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Evaporation Prediction of Ethanol Droplet by Statistical Rate Theory

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Abstract

Evaporation is one of common natural phenomenon which happens in everywhere. The application of evaporation, such as chemical industry and printing technology, affects human life everyday. However, the evaporation still cannot be predicted in an ideal method. It is found that the classical theory is not accurate and reliable enough for evaporation rate analysis. Statistical rate theory (SRT) was introduced to solve this problem. The SRT expression derived from the number of molecules transferred from the interfacial boundary between liquid and vapor phase, energy equilibrium and thermodynamics equilibrium. The final expression of evaporation rate of ethanol droplet was derived with all measurable parameter. In this study, the collected experimental data was used for SRT expression validation. The comparison between measured value and predicted value is analysed to prove that it is agreement for ethanol droplet evaporation process with SRT expression. Two terms in SRT expression was defined as phonon term and continuum term. Phonon term is depended on liquid and vapor interfacial temperature while the continuum term is because of continuum effects and its properties. The continuum term dominated evaporation rate while the condensation rate was decided by phonon term. Evaporation parameters, which are vapor phase interfacial temperature, liquid phase interfacial temperature, vapor phase pressure and drop size radius, are numerical analysed through SRT approach. For vapor phase and liquid phase interfacial temperature, the evaporation flux is slightly decreased when the vapor phase interfacial temperature is increasing. However, the increasing liquid phase interfacial temperature leads to increasing evaporation flux. Furthermore, the evaporation is decreased when the vapor phase pressure increasing. For droplet size, the evaporation flux behaves as constant when the drop size is not in nanometre scale. Once the droplet size comes into nanometre scale, the evaporation is increasing significantly. For the future work, more data from various conditions can be analysed. More materials such as methanol, glycol and acetone can be analysed via SRT approach.

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Contents

Abstract	ii
Acknowledgement	iii
Chapter 1: Introduction	1
1.1 Background	1
1.2 Motivation and Objective	1
1.3 Scope of report	2
Chapter 2: Literature Review	3
2.1 The mechanism of evaporation	3
2.2 The evaporation of droplet	6
2.3 The temperature distribution of a droplet	8
2.4 The flow in the droplet	9
2.4.1 The flow pattern of convection	10
2.4.2 The thermocapillary effect	11
2.5 The other models for droplet evaporation	12
2.6 Statistical rate theory	15
2.7 Summary	16
Chapter 3: Application of SRT in droplet evaporation	18
3.1 SRT Expression for the rate of Evaporation	18
3.2 An isolated system at an instant in time	18
3.3 Rate of interfacial molecular transfer	19
3.4 Equilibrium exchange rate between the liquid and vapor phases	25
3.5 Expression for the evaporation flux	27
3.6 Expressions for chemical potential and specific enthalpy	28
3.7 Expression for fluxes in terms of measurable variables	30
3.8 Summary	31
Chapter 4:Evaporation flux SRT Analysis	32
4.1 Experimental Setup	32
4.2 Experimental Procedures	34
4.3 Result and Discussion	35
4.4 Summary	39

Chapter 5:Parameters analysis through SRT approach.....	40
5.1 Effect of vapor-phase temperature	42
5.2 Effect of liquid-phase temperature	43
5.3 Effect of vapor-phase pressure	44
5.4 Effect of the droplet radius.....	46
5.5 Summary	47
Chapter 6: Conclusion and future work	49
6.1 Conclusions.....	49
6.2 Future work.....	49
References.....	51

Chapter 1: Introduction

1.1 Background

Evaporation is a process of transformation from liquid to vapour. Scientist studies this phenomenon for years, and applied it to many engineering field. Printing and refrigeration are two instances in daily life; besides, fabrication of new materials is a successful example of high technological evaporation. ^[1-3]

Evaporation is a complex process so that many scientists discovered the secret of this natural phenomenon. In 1820, John Dalton began experiments and studies on evaporation mechanism. ^[4] Temperature distribution, thermocapillary effect and many other effects are factors of liquid evaporation. A huge number of studies has been did, and countless experiments have been performed. But, the knowledge of evaporation is limited due to its complexity. More research and experiments are required for higher understanding of evaporation.

1.2 Motivation and Objective

Although many efforts have been devoted to the study of droplet evaporation project, as reviewed in chapter following, the evaporation process still have scientific value due to various materials and conditions. The traditional method was only focus on the thermal behaviour of evaporation process. However, the limitation of traditional thermal method was that it was hard to find the general coefficients in evaporation process. Therefore, it was hard to come out with the general equation in traditional thermal method. As the invention of computational method, numerical method has been developed fast to study this process behaviour. With the computational method, the general equation of evaporation process for

certain materials was determined. However, the evaporating behaviour was various from one materials to another. Therefore, in this project, evaporation properties of ethanol was studied. In addition, the statistical rate theory (SRT) has been applied to help analysis the property of ethanol in various evaporation environment.

In this study, the objectives to further understand the evaporation of ethanol droplet for the precise prediction in the potential application. First, the general equation of ethanol droplet evaporation with measurable parameters was derived through the statistical rate theory. Second, the equation was verified by comparison between the prediction values from equation and measured values from experiment. Then, the impacts of terms in evaporation equation were analyzed. Last, the properties of ethanol evaporation via the prediction were analyzed via the derived ethanol evaporation equation.

1.3 Scope of report

Chapter 2 is indicated the literature of the evaporation of droplet and the statistical rate theory (SRT).

Chapter 3 is the basic introduction to the SRT.

Chapter 4 is the experiment of fluid dynamic impact on the evaporation.

Chapter 5 is the experiment of thermal dynamic impact on the evaporation.

Chapter 6 is the experiment of the evaporation flux.

Chapter 7 is the experiment of the thermal properties of evaporation.

Chapter 8 is the conclusion and recommendation in the future

Chapter 2: Literature Review

2.1 The mechanism of evaporation

Evaporation condition is related to pressure and temperature. According to gases kinetic theory, the evaporation flux is defined as variances between the rate of molecular on the boundaries of liquid phase and vapour phase. Consider pressure, temperature, the rate of molecular from liquid to vapour, the rate of molecular from vapour to liquid can be represented as P_V, T_V, j_{LV}, j_{VL} .

Then, if

$$j_{LV} = j_{VL}, \quad (2.1)$$

it is called the equilibrium condition, which means the number of molecular transforming from liquid to gas is equal to the number of molecular transforming form gas to liquid. In addition to the rate of molecular, vapour temperature and liquid phase are considered as identical in equilibrium.

Maxwell-Boltzmann distribution defines the molecular speed distribution in vapour phase under certain temperature. Applied the Maxwell-Boltzmann distribution to an ideal vapour phase, the rate of molecular at unit time passing through a unit area can represented as [4]

$$j_{LV} = P_V \sqrt{\frac{M}{2\pi RT_V}} \quad (2.2)$$

where molecular mass is expressed as M and gas constant is expressed as R .

Furthermore, if the effect of molecular reflecting on interface between liquid and gas is ignored during this process, the unit rate of molecular from liquid phase to vapour phase, j_{LV} , is expressed as ^[5]

$$j_{LV} = P_V \sqrt{\frac{M}{2\pi RT_V}} \quad (2.3)$$

where P_{sat} is defined as saturation pressure and T_L is defined as liquid phase temperature.

For molecular rate from vapour phase to liquid phase, it can be considered as condensation rate. So, evaporation rate and condensation rate can be expressed and considered separately at non-equilibrium condition. j_{VL} is represented the evaporation rate flux from vapor phase to liquid phase The net rate can be represented as

$$j = j_{LV} - j_{VL} = \sqrt{\frac{M}{2\pi k_b}} \left(\frac{P_{sat}(T^L)}{\sqrt{T^L}} - \frac{P^L}{\sqrt{T^V}} \right) \quad (2.4)$$

At non-equilibrium evaporation, the number of molecular leaving from liquid is not as same as the number of condensing molecular from gases. Then, the evaporation rate can be explained as maximum number of molecular from liquid phase to vapour phase at equilibrium. For non-equilibrium evaporation, the evaporation rate could apply Maxwell-Stefan diffusion theory, which indicate the state of molecular near the boundary is main factor affecting the molecular diffusion. Hence, for non-equilibrium boundary, the net rate can be presented as the differences between the evaporation rate and condensation rate. Then, Hertz-Knudsen formula equation is ^[6]

$$j = j_{LV} - j_{VL} = \sqrt{\frac{M}{2\pi k_b}} \left(\sigma_e \frac{P_{sat}(T^L)}{\sqrt{T^L}} - \sigma_c \frac{P^L}{\sqrt{T^V}} \right) \quad (2.5)$$

where evaporation net rate is expressed as j , liquid phase is expressed as L , vapour is expressed as V , evaporation coefficient is defined as σ_e and condensation coefficient is defined as σ_c . Regarding to discussion mentioned above, evaporation coefficient is equal to condensation coefficient under equilibrium while they may not be same under non-equilibrium circumstances. ^[8,9] Regarding to Barrett and Clement research, liquid surface is the only factor affecting the value of evaporation coefficient. However, for condensation coefficient, it is determined by both liquid property and vapour property.

Schrage ^[10] believed that net bulk vapour velocity is a factor of distribution of vapour molecules. So, net rate expression can be modified by adding bulk vapour molecules velocity as

$$J = \frac{1}{\sqrt{2\pi M k}} \left(\frac{\sigma_e}{1-0.5\sigma_c} \frac{P_{sat}(T^L)}{\sqrt{T^L}} - \frac{\sigma_c}{1-0.5\sigma_c} \frac{P^V}{\sqrt{T^V}} \right) \quad (2.6)$$

where σ_c and σ_e value is not constant and determined by experiments ^[11,12]. And, many methods have been applied for coefficient value experiments. Quasi-steady evaporation is one of the most common experiment method applied for coefficient value.^[6] The method is to achieve maximum evaporation rate. Vacuum environment was used since Knudsen number of vacuum environment is larger than 1. Then, the maximum expression is

$$j_{VL} = \sigma_e P_L \sqrt{\frac{M}{2\pi R T_L}} \quad (2.7)$$

In fact, it is hard to control quasi steady state condition and temperature gradient is not accurate because of the error in evaporation. Eventually, Koffman^[13] and Marek ^[15] proved that coefficients was hard to predict since they were not follow particular pattern. Since the values of these coefficients cannot be determined, it is hard to finalize experimental results.

