * T)));
103 %         out = out*each(j);
104 %     end
105 for i = 1:numel(T)
106

```

```

107     out(i) = prod((exp(-hb .* vibfreq ./ (2 .* k .* T(i))))
    ./ ...
108     (1 - exp(-hb .* vibfreq ./ (k .* T(i)))));
109 end
110 end
111
112
113
114 function out = ke(TL, Pe, Ps, Vs, fluidName)
115 % return the molecular exchange rate of a fluid
116 global mpm k ;
117 % Pe = 6.8073*10^6;
118 out = mpm .* Ps .* exp(Vs/(k .* TL / mpm) .* ...
119     (Pe - Ps)) ./ sqrt(2 .* pi .* mpm .* k .* TL);
120
121
122
123 function out = Gamma(T, fluidName)
124 % return the surface tension of a fluid
125 if strcmpi (fluidName, 'ethanol') || strcmpi (fluidName, '
    C2H6O')

```

```

126     out = 0.03764 - 0.00002157.*T - 1.025 .*10.^(-7) .* T
        .^2;

127 elseif strcmpi (fluidName,'water') || strcmpi (fluidName,'
        H2O')

128     out = 235.8 .* (1 - T./647.096).^1.256.*(1 - 0.625.*(1
        - T./647.096));

129 end

130

131

132

133 function out = Vsat(T,fluidName)

134 % return the specific volume of a fluid

135 if strcmpi (fluidName, 'ethanol') || strcmpi (fluidName, '
        C2H6O')

136     out = (46.0684 .* 1.6288 ./ 0.27469.^(1 + (1 - T./514)
        .^0.23178)).^(-1);

137 elseif strcmpi (fluidName, 'water') || strcmpi (fluidName,
        'H2o')

138     out = 1./(322.*(1 + 1.99274064.*(1 - T./647.096)
        .^(1./3) +...

139     1.09965342 .* (1 - T./647.096).^(2./3) - ...

```

```
140      0.510839303.*(1 - T./647.096).^ (5./3) - ...
141      1.75493479.*(1 - T./647.096).^ (16./3) - ...
142      45.5170352.*(1 - T./647.096).^ (43./3) - ...
143      6.74694450.*10.^5.*(1 - T./647.096).^ (110./3)));
144 end
```

Appendix D

The Results of the temperature distribution measurements

The other groups of the measurements of the temperature distribution along the droplet interface are listed here:

Figure D.1: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol1 under steady state condition. $\Delta T_{max}^L = \pm 0.03^\circ\text{C}$ and $\Delta T_{max}^V = \pm 0.03^\circ\text{C}$.

Figure D.2: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol3 under steady state condition. $\Delta T_{max}^L = \pm 0.03^\circ\text{C}$ and $\Delta T_{max}^V = \pm 0.03^\circ\text{C}$.

Figure D.3: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol4 under steady state condition. $\Delta T_{max}^L = \pm 0.03^\circ\text{C}$ and $\Delta T_{max}^V = \pm 0.03^\circ\text{C}$.

Figure D.4: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol5 under steady state condition. $\Delta T_{max}^L = \pm 0.06^\circ\text{C}$ and $\Delta T_{max}^V = \pm 0.10^\circ\text{C}$.

Figure D.5: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol6 under steady state condition. $\Delta T_{max}^L = \pm 0.04^\circ\text{C}$ and $\Delta T_{max}^V = \pm 0.06^\circ\text{C}$.

Figure D.6: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol7 under steady state condition. $\Delta T_{max}^L = \pm 0.04^\circ\text{C}$ and $\Delta T_{max}^V = \pm 0.05^\circ\text{C}$.

Figure D.7: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol8 under steady state condition. $\Delta T_{max}^L = \pm 0.04^\circ\text{C}$ and $\Delta T_{max}^V = \pm 0.04^\circ\text{C}$.

Figure D.8: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol10 under steady state condition. $\Delta T_{max}^L = \pm 0.04^\circ\text{C}$ and $\Delta T_{max}^V = \pm 0.07^\circ\text{C}$.

Figure D.9: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol11 under steady state condition. $\Delta T_{max}^L = \pm 0.04^\circ\text{C}$ and $\Delta T_{max}^V = \pm 0.09^\circ\text{C}$.

Figure D.10: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol12 under steady state condition. $\Delta T_{max}^L = \pm 0.04^\circ\text{C}$ and $\Delta T_{max}^V = \pm 0.07^\circ\text{C}$.

Figure D.11: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol13 under steady state condition.

$$\Delta T_{max}^L = \pm 0.04^\circ\text{C} \text{ and } \Delta T_{max}^V = \pm 0.08^\circ\text{C}.$$

Figure D.12: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol14 under steady state condition.

$$\Delta T_{max}^L = \pm 0.04^\circ\text{C} \text{ and } \Delta T_{max}^V = \pm 0.08^\circ\text{C}.$$

Figure D.13: Temperature measured across the interface of the droplet at 4 horizontal positions of Exp No. Ethanol15 under steady state condition.

$\Delta T_{max}^L = \pm 0.03^{\circ}\text{C}$ and $\Delta T_{max}^V = \pm 0.08^{\circ}\text{C}$.

Appendix E

Core Code of Fuzzy Control

Method

The core code of the fuzzy control program (Matlab 2008) is shown as follows:

```
1  clc ;  
2  
3  %%  
4  % Use EraseMode ,draw dynamically . Change axis dynamically .  
5  % Multi-Line drawing line  
6  global fismat ;  
7  global i ;  
8  global t0 ;  
9  global t ;
```

```
10 global x;
11 global pressure;
12 global volume;
13
14 t0 = clock;
15 t = [0]; % initialize
16 pressure = [0]; % initialize
17 volume = [0];
18 i = 0;
19 x = -pi ;
20 setpressure = 800;
21
22 pressureFig=figure('Name','Pressure data');
23 pressureHline = plot(t,pressure,'EraseMode','background','
    MarkerSize',5);
24 title('Pressure vs Time');
25 xlabel('Tims (s)');
26 ylabel('Pressure Pa');
27 axis([x-5 x+5 0 1000]);
28 grid on;
29
```

```
30 %% Serial configuration
31
32 PressureCOM = serial('COM1'); % creat serial port obj
33 set(PressureCOM, 'BaudRate', 9600, 'DataBits', 8, 'StopBits
    ', 1, ...
34     'Parity', 'none'); % set properties for serial
35 PressureCOM.Terminator = 'CR/LF';
36 PressureCOM.Timeout = 1;
37 PressureCOM.InputBufferSize = 4096;
38 PressureCOM.BytesAvailableFcnMode = 'terminator'; % byte
    number or terminator
39 set(PressureCOM, 'BytesAvailableFcnCount', 4);
40 set(PressureCOM, 'BytesAvailableFcn', { @PressureCallback ,
    pressureHline });
41 fopen(PressureCOM);
42
43
44 setpressure = 800;
45 %%
46
47 fprintf(PressureCOM, 'MOD=FLOW');
```

```
48 pause(2);
49 fprintf(PressureCOM, 'PRI? ');
50 pause(2);
51 pressurefismat = readfis('fuzzy1.fis'); %fuzzy strategy of
    pressure
52
53 while ishandle(pressureFig)
54     ti = clock;
55
56     fprintf(PressureCOM, 'PRI? ');
57     pause(0.5);
58     if i>2
59         p = setpressure - pressure(i);
60         dpdt = (pressure(i - 1) - pressure(i)) / (t(i) -
            t(i-1));
61
62         valvePara=evalfis([p, dpdt], pressurefismat);
63         pressurestr = num2str(valvePara, '%3.2E');
64         pressurestr(end-2:end-2)='';
65         pressureOutput = ['FLO=', pressurestr, 'Pal/s'];
66         fprintf(PressureCOM, pressureOutput);
```

```
67
68     end
69         pause(0.5);
70 end
71 dlmwrite('t.txt', t, 'delimiter', ' ', 'precision', 8);
72 dlmwrite('pressure.txt', pressure, 'delimiter', ' ', '
        precision', 8);
73
74 fclose(PressureCOM);
75 delete(PressureCOM);
76 clear PressureCOM;
77 close all;
78 clear all;
79
80 %the callback function of pressure
81 function PressureCallback(PressureCOM, BytesAvailable,
        pressureHline)
82 global i;
83 global t;
84 global t0;
85 global x;
```



```

86 global pressure;

87 global t0;

88 global fismat;

89

90 out = fscanf(PressureCOM); %read data from s

91 if strfind(out, 'PRI=') ~= 0

92     %PRI= 2.87E+02Pa

93     pressureReg = regexp(out, '[+-]?[\d]+([\.\d]*)?([Ee]
        ][+-]?[0-9]{0,2})?','match');

94     p = str2double(pressureReg{1})

95     tn = clock;

96     time = etime(tn, t0);

97     t=[t time];    %0 0.1 0.2 0.3.. %Matrix 1*(i+1), column
        is increasing

98     pressure=[pressure p]; %Matrix 2*(i+1), 2row, i+1
        column.