2.2 The evaporation of droplet

Droplet surface is not flat but a curvature. A droplet surface is displayed in Fig. 2.1. From the figure, it is easy to classify into solid phase and liquid phase.^[31] Besides, the shape of it can be described as a circle theoretically. At the edge of liquid phase and solid phase, contact angle is defined. Also, they was classified into 3 elements: absorbed film, micro-region and macro-region^[32]. At absorbed film, the thickness of is around 100nm and the interaction of solid phase and liquid phase is determined by the Van Der Waals force^[31]. At the micro-region, it is determined by capillary force together with Van Der Waals force. And, this area is occupied 0.5% of extended area.^[33] At the macro-region, capillary force fully dominates it. According the experiments before, the evaporation happened at macro region for most of time.
[33-37]

In the process of evaporation, the state of droplet contact angle was transforming follow various patterns. Three of them happened mostly: constant contact area, constant contact angle and constant angle with area.^[38-42]

Figure 2.1: Different region during evaporation ^[43]

For a surface in perfect smooth status, once droplet placed on it, the radius of droplet expanded to maximum. Then, due to the evaporation process, the size of droplet would shrink. However, the contact angle of droplet was maintained for the same^[43]. If the surface is defined as smooth isothermal silicon surface^[44,45], the effect of flow in droplet can be ignored. So, the contact line only determined by the properties of the surface. However, the process of evaporation was still various, even at a hydrophobic surface; because contact angle may increase or decrease at first stage^[46-48]

For non-ideal substrate, surfactant effect influenced the process of evaporation. Therefore, in real, the process of droplet evaporation initiated with pinned contact line. In the process of evaporation, the angle of contact line reduced to its minimum value. The contact line did not change the contact angle^[49,50] The reason why pinned contact evaporation initiated is because of the surface properties.^[51,52]

The energy barrier from the chemical heterogeneities and substrate roughness are main factors of pinned contact line^[53] When the contact angle remain certain value, the free energy of surface is minimum. Thus, the free energy of surface may change due to pinned contact line when the droplet volume was shrinking. Therefore, pinned status would be transfer to unpinned status in order to release the extra free energy. In the process of evaporation, the pinned and unpinned status changed to each other frequently.

For unpinned process of evaporation, it is different from high evaporation rate and low evaporation rate. For high rate circumstances, the degree of contact angle increased because of the reduced radius of droplet. In addition, for low evaporation rate, the degree of contact angle remain the same but the radius of droplet was reduced slowly. Moreover, impurities of the droplet would be a factor affecting the evaporation rate. As well as outside environment, the temperature of environment and the pressure of environment are all factors affecting the

evaporation rate^[45] And, if the surface is rough enough and the surfactant condition is highly concentrated, only pinned process is initiated in high temperature.

2.3 The temperature distribution of a droplet

In evaporation process, the temperature of interface between liquid and vapour is decreased because of the energy transfer of vaporization. And the energy difference between liquid phase and vapour phase is equal to the heat conduction of liquid phase. And the heat resistance in the liquid phase depends on heat conduction length. The longer length, the higher resistance; and it is harder for energy transfer. For the distribution of temperature in droplet, two theories are most famous. One theory indicated that the temperature distribution is determined by the heat conduction.^[52] The lowest temperature should be located at the longest conduction route. And, the longest route in the droplet is the tip of it. Hence, the temperature in tip should be the lowest temperature and the temperature should increase from tip to contact line. The other theory indicated that the dominant factor of temperature distribution was the uneven evaporation flux. Deegan studied the pattern of droplet and he mentioned that the contact line was always fixed in droplet.^[52]

According to the water temperature distribution experiment measured by Hohmann and Stephan^[49], 0.08K-0.2K temperature difference drop was observed at micro region. They believed this effect was due to the intensive evaporation at micro region. And, Steinchen and Sefiane^[48] did experiment of 600um diameter droplet in a capillary, and ensured the temperature of environment was kept at 298K. The temperature of contact line was about 0.4K lower than the tip temperature. Also, the temperature distribution of droplet with respect to time was concluded by Savino and Fico^[60]. The temperature distribution of evaporation droplet was changing by second and they found the hottest area of evaporation droplet is the tip of droplet.

For volatile liquids such as methanol and pentane, Buffone and Sefiane^[51] studied the temperature distribution of it by installing an infrared camera in capillary. In the condition of pure evaporation, the temperature raised from surface of border, it came to the maximum value at the middle of it; then, the temperature began decreasing from boundary to center. But, they believed that this outcome was not accurate. They thought the coldest point was due to the infrared camera technical problem, because the infrared camera cannot focus on two places at same time. The theoretical temperature distribution should raising continuously from surface to the centre of it .

Hu and Larson^[33] studied the temperature distribution in evaporation process by simulating the evaporating process of a water droplet. As the result of it, they proved the contact angle was the factor of surface temperature of droplet. For contact angle smaller than the critical value, the temperature distribution was determined by the evaporation process so that the temperature was rising from contact line to the tip of droplet. While contact angle was larger than the critical value. Then, the temperature was decreasing from contact line until to the tip of droplet. And, heat conduction dominated the temperature distribution. Girard^[52] proved the lowest temperature point was located at the centre of the droplet through the recording of the sessile water evaporating process. In addition, Sefiane^[33] also found that the hydrothermal waves was because of the thermocapillary effect.

2.4 The flow in the droplet

For the inside of droplet, it is a complex process of properties of surface, properties of liquid and capillary effect and so on.

2.4.1 The flow pattern of convection

First of all, it is easier to explain the evaporation process contact line by eliminating the effects of gravity factor and surface tension factor. The value of contact angle at this situation was not zero degree when pinned contact line in the evaporation process happened. Thus, the flow from another area should compensate in order to keep stability at the contact line. And, Deegan found that the mean velocity of contact line flow should follow the below rules:

$$\bar{u} \sim (r - l)^{-\lambda}, \text{ where } \lambda = \frac{(\pi - 2\theta)}{(2\pi - 2\theta)} \quad (2.8)$$

where the contact angle is presented as θ and radius of droplet is presented as r . From the equation, if contact angle is 0, the λ is 0.5.

It is hard to determined the relationship between the contact angle, flux distribution and the flow inside droplet^[37] For the flow direction, it is point to the centre of droplet when maximum value of evaporation rate is applied. For the condition of contact angle was smaller than $\pi/2$ and evaporation flux was distributed evenly, the flow with the pinned contact line moved direct to the contact line. However, if the contact line was unpinned and the contact angle was fixed degree, the flow moved towards to the centre of the droplet. On the other hand, for the condition of contact angle was larger than $\pi/2$, the flow direct to the contact line of droplet, In conclusion, the pattern of flow inside droplet was mainly determined by flow contact angle. Hence, the critical angle was defined as the special degree to convection. According to the experiments, violent convection was generated if the contact angle was 14 degree higher than critical degree value^[53]. For the contact angle smaller than critical value, the convection effect would not be a factor of droplet flow. So, the flow direct to the droplet edge.

For PIV method, one factor which affected the measurement of the illuminated particles located at the inside of droplet. It is the different refractive indices of liquid phase and vapour phase. So, the flow recorded by camera was various to the real flow in droplet. In order to ensure the accuracy of experiment, all raw data should be modified and corrected before PIV analysis. But, only limited research applied the correct data for their experiment. Finally, Kang^[42] developed one analytical method to solve this issue. However, the flow data located near the interface cannot calculate. It is important to study evaporation process due to data missing. Moreover, the pre-request of this correction was to assume all the shape of droplet as hemispherical shape. But in real experiment, the shape of droplet may various to each other; hence, the different shape may receive an error.

2.4.2 The thermocapillary effect

The reason of thermocapillary effect is the tension gradient of the surface of liquid phase and vapour phase. The tension gradient of the surface would cause flow and the direction was from low tension gradient place to high tension gradient place. If the evaporation rate is not even, the temperature gradient may various in the droplet. Therefore, the convection in the droplet generate and this kind of thermocapillary flow is defined as Marangoni flow.

The convection triggered by surface tension can be expressed by Marangoni number. It is the ratio between viscous force and surface tension. So, it shown as

$$M_a = \left(-\frac{\partial \gamma}{\partial T}\right) \left(\frac{\partial T}{\partial D}\right) \frac{D^2}{\eta \alpha L} \quad (2.9)$$

where Marangoni Number is expressed as M_a , temperature gradient is expressed as $\frac{\partial T}{\partial D}$, the thermal diffusivity is expressed as αL , surface tension is expressed as γ , the dynamic viscosity is expressed as η , the thickness is expressed as D . According to the research, when silicone oil

droplet placed on solid plate with constant temperature, the Marangoni number is about 80 for a thermocapillary flow.

Since the thermocapillary flow was depend on the type of liquid, it is hard to be observed in the water. And, thermocapillary effect was determined by the contamination of the surfactant. For evaporating water droplet, Xu and Luo ^[46] researched for thermocapillary flow of it. And, it is because of two reasons. One was the thermal conductivities of the liquid as well as substrate. The other one was the ratio value between the radius of contact line in the droplet and the thickness of substrate.

2.5 The other models for droplet evaporation

Researcher have studied the process of evaporation for centuries by established their own models ^[20]. The evaporating rate of droplet was affected by the droplet diameter. In addition, the linear relationship has been proved by the diameter of liquid droplet and the pinned liquid evaporating droplet. For the liquid droplet with constant volume, the relationship has been studied as parabolic curve.

If the temperature in the spherical droplet is smaller than critical value and distributed evenly, both vapour phase and liquid phase achieved at condition of quasi-steady state. Besides, D^2 law is applied if the convection can be ignored , the diameter of droplet changing rate is a constant.

$$\frac{dD^2}{dt} = -K \quad (2.10)$$

where the evaporation K remain the unchanged value and time is expressed as t . However, this situation is limited and hard to achieve, and it is a special type of liquid evaporation.

Murisc and Knodic ^[25] concluded the model type at a slow evaporating rate, two types of evaporation of droplet had been defined: Lens model and non-equilibrium on one side model (NEOS).

For the Lens model^[25], one of the simplest model is isothermal droplet with the shape of sphere. The evaporation is only influenced by the vapour diffusion. So, the vapour diffusion is at quasi steady state and the evaporating is at equilibrium. To calculate the rate of the evaporation, a conductor with constant potential was used. If the effect of changing temperature is eliminated and evaporation flux is stable, Lens model can calculate for non-isothermal evaporation. For a heated substrate, the temperature difference is large and the interface between vapour phase and liquid phase cannot at equilibrium. Therefore, the Lens model cannot apply for a heated substrate.

For the vapour phase, if the molecules can only move because of diffusion, a model has been proposed. This model is analogy analysis of the evaporation flux together with electric field. In steady state, the evaporating rate of droplet was connected to the diffusivity of vapour phase ^[67,68]. Since the electrostatic potential and evaporation concentration are similar to each other, the flux of evaporation can be treated as electrostatic flux in order to solve problem. Hence, for the area around contact angle, the evaporation flux is:

$$j(r, t) \sim (r - l)^{-\lambda} \quad (2.11)$$

where the distance travelled from the center of droplet is expressed as l , the contact angle is expressed as θ , the radius of droplet is expressed as r and the time is expressed as t . if the value of contact angle was limited to 0, the value of λ is equal to 0.5. Therefore, the value of evaporating flux is large at the area close to the contact line. And, the reason of this phenomenon is higher possibility of evaporation at this area compared to the top cap of droplet.

For the NEOS model, the non-equilibrium situation has happened for interface between liquid phase and vapour phase ^[29]. NEOS model assumed the uniformly vapor distribution for all areas including infinity of droplet. So, the evaporation rate was defined as the molecules transfer across the liquid-vapour interface. Thus, the main factors affected evaporation rate are the liquid thermal diffusivities and the substrate thermal diffusivities. So, NEOS model can build the heated boundary data properly. The evaporation flux is

$$j \propto \frac{1}{h+k_L+k_S} \quad (2.12)$$

where the thickness of film is expressed as h , the heat transferring to the liquid is expressed as K_L and the heat transferring to the substrate is expressed as K_S .

For the experiment created by Murisic and Konic, the results of water evaporating from the Lens model was almost as same as the results from NEOS model. The only difference was the value from contact line. The NEOS model concluded the heat loss from evaporation was smaller than conduct of surface. While, the Lens model concluded the temperature at contact line was much smaller because of evaporation flux. For the alcohol evaporating process, the Lens model concluded the lower temperature at contact line. Sefiane et al ^[27] mentioned the evaporation of alcohol was volatility due to the larger Biot number. Two models have been supported from several experiments. The NEOS model was supported by Hu, Larson ^[13] and Girard ^[64,65]. They proved the temperature increasing from droplet center to contact line. And Ristenpart ^[24] recorded the temperature at some significant area, the result proved that the temperature gradient kept changing positive and negative value.

Furthermore, many models have been developed to explain the evaporating process. For instance, Maruyama built model which related the molecular dynamics to the process of

evaporation^[98]. And, the contact angle was same for both evaporation and condensation at equilibrium.

2.6 Statistical rate theory

Fang and Ward had studied the evaporation of two hydrocarbons in order to validate the credibility of SRT based expression in calculating liquid-vapor phase transition for other liquids. These hydrocarbons comprises differently shaped molecules, octane and methylcyclohexane. because of hydrocarbons' more volatile property than water with the same temperature, it allows us to study higher evaporation rates; though it is more difficult to determine the temperature at the interface in different phases. since the convective effects in the hydrocarbons is non-negligible, interface's temperature calculation has to be determined using a numerical procedure which is different from using water instead.^[27]

The results are showing predictions calculated based on SRT and the real measurements are highly consistent. The maximum difference between the prediction and measured result is only 1.0 °C at all phases. However the question of the essentialness of quantum mechanical description when it comes to describing the condition at the interface of an evaporating liquid also emerges.^[27]

One new method was raised by Duan et al.^[41] in 2007 to determine saturation vapor pressure $P_s(T)$, of water below its triple point conditions. In this new expression developed using SRT, the Pressure is used as a parameter for the net evaporation flux. in 50 different experiments, SRT were used to measure the interfacial conditions in both steady-state evaporation and condensation experiments in order to calculate $P_s(T)$. Liquid-vapor latent heat $L_{lv}(T)$ calculation expression was then developed using $P_s(T)$ values.

A series of studies are conducted with attempt to determine the validity of SRT

expressions for $L_{lv}(T)$. The results are showing a good agreement between predicted values and measurements.^[41]

2.7 Summary

In this chapter, the classical approach was studied. Evaporation condition is related to pressure and temperature. According to gases kinetic theory, the evaporation flux is defined as variances between the rate of molecular on the boundaries of liquid phase and vapour phase. Then, , Hertz-Knudsen formula equation was invented to evaluate the evaporation process. However, in this classical approach, coefficients were hard to determine their values. The research proved that the coefficients value were not constants and depended on experimental environment. Therefore, the classical theory was not accurate enough to describe the evaporation process.

Then, the literature about evaporation was studied. In the process of evaporation, the state of droplet contact angle was transforming follow various patterns. Three of them happened mostly: constant contact area, constant contact angle and constant angle with area. Besides, the temperature distribution of droplet was studied. The temperature of interface between liquid and vapour is decreased because of the energy transfer of vaporization. The contact angle was one factor of temperature distribution of droplet.

In addition, the flow pattern of convection and thermocapillary effect was studied in this chapter. It explained the evaporation process contact line by eliminating the effects of gravity factor and surface tension factor. The tension gradient of the surface would cause flow and the direction was from low tension gradient place to high tension gradient place.

Lastly, various models was introduced in this chapter. Murisc and Knodic^[25] concluded the model type at a slow evaporating rate, two types of evaporation of droplet had been defined:

Lens model and non-equilibrium on one side model (NEOS). And, SRT approach was introduced in this chapter. Since the SRT approach was not coefficient determined method, it was accurate enough to describe the evaporation process. The chapter 3 would introduce and evaluated the SRT expression for ethanol evaporation process.

Chapter 3: Application of SRT in droplet evaporation

3.1 SRT Expression for the rate of Evaporation

Statistical Rate Theory (SRT) was applied in this project to analysis the evaporation rate of the liquid of Ethanol.

First of all, a system with single-component has been built and the evaporation was at the state of steady. The liquid temperature is T^L , the liquid pressure is P^L , the vapor temperature is T^V , the vapor pressure is P^V . The liquid received the energy from surroundings to ensure that the temperature is T^L at the interface between liquid and vapor. Therefore, the evaporation flux expression was proposed.

3.2 An isolated system at an instant in time

Assume small unit of droplet and the liquid temperature is T^L . And, for the surface of droplet, the effect of adsorption was ignored.

For a single molecule, it is located at either the vapor phase or the liquid phase. Assume that both liquid and vapor phase are distributed uniformly and the thermodynamic properties remain the same for each unit of phases. Then, the phase depth is expressed as δL^a and the surface area is δA .

Assume the number of molecules in the vapor phase was N^L and the number of molecules in the liquid phase was N^V . Since it was a steady-state system, the temperature of vapor phase T^V was equal to the temperature of liquid phase T^L . So, the same variables from liquid phase and vapor phase should have same value since it is a steady-state system.

As a result, if all above assumption can be achieved, the evaporation rate of the small unit system was equal to the evaporation rate at the steady-state system at the instant time t . Thus, the expression of the evaporation rate of small unit system was valid and the same as expression at steady state system.

An isolated system was created by the small volume of droplet and the properties of this system was determined by steady-state system.

In statistical rate theory, thermodynamic equilibrium was an essential state for the isolated system [37, 39, 42]. According to the properties of isolated system, the pressure and the temperature at the final stage were represented as P_e^V , T^L . The pressure at the final stage P_e^V was not the pressure at the instant time P^V .

3.3 Rate of interfacial molecular transfer

For the equilibrium approximation, the unit system of entire system can be analysis independently. As the value of phase temperature from each unit indicated, the mechanical energies ΔE^α interval can be expressed as following: [43].

$$(\Delta E^\alpha)^2 = \overline{(\Delta E^\alpha)^2} - (\overline{\Delta E^\alpha})^2 \quad (3.1)$$

where $\overline{E^\alpha}$ is total average energy and it is as same as the internal energy of phase α , U^α . And, $\overline{(E^\alpha)^2}$ is the average of the energy square.

For each phase, the energy is

$$(\Delta E^\alpha) = \pm T^\alpha \sqrt{k C_V^\alpha} \quad (3.2)$$

where α is expressed the phase analysis, C_V^α is the specific heat of unit volume. Hence, the energy should stay in the interval of $U^\alpha \pm \Delta E^\alpha$.

The number of liquid phase molecules is N^L while the number of vapor phase molecules is N^V . For a unit system with the molecular distribution of λ_j , the energy range of unit system can expression as below where $u_v(\lambda_j)$ is unit state of system

$$1 \leq v \leq \Omega(\lambda_j) \quad (3.3)$$

The number of molecule from liquid phase travels to the vapor phase at the time t. Then, the molecular distribution λ_k

$$\lambda_k : N^L - 1, N^V + 1 \quad (3.4)$$

Assume $\Omega(\lambda_k)$ is represented the number of mechanical states in isolated system. Besides, $u_\epsilon(\lambda_k)$ is the number of the unperturbed mechanical states. Therefore, the expression below can be concluded for this situation

$$1 \leq \epsilon \leq \Omega(\lambda_k) \quad (3.5)$$

For the unit system, Schrödinger equation was applied to analyze the probability of transition at unit area from the difference of molecular distribution ^[37,39]. For one state, the molecular distribution is λ_j , and the molecular distribution of another state is expressed as λ_k . When the state is λ_j , the time at instant is defined as t. When time travel to the δt , the perturbation is applied for the isolated system. As a result,

$$K[\lambda_j(u_v), \lambda_k(u_\epsilon)] = \frac{(2\pi)|V_{v\epsilon}|^2 \zeta \delta t}{\hbar \delta A} \quad (3.6)$$

where the energy density is expressed as ζ at this state, the matrix element is expressed as $|V_{v\epsilon}|$

from the λ_j state to λ_k state. Define the value of $\hbar$ is equal to the Planck Number over 2π , then we will have

$$\delta t(\Delta E^L + \Delta E^V) \gg 2\pi\hbar \quad (3.7)$$

Therefore, for all unit system located at the interval $(\Delta E^L, \Delta E^V)$, the value of $K[\lambda_j(u_v), \lambda_k(u_\epsilon)]$ is a constant at all states^[37, 39].