99

100     set(pressureHline, 'XData', t, 'YData', pressure(1,:));

101

102     x = x + 1;    % x = x+0.1

103     axis([x-5 x+5 0 1000]);

```

```

104     drawnow
105     pause(0.5);
106
107     i = i+1;
108     elseif strfind(out,'FLO=') ~= 0
109         %      FLO=1.00E+00Pal/s
110         flowrateReg = regexp(out,'[+-]?[\d]+([\.\d]*)?([Ee][+-]?[0-9]{0,2})?','match');
111         flowrate = str2double(flowrateReg{1});
112         pause(0.5);
113     end
114 end

```

Appendix F

Core Code of the Recovery Program

Due to the length of the program, only the main tracing code for image recovery (Visual C++ 2010) is shown as follows:

```
1 Primitive* Engine::Raytrace( Ray& a_Ray, Color& a_Acc, int
    a_Depth, real a_RIndex, real& a_Dist, real a_Samples,
    real a_SScale, Color& store_color, int workMode, int
    checkScale )
2 {
3     // trace primary ray
4     a_Dist = 10000.0f;
5     Primitive* prim = 0;
```

```
6         int result ;
7         // find the nearest intersection
8         if (!(result = FindNearest( a_Ray, a_Dist , prim ))
           ) return 0;
9
10        // determine color at point of intersection
11        vector3 pi = a_Ray.GetOrigin() + a_Ray.
           GetDirection() * a_Dist;
12        Color color = prim->GetColor( pi );
13        vector3 N = prim->GetNormal( pi );
14        double d = 0;
15
16        switch (prim->GetType() + workMode)
17        {
18            //workMode: 0 is false , 1 is align mode,
19            //10 is demo mode
20
21            //1 is sphere , 3 is triangle , 5 is target
22            plane
23
24        case 2:
25            //Primitive::SPHERE
```

```
23         //record only in align mode: 1 + 1 = 2
24         cacheImageData(pi, Color(0,255,125));
25         return prim;
26         break;
27     case 4:
28         //Primitive::TRIANGLE
29         //record only in align mode: 3 + 1 = 4
30         cacheImageData(pi, Color(0,255,125));
31         return prim;
32         break;
33     case 5:// Primitive::TARGET
34         // record in normal mode
35         cacheImageData(pi, store_color);
36         return prim;
37         break;
38     case 6:// Primitive::TARGET
39         //record in align mode: 5 + 1 = 6
40         cacheImageData(pi, store_color);
41         return prim;
42         break;
43     case 15:// Primitive::TARGET
```

```

44         //record in demo mode: 5 + 10 = 15
45         d=abs(( floor(pi.x * checkScale) + floor(pi
           .y * checkScale))));
46         d=fmod(d,2);
47         a_Acc += d < 1 ? Color(0,0,0) : Color
           (1,1,1);
48         //cacheImageData(pi, a_Acc*255);
49         return prim;
50         break;
51     default:
52         break;
53 }
54 // calculate refraction
55 real refr = prim->GetMaterial()->GetRefraction();
56 if ((refr > 0) && (a_Depth < TRACEDEPTH))
57 {
58     real rindex = prim->GetMaterial()->
           GetRefrIndex();
59     real n = a_RIndex / rindex;
60     vector3 N = prim->GetNormal( pi ) * (real)
           result;

```

```

61         real cosI = -DOT( N, a_Ray.GetDirection()
           );
62         real cosT2 = 1.0f - n * n * (1.0f - cosI *
           cosI);
63         if (cosT2 > 0.0f)
64         {
65             vector3 T = (n * a_Ray.
           GetDirection()) + (n * cosI -
           _sqrt( cosT2 )) * N;
66             Color rcol( 0, 0, 0 );
67             real dist;
68             Raytrace( Ray( pi + T * EPSILON, T
           ), rcol, a_Depth + 1, rindex,
           dist, a_Samples * 0.5f,
           a_SScale * 2, store_color,
           workMode, checkScale );
69             m_RaysCast++;
70             a_Acc += rcol * transparency;
71
72         }
73     }

```

```
74         // return pointer to primitive hit by primary ray
75     return prim;
76 }
```