At the time within the period of δt , the probability of the number of molecules travelling from λ_j state to λ_k state is expressed as $\tau[\lambda_j, \lambda_k]$.

$$\tau[\lambda_j, \lambda_k] = \frac{k_{LV}\Omega(\lambda_k)\delta A}{\Omega(\lambda_j)\delta t} \quad (3.8)$$

For the equation above, the Boltzmann entropy theory can be applied to it. So, the new expression is

$$\tau[\lambda_j, \lambda_k] = \frac{k_{LV}\delta A}{\delta t} \exp\left[\frac{S(\lambda_k) - S(\lambda_j)}{k}\right] \quad (3.9)$$

where the Boltzmann constant is expressed as k , the isolated system entropy is expressed as $S(\lambda)$ with the distribution of molecules λ .

For the move of molecules, it is not an one-way transport. The certain number of molecules would travel from vapor phase to the liquid phase. If the distribution of molecules is defined as λ_i , the expression of it:

$$\lambda_i: N^L + 1, N^V - 1 \quad (3.10)$$

The same analysis is applied to this situation, then the probability of the number of molecules travelling from λ_j state to λ_i state is expressed as $\tau[\lambda_j, \lambda_i]$.

$$\tau[\lambda_j, \lambda_i] = \frac{k_{VL}\delta A}{\delta t} \exp\left[\frac{S(\lambda_i) - S(\lambda_j)}{k}\right] \quad (3.11)$$

When the distribution of molecules varies from state λ_j to state λ_k , the quantity of the liquid molecules is

$$N^L(\lambda_k) - N^L(\lambda_j) = -1 \quad (3.12)$$

On the other hand, the quantities of vapor molecules also

$$N^V(\lambda_k) - N^V(\lambda_j) = 1 \quad (3.13)$$

For the state transformation from state λ_j to state λ_k , the isolated system entropy is expressed as below:

$$S(\lambda_k) - S(\lambda_j) = \sum_{i=L,V,R} [S^i(\lambda_k) - S^i(\lambda_j)] \quad (3.14)$$

where the reservoir is expressed as R . As mentioned above, the L , V and R are independent variables of the entropy. For this condition, it can apply Euler relationship.

$$S^i = \frac{H^i}{T^i} - \frac{\mu^i N^i}{T^i} \quad (3.15)$$

where the chemical potential is expressed as μ , the enthalpy of the system is expressed as H . For the unit system, when the distribution of molecules set as various value, the temperature remains the unchanged value at each phases as well as chemical potential. Thus, the number of molecules from unit system does not transfer to reservoir. Together with Eq. (3.15) and Eq. (3.14).

$$S(\lambda_k) - S(\lambda_j) =$$

$$\left(\frac{H^L(\lambda_k)}{T^L} - \frac{H^L(\lambda_j)}{T^L} \right) + \left(\frac{H^V(\lambda_k)}{T^V} - \frac{H^V(\lambda_j)}{T^V} \right) + \left(\frac{\mu^L}{T^L} - \frac{\mu^V}{T^V} \right) + \left(\frac{U^R(\lambda_k)}{T^L} - \frac{U^R(\lambda_j)}{T^L} \right) \quad (3.16)$$

For the reservoir, the pressure and the volume do not change in the unit system. When the molecule distribution from state λ_j to state λ_k , only single molecule transfer to the other phase.

For isolated system, the condition is defined as below

$$[H^L(\lambda_k) - H^L(\lambda_j)] + [H^V(\lambda_k) - H^V(\lambda_j)] + [U^R(\lambda_k) - U^R(\lambda_j)] = 0 \quad (3.17)$$

Apply Eq. (3.17) into Eq. (3.16),

$$S(\lambda_k) - S(\lambda_j) = \left(\frac{\mu^L}{T^L} - \frac{\mu^V}{T^V} \right) + \left(\frac{1}{T^V} - \frac{1}{T^L} \right) [H^V(\lambda_k) - H^V(\lambda_j)] \quad (3.18)$$

By introducing the number of molecules in each phase, the total enthalpy of each phase H may be expressed in terms of the enthalpy per molecule, h

After the discussion of the molecules number in each phases, the total enthalpy H is concluded from the enthalpy from each molecule which is expressed as h

$$H^i = h^i N^i, \quad i = L, V; \quad (3.19)$$

Apply Eq. (3.18) into Eq. (3.19)

$$S(\lambda_k) - S(\lambda_j) = \left(\frac{\mu^L}{T^L} - \frac{\mu^V}{T^V} \right) + h^V \left(\frac{1}{T^V} - \frac{1}{T^L} \right) \quad (3.20)$$

By same method, the change of entropy also can be analyze from the distribution from state λ_j to state λ_i

$$S(\lambda_i) - S(\lambda_j) = -[S(\lambda_k) - S(\lambda_j)] \quad (3.21)$$

And

$$S(\lambda_i) - S(\lambda_j) = -\left(\frac{\mu^L}{T^L} - \frac{\mu^V}{T^V} \right) - h^V \left(\frac{1}{T^V} - \frac{1}{T^L} \right) \quad (3.22)$$

Regarding to the analysis of change of distribution from state λ_j to state λ_i as well as state λ_j and state λ_i , the thermodynamic properties can derived in terms of the differences of entropy when the molecular distribution of unit system is defined as λ_j .

Apply Eq. (3.20) and Eq. (3.22) into Eq. (3.9) and Eq. (3.11), the probability of the single molecule which travelling from liquid phase to the vapor phase at any time is expressed as below

$$\tau[\lambda_j, \lambda_k] = \frac{k_{LV} \delta A}{\delta t} \exp \left[\left(\frac{\mu^L}{k T^L} - \frac{\mu^V}{k T^V} \right) + \frac{h^V}{k} \left(\frac{1}{T^V} - \frac{1}{T^L} \right) \right] \quad (3.23)$$

On the other hand, the probability of single molecule travelling from vapor phase to liquid phase at any time is expressed as below

$$\tau[\lambda_j, \lambda_i] = \frac{k_{VL}\delta A}{\delta t} \exp\left[-\left(\frac{\mu^L}{kT^L} - \frac{\mu^V}{kT^V}\right) - \frac{h^V}{k}\left(\frac{1}{T^V} - \frac{1}{T^L}\right)\right] \quad (3.24)$$

Therefore, for the number of molecules ΔN_{LV} , if the molecules remain at same number, the evaporation rate is derived from the properties of liquid phase and vapor phase. And, Δt is represented as the time needed for travelling from one phase to the other. When $\tau[\lambda_j, \lambda_i]$ keeps as a constant value, the product of $\tau[\lambda_j, \lambda_i]$ and Δt has relationship of proportional to ΔN_{LV} .

$$\Delta N_{LV} = K_{LV} \exp\left[\left(\frac{\mu^L}{kT^L} - \frac{\mu^V}{kT^V}\right) + \frac{h^V}{k}\left(\frac{1}{T^V} - \frac{1}{T^L}\right)\right] \Delta t \quad (3.25)$$

According to the Eq. (3.6)

$$K_{LV} = C \frac{(2\pi)^{1/2} |V_{v\epsilon}|^2 \zeta}{h} \quad (3.26)$$

where C is represented as proportionality constant.

Since Δt is limited, the flux of evaporation is

$$j^{LV} = K_{LV} \exp\left[\left(\frac{\mu^L}{kT^L} - \frac{\mu^V}{kT^V}\right) + \frac{h^V}{k}\left(\frac{1}{T^V} - \frac{1}{T^L}\right)\right] \quad (3.27)$$

In order to ensure the valid of equation above, the quantity of molecules is far smaller than the quantity of molecules from liquid phase and vapor phase

$$N^\alpha \gg \Delta N_{LV}, \quad \alpha = L \text{ or } V \quad (3.28)$$

According to the same method of analysis, the other directional process can be concluded. For this direction, it is defined as condensation rate.

$$j^{VL} = K_{VL} \exp\left[-\left(\frac{\mu^L}{kT^L} - \frac{\mu^V}{kT^V}\right) - \frac{h^V}{k}\left(\frac{1}{T^V} - \frac{1}{T^L}\right)\right] \quad (3.29)$$

3.4 Equilibrium exchange rate between the liquid and vapor phases

In isolated system, it has two parts: one is the small volume unit system, the other is the reservoir. Then, when total virtual entropy ($S^L + S^V + S^R$) arrive the maximum value, the system is at a state of thermodynamic equilibrium. Therefore, in order to thermodynamic equilibrium, the following conditions should achieve.

$$\frac{\mu_e^L}{T_e^L} = \frac{\mu_e^V}{T_e^V}, \quad \frac{1}{T_e^L} = \frac{1}{T_e^V} = \frac{1}{T^L} \quad (3.30)$$

where for all parameter at thermodynamic equilibrium circumstances, the subscript e is used to identify. In order to remain equilibrium of system, the temperature as well as molecular distribution are changed to new values. However, K_{LV} and K_{VL} keep unchanged value at the range of temperature and distribution. ^[47].

At the thermodynamic equilibrium, the small unit system and the reservoir is defined. Assume that λ_e is represented as the distribution of molecules, λ_f is represented as the molecular distribution from the liquid phase to vapor phase, λ_d is represented as the molecular distribution from the vapor phase to liquid phase. So, these notation are applied to the equilibrium situation, the expression is

$$S(\lambda_f) - S(\lambda_e) = \left(\frac{\mu_e^L}{T_e^L} - \frac{\mu_e^V}{T_e^V} \right) + h_e^V \left(\frac{1}{T_e^V} - \frac{1}{T_e^L} \right) \quad (3.31)$$

And

$$S(\lambda_d) - S(\lambda_e) = - \left(\frac{\mu_e^L}{T_e^L} - \frac{\mu_e^V}{T_e^V} \right) - h_e^V \left(\frac{1}{T_e^V} - \frac{1}{T_e^L} \right) \quad (3.32)$$

Therefore, $S(\lambda_f) - S(\lambda_e)$ item was eliminated in the equation as well as $S(\lambda_d) - S(\lambda_e)$. Also, K_{LV} and K_{VL} remain the unchanged value as constant. The evaporation rate expression at the equilibrium state is

$$j_e^{LV} = K_{LV} \quad (3.33)$$

And

$$j_e^{VL} = K_{VL} \quad (3.34)$$

at equilibrium, the evaporation rate from liquid phase to vapor phase is equal to the condensation rate from vapor phase to liquid phase. Thus, the following equation

$$K_{LV} = K_{VL} = K_e \quad (3.35)$$

where K_e is defined as the transfer rate from either liquid or vapor phase to the other phase.

For the circumstances discussed above, classical kinetic theory is introduced to calculate the rate of molecular travelling from vapor phase to surface between two phases. And, it is also applied to the rate of molecules from the surface to the liquid phase.

At equilibrium, P_e^V is represented as the pressure of vapor, m is represented as the mass of molecules. Then, the exchange rate of molecules from each phases at the equilibrium is introduced as following:

$$K_e = \frac{P_e^V}{\sqrt{2\pi mkT^L}} \quad (3.36)$$

Referring to the Eq. (3.30), the chemical potential from liquid phase is same as the one from vapor phase at the equilibrium. Then,

$$\kappa[P^L - P_\infty(T^L)] \ll 1 \quad (3.37)$$

where the isothermal compressibility is expressed as κ , the pressure of saturation vapor is expressed as $P_\infty(T^L)$, the temperature is expressed as T^L .

Therefore, if the liquid is compressible, a special state is applied to this equation and this state is named as reference state. Hence, for saturation condition, if it is the reference state, the expression has been modified as

$$\mu^L(T^L, P_e^V) = \mu[T^L, P_\infty(T^L)] + v_\infty^L [P_e^L - P_\infty(T^L)] \quad (3.38)$$

where the volume v_∞^L is represented the value at saturated liquid phase.

Assume the gas in vapor phase is ideally, the chemical potential expression can obtain by the reference state:

$$\mu^V(T^L, P_e^V) = \mu[T^L, P_\infty(T^L)] + kT^L \ln\left(\frac{P_e^V}{P_\infty}\right) \quad (3.39)$$

Apply Eq. (3.38) and Eq. (3.39) into Eq. (3.30),

$$P_e^V = \eta P_\infty(T^L) \quad (3.40)$$

where the expression of η

$$\eta = \exp\left(\frac{v_\infty^L}{kT^L} [P_e^L - P_\infty(T^L)]\right) \quad (3.41)$$

Thus, the expression of K_e

$$K_e = \frac{\eta P_\infty(T^L)}{\sqrt{2\pi m k T}} \quad (3.42)$$

To be conclude, the evaporation flux is Eq. (3.42). at the equilibrium. If so, the Eq. (3.35) is valid equation to apply. ^[49].

3.5 Expression for the evaporation flux

When the distribution of molecules in the system is λ_j , the net flux of the evaporation can be expressed as

$$j(\lambda_j) = j^{LV} - j^{VL} \quad (3.43)$$

Applying Eqs. (3.20), (3.22), (3.27), and (3.35), the expression can be modified to more complex as

$$j(\lambda_j) = \frac{K_e}{\Omega(\lambda_j)} [\Omega(\lambda_k) - \Omega(\lambda_i)] \quad (3.44)$$

For the expression above, it can briefly explain the reason of evaporation or condensation. At the instant time, the molecules distributed in the liquid phase may travel to the vapor phase at certain probability. On the other hand, the molecules distributed in the vapor phase can travel to the liquid phase at certain probability. Hence, the higher probability will dominant the process. If the more molecules travel to liquid phase compared to that to vapor phase, it is a condensation process. Otherwise, it is defined as evaporation process. [25]

Applying Eqs. (3.20), (3.22), (3.27), (3.29), and (3.43)

$$j(\lambda_j) = K_e \left\{ \exp \left[\frac{\mu^L}{T^L} - \frac{\mu^V}{T^V} + h^V \left(\frac{1}{T^V} - \frac{1}{T^L} \right) \right] - \exp \left[-\frac{\mu^L}{T^L} + \frac{\mu^V}{T^V} - h^V \left(\frac{1}{T^V} - \frac{1}{T^L} \right) \right] \right\} \quad (3.45)$$

The evaporation expression above is determined by the properties of phases. And, they present same value when the system in the state of steady-state.

3.6 Expressions for chemical potential and specific enthalpy

According to the research, the boundary of liquid-vapor interface is curve, the radius of droplet was related to the liquid pressure. If the shape of droplet is defined as spherical, the evaporation flux can expressed by Laplace equation

$$P^L = P^V + \frac{2\gamma^{LV}}{R_c} \quad (3.46)$$

where the radius is expressed as R_c and the surface tension is expressed as γ^{LV} .

Eq. (3.46) and Eq. (3.38),

$$\frac{\mu^L(T^L, P^L)}{T^L} = \frac{\mu[T^L, P^\infty(T^L)]}{T^L} + \frac{v_\infty^L}{T^L} \left(P^V + \frac{2\gamma^{LV}}{R_c} - P^\infty(T^L) \right) \quad (3.47)$$

For the ideal gas in the vapor phase, Born-Oppenheimer method and Boltzmann statistics were applied for the chemical potential. Then, the expression can be derived as below

[26, 43]

$$\frac{\mu^V(T^V, P^V)}{T^V} = -k \ln \left[\left(\frac{m}{2\pi\hbar^2} \right)^{3/2} \frac{(kT^V)^{5/2}}{P^V} \right] - k \ln(q_{vib}q_{rot}q_{elec}) \quad (3.48)$$

The partition of electronic function is

$$q_{elec} = g_e \exp \left(\frac{D_e}{kT^V} \right) \quad (3.49)$$

where the state degeneracy is expressed as g_e and the minimum of potential is expressed as D_e .

For the ideal circumstances, the partition function of vibration and rotation is

$$q_{vib} = \prod_{l=1}^{n'} \frac{\exp(-\Theta_l/2T^V)}{1 - \exp(-\Theta_l/T^V)} \quad (3.50)$$

$$q_{rot} = \left(\frac{2kT^V}{\hbar^2} \right)^{1.5} \frac{(\pi I)^{0.5}}{\sigma_s} \quad (3.51)$$

where the temperature of vibration is expressed as Θ_l , the degree of freedom is expressed as n' , the product of inertia is expressed as I , the vibration symmetry factor is expressed as σ_s .

By subtracting Eq. (3.48) from Eq. (3.47)

$$\begin{aligned} \frac{\mu^L(T^L, P^L)}{T^V} - \frac{\mu^V(T^V, P^V)}{T^V} &= \frac{v_\infty^L}{T^L} \left(P^V + \frac{2\gamma^{LV}}{R_c} - P_\infty(T^L) \right) - D_e \left(\frac{1}{T^L} - \frac{1}{T^V} \right) + \\ &k \ln \left[\left(\frac{T^V}{T^L} \right)^4 \left(\frac{P_\infty(T^L)}{P^V} \right) \right] + k \ln \left(\frac{q_{vib}(T^V)}{q_{vib}(T^L)} \right) \end{aligned} \quad (3.52)$$

For the enthalpy of single molecule in vapor phase, the expression can be derived from the function of partition^[43]

$$h^V = 4kT^V - D_e + k \sum_{l=1}^3 \frac{\Theta_l}{2} + k \sum_{l=1}^3 \frac{\Theta_l}{\exp(\Theta_l/T^V) - 1} \quad (3.53)$$

3.7 Expression for fluxes in terms of measurable variables

From Eqs. (3.27), (3.29), (3.42), and (3.43), the net evaporation rate is expressed as

$$j = \frac{\eta P_{\infty}(T^L)}{\sqrt{2\pi mkT^L}} \left(\exp \frac{\Delta S}{k} - \exp \frac{-\Delta S}{k} \right) \quad (3.54)$$

where

$$\Delta S = \left(\frac{\mu^L}{T^L} - \frac{\mu^V}{T^V} \right) + h^V \left(\frac{1}{T^V} - \frac{1}{T^L} \right) \quad (3.55)$$

And apply Eqs. (3.52) and (3.53),

$$\begin{aligned} \Delta S = k \left\{ 4 \left(1 - \frac{T^V}{T^L} \right) + \left(\frac{1}{T^V} - \frac{1}{T^L} \right) \sum_{l=1}^3 \left(\frac{\Theta_l}{2} + \frac{\Theta_l}{\exp(\Theta_l/T^V) - 1} \right) + \frac{v_{\infty}^L}{kT^L} \left(P^V + \frac{2\gamma^{LV}}{R_c} - \right. \right. \\ \left. \left. P_{\infty}(T^L) \right) + \ln \left[\left(\frac{T^V}{T^L} \right)^4 \frac{P_{\infty}(T^L)}{P^V} \right] + \ln \left(\frac{q_{vib}(T^V)}{q_{vib}(T^L)} \right) \right\} \end{aligned} \quad (3.56)$$

The equation above is the final outcome of SRT for the net rate of evaporation. The variable in the equation can be received from experiment.

Besides, the vibration characteristic temperature is

$$\Theta_l = \frac{(\text{vibrational frequency})}{k} \quad (3.57)$$

where ethanol molecules vibrational frequencies are 6.94879×10^{14} , 5.63023×10^{14} , 2.7426×10^{14} , 2.62016×10^{14} , 2.48642×10^{14} , 2.3395×10^{14} , 2.00986×10^{14} , 1.959×10^{14} , 1.65196×10^{14} , 8.04319×10^{13} , 5.2535×10^{14} , 2.7426×10^{14} , 2.39224×10^{14} , 2.07955×10^{14} , and 1.5088×10^{14} . Overall, SRT expression of evaporation process established and the following will apply this expression to analyse the ethanol droplet evaporation.

Besides, the expression from SRT method apply both overhanging and upright sessile type droplets. From the expression, it indicated that no parameter was related to the shape of

droplets. In SRT expression, all parameters were from the interface between liquid phase and vapor phase. Therefore, the evaporation expression derived from SRT works for both overhanging and upright sessile type of droplets.

3.8 Summary

In this chapter, SRT approach was studied and the SRT expression for ethanol evaporation process was evaluated. Firstly, an isolated system at an instant time was studied. For the single molecule, it is either located at vapor phase or liquid phase. Then, the rate of interfacial molecular transferred was studied. Therefore, the equilibrium exchange rate between the vapor phase and liquid phase can be determined. Therefore, the expression for the ethanol evaporation flux was imitated. Together with the chemical potential and specific enthalpy expression, the SRT expression for ethanol evaporation flux in terms of measured variables can be determined.

Chapter 4:Evaporation flux SRT Analysis

The objective of this experiment was to find out the SRT expression of evaporation for the ethanol droplet. Therefore, some variables were predefined with certain value. In this experiment, T^L , T^V , R_c and $\bar{J}$ were selected for predefined value. The value will discussed in the following experiment and respective experimental equipment did set up.

From the conclusion of previous two experiment, the evaporating area of droplet and the droplet volume can be measured in improved experiment. Together with property of Ethanol such as the density, the evaporation flux $\bar{J}$ had been determined.

4.1 Experimental Setup

In this experiment, several apparatus were applied for the better results. For copper rig, the 4mm diameter copper rig was chosen for this experiment. It was easier and more accurate to observe ethanol droplet by syringe pump. So, one syringe pump was installed on the top of rig in order to provide the ethanol droplet. At the bottom of copper rig, one controlled handle was implemented to move copper rig up and down. The most importantly, the Data Acquisition (DAQ) device was implemented and connect to the system in order to collect the data. Therefore, parameters like P^V , T^L , T^V , R_c and $\bar{J}$ was recorder and calculated for the experiment results analysis. Last but not least, one high speed camera also installed at the side of copper rig to provide the clear pictures of this experiment as shown in Fig. 4.1.

Figure 4.1: Experiment set up

In this experiment, the only point that data collected was located at the center of ethanol droplet. As Fig. 4.2,

Figure 4.2: The measured point in ethanol droplet

During the process of experiment, the Ethanol droplet was placed at the center of copper rig by a medical syringe with extra fine needle. The shape of droplet was confirmed as semi spherical. And, the Fig. 4.3 was captured by the camera used in this experiment. It was clear enough for this experiment. In this experiment, overhanging type droplet was chosen as the object of experiment. The droplet was controlled to half circle shape. Therefore, the expression derived from SRT can apply to this experiment also.

Figure 2.3: Image captured by the high speed camera

4.2 Experimental Procedures

In this experiment, all parameters data need to be collected properly and accurate enough for further analysis.

Therefore, the first step of experiment was to set desired temperature droplet. The temperature-controlled system was set for this experiment in order to provide the droplet with expected temperature. Second, the position of high speed camera was adjusted for several times so that the clearest and sharpest results can be captured. And, this step was important because the result only can be analyzed if the result was qualified for this experiment. The following step was to place a droplet of desired material, Ethanol in this experiment, on the center of substrate by a syringe. If the droplet was not place on the exact center of substrate, this step was repeated for better experiment result. Finally, the data was collected and checked for result.

After collection of first group data, the steps above need to repeat for several times to collect enough sets of data for experiment analysis. Then, computer software, *Mathmatica* , was installed for SRT method analysis. The following comparison with

measured and predicted vapour pressure, SRT expression term analysis and the impact of vapour pressure changes for evaporation flux.

4.3 Result and Discussion

In this experiment, the real pressure at vapour phase was measured by DAQ devices. In order to verify SRT method, the calculated pressure at same location was determined by same group parameters except pressure value. In order to achieve accurate results, the results from Hebin have been quoted and applied for analysis ^[49]. All parameters value are shown in Table 4.1.

Table 4.1: Experiments Results Sets

Exp. No.	T_l^L (°C)	T_l^V (°C)	$\bar{j}$ (g/m ² s)	R (mm)	P_{meas}^V (Pa)
EH1	8.5±0.03	8.8±0.03	3.5	3.97±0.03	2909±19
EH2	6.9±0.03	7.2±0.08	4.6	3.81±0.02	2535±9
EH3	6.6±0.05	7.0±0.08	5.7	3.58±0.02	2488±15
EH4	6.3±0.03	6.7±0.04	4.9	3.75±0.02	2371±16
EH5	4.4±0.03	5.7±0.03	6.2	4.12±0.03	2151±17
EH6	3.6±0.02	4.8±0.08	6.0	3.84±0.04	2128±8
EH7	3.0±0.03	5.1±0.07	6.1	4.03±0.02	2018±19
EH8	2.2±0.02	4.3±0.06	6.0	4.46±0.01	1985±18

As shown in table, 8 sets of experiment parameters were chosen for the further comparison analysis. Then, all measured pressure value and predicted pressure value are displayed as Fig. 4.4. P-m represented measured pressure with error bar while the predicted pressure is defined as P-c.

Figure 4.4: Measured and predicted pressure in various experiment sets

In this figure, the X-axis indicated the experiment index number while the pressure was shown as Y-axis value. However, it is not easy to judge the various between the measured pressure and predicted pressure. Therefore, another figure was decided to be analysed the pressure shown as Fig. 4.5.

Figure 4.5: Predicted pressure versus measured pressure

The X-axis is represented by the predicted vapour phase pressure value while the measured vapour phase pressure value describes the Y-axis. Besides, the graph of $y = x$ was displayed. So that, it is straight and clearly to show the results of various of predicted pressure and measured pressure.

For this experiment, the average difference between predicted and measured pressure was around 2.64%. Thus, the SRT method demonstrated agreement with the experiment results.

In order to better understanding of SRT approach, the magnitude of the SRT terms analysis was done for evaporation of ethanol droplet. At the molecular level, the entropy change leads to two terms change, named as phonon term and continuum term. ^[51] All values calculated for phonon term and continuum term was shown in Table 4.2.

Table 4.2: The values of phonon term, continuum term and evaporation flux from all experiment sets

Exp. No.	Phonon Term(g/m ² s)	Continuum Term(g/m ² s)	Evaporation Flux(g/m ² s)
EH1	-62.38	65.88	3.5
EH2	-63.54	70.14	4.6
EH3	-84.87	90.57	5.7
EH4	-85.04	89.94	4.9
EH5	-278.44	284.64	6.2
EH6	-258.50	265.3	6.8
EH7	-453.43	459.53	6.1
EH8	-455.99	461.99	6.0

The phonon term is

$$\frac{\Delta Sp}{k} = \left\{ 4 \left(1 - \frac{T^V}{T^L} \right) + \left(\frac{1}{T^V} - \frac{1}{T^L} \right) \sum_{l=1}^3 \left(\frac{\theta_l}{2} + \frac{\theta_l}{\exp(\theta_l/T^V) - 1} \right) + \ln \left[\left(\frac{T^V}{T^L} \right)^4 \frac{P_\infty(T^L)}{P^V} \right] \right\} \quad (4.1)$$

It mainly depended by the liquid and vapour interfacial temperatures. From the table, all phonon terms are negative value, which means energy contribution of ethanol molecular phone to the entropy at the temperature of liquid was smaller than at the temperature of vapour.

$$\frac{\Delta Sc}{k} = k \left\{ + \frac{v_\infty^L}{kT^L} \left(P^V + \frac{2\gamma^{LV}}{R_c} - P_\infty(T^L) \right) + \ln \left(\frac{q_{vib}(T^V)}{q_{vib}(T^L)} \right) \right\} \quad (4.2)$$

For the continuum term, it is represented by continuum effects and the liquid properties. From the table, all continuum terms indicated positive value. Besides, this term was lead the evaporation effect of ethanol droplet from liquid phase to vapour phase.

Figure 4.6: Phonon term and continuum term

As Fig. 4.6 shown, all phonon term in ethanol SRT expression led to condensation direction while all continuum term led to the evaporation process. Besides, the sum of phonon term and continuum term were value of the evaporation flux.

4.4 Summary

In this experiment, all parameters of ethanol droplet evaporation were collected under steady state equilibrium. The SRT expression of ethanol droplet evaporation has been verified by comparison the measured vapour pressure value and predicted vapour pressure value. As results, the SRT expression had a excellent agreement with the measured value. Besides, two terms, phonon term and continuum term was defined in SRT expression. The impact of two terms for evaporation process has been analysed. Furthermore, the SRT expression was applied for the impact of pressure change for ethanol droplet evaporation.

Hence, for improvement of experiment, more parameters can be analysed by SRT expression, such as vapour phase temperature, liquid phase temperature, radius and so on. Besides that, the comparison of various materials can be analysed for study of evaporation process in future.

Chapter 5: Parameters analysis through SRT approach

The evaporation results of experiment under steady state equilibrium are listed in Table 5.1. For temperature, the centerline temperature of droplet were measured and recorded. For vapor phase temperature, it performed a linear decrease to the interface between vapor phase and liquid phase. And, the interface temperature also reduced when the pressure at lower value.

The vapor phase is the one factor affecting the evaporation process. It can be calculated if the average evaporation flux is distributed evenly at the boundary interfaces where the evaporation process happened.

Table 5.1: Experiments Sets Data for SRT

Exp. No.	T_I^L (°C)	T_I^V (°C)	R (mm)	P_{meas}^V (Pa)
EX1	2.2±0.02	4.3±0.06	4.46±0.01	1985±18
EX2	3.0±0.03	5.1±0.07	4.03±0.02	2018±19
EX3	3.6±0.02	4.8±0.08	3.84±0.04	2128±8
EX4	4.4±0.03	5.7±0.03	4.12±0.03	2151±17
EX5	6.3±0.03	6.7±0.04	3.75±0.02	2371±16
EX6	6.6±0.05	7.0±0.08	3.58±0.02	2488±15
EX7	6.9±0.03	7.2±0.08	3.81±0.02	2535±9
EX8	8.5±0.03	8.8±0.03	3.97±0.03	2909±19

Data under various condition displayed in Table 5.1 above. From the table, the liquid phase interfacial temperature range is from 2.2 °C to 8.5 °C. While, the vapor phase interfacial temperature range is from 4.3 °C to 8.8 °C. The radius size were around 4 mm, which the minimum radius is 3.58 mm and maximum radius is 4.46 mm. In addition, the pressure were from 1985 Pa to 2909 Pa.

In order to study the evaporation process at steady state equilibrium for ethanol. The following subchapter discuss the effect of vapor-phase temperature at interface, liquid phase temperature at interface, the vapor phase pressure and the radius of the droplet. Other variables were controlled as constant value in order reduce the error in experiment.

5.1 Effect of vapor-phase temperature

For vapor phase temperature, the study focused on the temperature on from -1°C to 2.5°C with the step of 0.5°C . Other factors, such as liquid phase temperature, vapor phase pressure and droplet radius, were kept as constant value in order to apply SRT to calculate the evaporation flux. The relationship between the evaporation flux rate and vapor phase temperature display in figure below.

Figure 5.1: Evaporation flux under various vapor phase temperature

From the figure, the evaporation rate slightly decreased when the vapor interfacial temperature was increasing. In vapor phase, the enthalpy was increasing when the vapor phase temperature was increasing. For ethanol, increasing vapor phase interfacial temperature leads to higher energy gap. Thus, the molecules were escaped from liquid phase to vapor phase, the evaporation rate was decreasing slightly.

Compared various dataset under equilibrium, the evaporation flux had a trend to evaporation from condensation when the vapor phase interfacial temperature was increasing.

However, the evaporation flux was not always increasing with larger vapor temperature. Therefore, the impact of vapor phase interfacial temperature was one evaporation flux factor; but, the impact was not significant since the evaporation flux was increasing slightly.

5.2 Effect of liquid-phase temperature

For the liquid phase temperature, the study conducted in the same method except the temperature range from -1°C to 2.5°C with step of 0.5°C . As same as vapor phase temperature experiment, vapor phase pressure and radius of droplet kept as constant. The evaporation flux from the selected group display in figure below.

In the one dataset simulation, the evaporation flux was increasing when the liquid phase interfacial temperature was increasing. For instance, in dataset EX5, the evaporation flux was $4.32\text{ g/m}^2\text{s}$ when the liquid phase interfacial temperature was 5.2°C , which applied -1°C to original temperature. And, the evaporation flux was raising to $6.53\text{ g/m}^2\text{s}$ when temperature was 8.8°C .

Compared evaporation flux in various dataset under equilibrium, the impact of liquid phase interfacial temperature on evaporation flux was evaporation trend. Similar with vapor phase interfacial temperature, the evaporation flux had higher possibility with higher liquid phase interfacial temperature.

Figure 5.2: Evaporation flux under various liquid phase temperature

From the figure, it can be easily concluded that the liquid phase temperature changes affected the evaporation flux increase larger compared to the same condition at vapor phase temperature. As discussed, the phonon term in ethanol droplet behaves condensation process. Therefore, when the temperature of liquid was increasing, the absolute value of phonon term was decreasing. Then, the evaporation rate of ethanol was increasing. Besides, compared to the vapor phase interfacial temperature, the liquid phase interfacial temperature lead to the larger gap of evaporation rate change.

5.3 Effect of vapor-phase pressure

For vapor phase pressure study, the pressure range is from 1985Pa to 2909Pa and the variance to each vapour phase pressure is range from -300 Pa to 400 Pa with step of 100Pa. Meantime, the vapor phase temperature, liquid phase temperature and radius of droplet kept as constant. Therefore, the relationship between vapor phase pressure and average evaporation rate can be determined and displayed as figure below.

Figure 5.3: Evaporation flux under various pressure

From the figure, the trend of evaporation rate is as different as vapor phase temperature study and liquid phase temperature study. The evaporation flux was decreasing while the pressure was increasing. For EX5 as instance, The evaporation flux dropped from 25.08 $\text{g/m}^2\text{s}$ to -19.52 $\text{g/m}^2\text{s}$. This behaviour may because the entropy was changed. Since the pressure had higher value, the molecules escaping from liquid phase to vapor phase were required higher energy level. So, less molecules evaporated from liquid phase with higher pressure compared to lower pressure level.

Besides, compared evaporation flux in various dataset under equilibrium, the impact of pressure on evaporation flux had evaporation trend, which is similar to vaopr phase and liquid phase interfacial temperature. The evaporation flux had higher possibility to achieve higher level when the pressure value was increasing.

However, the parameters are dependable in this study. Although the vapor phase temperature was the only variable desired to change, the other parameters passively changed

as well. Overall, the average evaporation rate changed dramatically when vapor phase pressure changed.

5.4 Effect of the droplet radius

The radius of droplet is the factor of evaporation flux rate. As same analysis above, SRT method applied to radius of droplet analysis. The figure below indicated the relationship between the droplets radius and average evaporation flux. At the steady state equilibrium, the radius was around 1 mm in the experiment. For the SRT analysis, the radius changed from 10 millimeter to 1 nanometer. However, the shape of droplet, vapor phase temperature, liquid phase temperature and liquid phase pressure maintained as constant value. From the figure, the evaporation flux rate dropped to extreme small value in nano scale. Besides, the evaporation flux rate maintained as almost constant value when the radius of droplet changed to nanometre scale.

Figure 5.4: Evaporation flux under various radius size

As the droplet size shrinks, the surface tension term would increase. Before the radius is larger than the micro size, the temperature terms dominate. Accordingly, the average evaporation flux does not change much. However, as the droplet radius is further reduced, the surface tension term becomes significantly larger, and dominates the entropy change.

In addition, for the experiments at a higher vapor-phase pressure, the temperature jump is smaller, resulting in a higher average evaporation flux. Note that the surface area per volume liquid would increase if we can separate the volume liquid into droplets with a smaller size. We can find that both the evaporation flux and droplet surface area are larger with a decrease of the droplet size. Thus, the evaporation rate would increase, especially as the droplet is in the nano size.

5.5 Summary

The evaporation flux experiment of ethanol were validated and analyzed by SRT method. As discussed above, the study is focused on the factor of vapor phase temperature, liquid phase temperature, vapor phase pressure and radius of droplets. The larger temperature leads to a larger average evaporation flux. Compare vapor phase temperature and liquid phase temperature, the liquid phase temperature jump leads to a larger evaporation rate changes. For vapor phase pressure, the average evaporation flux rate is decreasing while the vapor phase pressure is increasing. If the pressure changed large enough, the evaporation process will change to condensation process as well. For radius of droplet, the behaviour has two states. At the first state, the evaporation flux rate drop dramatically when the radius reduced before nano size. At the second state, the flux rate is increasing slowly when the radius was decreasing at the nano size. This is because the surface area at the unit liquid volume was increasing so that the flux rate raised. In addition, the condition with higher vapor phase interfacial temperature,

higher liquid phase interfacial temperature and higher pressure under equilibrium, the evaporation flux has higher possible to be increasing.

Chapter 6: Conclusion and future work

6.1 Conclusions

In this project, the objective were to study the ethanol evaporation process by statistical rate theory (SRT). The evaporation of ethanol has been studied. The focus area was to comparison with measured vapour phase pressure and predicted vapour phase pressure. As the result of experiment, the error between measured and predicted value was around 2.64%. Therefore, the SRT expression described the process of ethanol droplet evaporation. Within the expression, two terms were analysed. The phonon term were always negative value while continuum term led to the positive value and they dominated the process direction. Besides, the impact of various parameters change were analysed in ethanol SRT expression. For the vapor and liquid phase interfacial temperature, the evaporation flux was increasing while the temperature was increasing. However, the liquid phase interfacial temperature led to larger jump of evaporation flux changes. For the pressure, the evaporation was decreasing while the pressure was larger value. Finally yet importantly, the evaporation flux was drop dramatically when the radius change in nano size scale. However, when the radius was large enough, the evaporation flux kept almost as constant.

6.2 Future work

For the future work, different materials, such as methanol, glycol and acetone, can be involved. First, the different material can analyse and compare the outcomes. As far as I know, the evaporation behaviour may different from materials. For instance, the phonon term in water lead to the evaporation direction. However, the phonon term in ethanol droplet behaved as condensation process. Therefore, more valuable results we may conclude from the comparison experiment.

Second, the data used in this report was below 10°C. The ethanol behaviour in around 25°C can be analysed and compared to the SRT expression also. For the various temperature set, the effects of various parameters can still be discussed and studied.

References

- [1]Duan, F., Crivoi, A. and He, B. (2010). "Thermal properties of deuterium oxide near the triple point predicted from nonequilibrium evaporation." *Journal of Chemical & Engineering Data*, 55(9), pp.3674-3679.
- [2]Y.-Y. Yan and T.-F. Lin, "Evaporation heat transfer and pressure drop of refrigerant R-134a in a plate heat exchanger," *Journal of Heat Transfer*, vol. 121, no. 1, pp. 4183–4194, 1999.
- [3]J. Park and J. Moon, "Control of colloidal particle deposit patterns within picoliter droplets ejected by ink-jet printing," *Langmuir*, vol. 22, no. 8, pp. 3506–3513, 2006.
- [4]S. Narayanan, J. Wang, and X.-M. Lin, "Dynamical self-assembly of nanocrystal superlattices during colloidal droplet evaporation in situ small angle X-ray scattering," *Physical Review Letters*, vol. 93, no. 13, 2004.
- [5]M. Teitel, D. Schwabe, and A. Y. Gelfgat, "Experimental and computational study of flow instabilities in a model of Czocharlski growth," *Journal of Crystal Growth*, vol. 310, no. 7-9, pp. 1343–1348, 2008.
- [6]H. K. Cammenga, *Evaporation mechanisms of liquids. Current topics in materials science v 5*, Amsterdam ; New York: North-Holland Pub. Co.,1980.
- [7]J. Barrett and C. Clement, "Kinetic evaporation and condensation rates and their coefficients," *Journal of Colloid and Interface Science*, vol. 150, no. 2, pp. 352–364, 1992.
- [8]J. Young, "The condensation and evaporation of liquid droplets in a pure vapour at arbitrary Knudsen number," *International Journal of Heat and Mass Transfer*, vol. 34, no. 7, pp. 1649–1661, 1991.
- [9]J. Young, "The condensation and evaporation of liquid droplets at arbitrary Knudsen number in the presence of an inert gas," *International Journal of Heat and Mass Transfer*, vol. 36, no. 11, pp. 2941–2956, 1993.
- [10]R. W. Schrage, "A theoretical study of interphase mass transfer." *New York:Columbia University Press*, 1953.
- [11]A. F. Mills and R. A. Seban, "The condensation coefficient of water," *International Journal of Heat and Mass Transfer*, vol. 10, no. 12, pp. 1815–1827,1967.
- [12]K. Wylie and R. S. Brodkey, "Transport phenomena at the liquid–vapor interface of mercury using a radioactive tracer," *Proceedings of the International Symposium on Two-Phase Systems*, pp. 195–206, 1972.
- [13]L. D. Koffman, M. S. Plesset, and L. Lees, "Theory of evaporation and condensation," *Physics of Fluids*, vol. 27, no. 4, pp. 876–880, 1984.
- [14]C. Cercignani, W. Fiszdon, and A. Frezzotti, "The paradox of the inverted temperature profiles between an evaporating and a condensing surface," *Physics of Fluids*, vol. 28, pp. 3237–3240, 1985.
- [15]R. Marek and J. Straub, "Analysis of the evaporation coefficient and the condensation coefficient of water," *International Journal of Heat and Mass Transfer*, vol. 44, no. 1, pp. 39–53, 2001.
- [16]Y. P. Pao, "Application of kinetic theory to the problem of evaporation and condensation," *Physics of Fluids*, vol. 14, no. 2, p. 306, 1971.
- [17]Y. P. Pao, "Temperature and density jumps in the kinetic theory of gases and vapors," *Physics of Fluids*, vol. 14, no. 7, p. 1340, 1971.
- [18]C. E. Siewert and J. R. Thomas, "Half-space problems in the kinetic theory of gases," *Physics of Fluids*, vol. 16, pp. 1557–1559, 1973.
- [19]J. W. Cipolla, H. Lang, and S. K. Loyalka, "Kinetic theory of condensation and evaporation ii," *Journal of Chemical Physics*, vol. 61, pp. 69–77, 1974.
- [20]Y. Onishi, "The spherical-droplet problem of evaporation and condensation in a vapor gas-mixture," *Journal of Fluid Mechanics*, vol. 163, pp. 171–194,1986.

- [21]K. Aoki and N. Masukawa, "Gas flow caused by evaporation and condensation on two parallel condensed phases and the negative temperature gradient: Numerical analysis by using a nonlinear kinetic equation," *Physics of Fluids*, vol. 6, pp. 1379–1395, 1994.
- [22]L. J. F. Hermans and J. J. M. Beenakker, "The temperature paradox in the kinetic theory of evaporation," *Physics of Fluids*, vol. 29, pp. 4231–4232, 1986.
- [23]D. Bedeaux, L. J. F. Hermans, and T. Ytrehus, "Slow evaporation and condensation," *Physica A*, vol. 169, pp. 263–280, 1990.
- [24]P. N. Shankar and M. D. Deshpande, "On the temperature distribution in liquid-vapor phase between plane liquid surfaces," *Physics of Fluids a-Fluid Dynamics*, vol. 2, pp. 1030–1038, 1990.
- [25]K. Hisatake, S. Tanaka, and Y. Aizawa, "Evaporation rate of water in a vessel," *Journal of Applied Physics*, vol. 73, pp. 7395–7401, 1993.
- [26]G. Fang and C. A. Ward, "Temperature measured close to the interface of an evaporating liquid," *Physical Review E*, vol. 59, pp. 417–428, 1999.
- [27]G. Fang and C. A. Ward, "Examination of the statistical rate theory expression for liquid evaporation rates," *Physical Review E*, vol. 59, pp. 441–453, 1999.
- [28]C. A. Ward and G. Fang, "Expression for predicting liquid evaporation flux: Statistical rate theory approach," *Physical Review E*, vol. 59, pp. 429–440, 1999.
- [29]C. A. Ward and D. Stanga, "Interfacial conditions during evaporation or condensation of water," *Physical Review E*, vol. 64, no. 5, 2001.
- [30]A. H. Persad and C. A. Ward, "Statistical rate theory examination of ethanol evaporation," *The Journal of Physical Chemistry B*, vol. 114, no. 18, pp. 6107–6116, 2010.
- [31]R. R. Mazzoco and P. C. Wayner, "Aqueous wetting films on fused quartz," *Journal of Colloid and Interface Science*, vol. 214, no. 2, pp. 156–169, 1999.
- [32]M. Potash Jr and P. C. Wayner Jr, "Evaporation from a two-dimensional extended meniscus," *International Journal of Heat and Mass Transfer*, vol. 15, no. 10, pp. 1851–1863, 1972.
- [33]K. Park and K.-S. Lee, "Flow and heat transfer characteristics of the evaporating extended meniscus in a micro-capillary channel," *International Journal of Heat and Mass Transfer*, vol. 46, no. 24, pp. 4587–4594, 2003.
- [34]P. C. Stephan and C. A. Busse, "Analysis of the heat transfer coefficient of grooved heat pipe evaporator walls," *International Journal of Heat and Mass Transfer*, vol. 35, pp. 383–391, 1992.
- [35]J. A. Schonberg, S. Dasgupta, and P. C. Wayner, "An augmented young-laplace model of an evaporating meniscus in a microchannel with high heat flux," *Experimental Thermal and Fluid Science*, vol. 10, pp. 163–170, 1995.
- [36]V. Sartre, M. C. Zaghoudi, and M. Lallemand, "Effect of interfacial phenomena on evaporative heat transfer in micro heat pipes," *International Journal of Thermal Sciences*, vol. 39, pp. 498–504, 2000.
- [37]H. Hu and R. G. Larson, "Evaporation of a sessile droplet on a substrate," *Journal of Physical Chemistry B*, vol. 106, pp. 1334–1344, 2002.
- [38]K. Sefiane, L. Tadrist, and M. Douglas, "Experimental study of evaporating water-ethanol mixture sessile drop: influence of concentration," *International Journal of Heat and Mass Transfer*, vol. 46, pp. 4527–4534, 2003.
- [39]K. Sefiane, "Effect of nonionic surfactant on wetting behavior of an evaporating drop under a reduced pressure environment," *Journal of Colloid and Interface Science*, vol. 272, pp. 411–419, 2004.
- [40]V. Dugas, J. Broutin, and E. Souteyrand, "Droplet evaporation study applied to DNA chip manufacturing," *Langmuir*, vol. 21, no. 20, pp. 9130–9136, 2005.

- [41] T. Kajiya, E. Nishitani, T. Yamaue, and M. Doi, "Piling-to-buckling transition in the drying process of polymer solution drop on substrate having a large contact angle," *Physical Review E*, vol. 73, p. 011601, 2006.
- [42] J. Fukai, H. Ishizuka, Y. Sakai, M. Kaneda, M. Morita, and A. Takahara, "Effects of droplet size and solute concentration on drying process of polymer solution droplets deposited on homogeneous surfaces," *International Journal of Heat and Mass Transfer*, vol. 49, pp. 3561–3567, 2006.
- [43] D. M. Anderson and S. H. Davis, "The spreading of volatile liquid droplets on heated surfaces," *Physics of Fluids*, vol. 7, pp. 248–265, 1995.
- [44] C. Poulard, O. Benichou, and A. M. Cazabat, "Freely receding evaporating droplets," *Langmuir*, vol. 19, no. 21, pp. 8828–8834, 2003.
- [45] C. Poulard and P. Damman, "Control of spreading and drying of a polymer solution from marangoni flows," *Europhysics Letters*, vol. 80, no. 6, 2007.
- [46] G. McHale, S. M. Rowan, M. I. Newton, and M. K. Banerjee, "Evaporation and the wetting of a low-energy solid surface," *The Journal of Physical Chemistry B*, vol. 102, no. 11, pp. 1964–1967, 1998.
- [47] G. McHale, H. Y. Erbil, M. I. Newton, and S. Natterer, "Analysis of shape distortions in sessile drops," *Langmuir*, vol. 17, no. 22, pp. 6995–6998, 2001.
- [48] G. McHale, S. Aqil, N. J. Shirtcliffe, M. I. Newton, and H. Y. Erbil, "Analysis of droplet evaporation on a superhydrophobic surface," *Langmuir*, vol. 21, no. 24, pp. 11053–11060, 2005.
- [49] E. F. Crafton and W. Z. Black, "Heat transfer and evaporation rates of small liquid droplets on heated horizontal surfaces," *International Journal of Heat and Mass Transfer*, vol. 47, pp. 1187–1200, 2004.
- [50] R. G. Picknett and R. Bexon, "The evaporation of sessile or pendant drops in still air," *Journal of Colloid and Interface Science*, vol. 61, no. 2, pp. 336–350, 1977.
- [51] P. G. de Gennes, "Wetting: statics and dynamics," *Rev. Mod. Phys.*, vol. 57, pp. 827–863, 1985.
- [52] R. D. Deegan, "Pattern formation in drying drops," *Phys. Rev. E*, vol. 61, pp. 475–485, Jan 2000.
- [53] M. E. R. Shanahan, "Simple theory of stick-slip wetting hysteresis," *Langmuir*, vol. 11, pp. 1041–1043, 1995.
- [54] C. Bourgesmonnier and M. E. R. Shanahan, "Influence of evaporation on contact-angle," *Langmuir*, vol. 11, pp. 2820–2829, 1995.
- [55] K. Sefiane and J. Cameron, "Modelling of heat and fluid flow during the evaporation of volatile drops on hot substrates," *Progress in Computational Fluid Dynamics*, vol. 6, pp. 363–370, 2006.