Optical and Thermal Techniques for Analyzing Evaporation of Methanol Sessile Droplet

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Abstract - An experimental apparatus is designed and realized in order to analyze the behavior of the kinetics and the dynamics of methanol droplet evaporation. Two experimental techniques are used. One is optical and relies on video recording and image processing and the other one is a thermal technique based on heat flux measurements with a heat flux sensor. The case of pure methanol, a more volatile liquid, seems to be more complicated and more intriguing than that of water. Indeed, for that case, the evaporation kinetics is very fast and instabilities appear during evaporation. 96% of the droplet volume evaporate in the first 61% of the droplet lifetime where the contact line is first pinned then the contact radius decreases sharply. The droplet contracts to form a smaller droplet with a higher contact angle. The capillary effects are substantial and produce instabilities. The remaining 4% of the volume evaporate in a second step lasting for 39% of the droplet lifetime with decreasing contact angle, height and contact radius until the drop disappears. The effects of the substrate temperature on the different stages of wetting and the physical mechanisms related to the evaporation of methanol have been identified and discussed. The use of optical method to evaluate the evaporation kinetics based on the elementary volume variation during evaporation showed its limits in the transient stage characterized by the flattening of the drop to form a liquid film and the appearance of instabilities in the liquid-gas interface. On the other hand, the thermal method showed its efficiency and validity in this stage for estimating the mass and heat transfer rate exchanged during all the process of evaporation.

Keywords: Droplet Evaporation, Methanol, Visualization, Heat Flux Sensor, Bond number.

1. Introduction
The evaporation of a sessile droplet has been the subject of growing interest in recent years because of its importance in many applications. This process is an important physics problem due to the complexity of the associated mechanisms: fluid dynamics, substrate physico-chemistry, heat and mass transfer. In this context, several studies have been carried out to analyze the evaporation of volatile fluid. Sefiane et al. [1] experimentally studied the evaporation of water-ethanol binary sessile drops on polytetrafluoroethylene (PTFE) in a controlled pressure environment. In the case of pure ethanol, results of the variations of contact angle, base radius and the drop volume as a function of time are presented. When evaporation occurs, the pure ethanol contact angle decreases continuously with time. At the end of the drop lifetime where a sudden jump in the contact angle is observed. This behaviour it explained by the decrease of the drop base radius. This is related to the depinning of the triple line. The drop volume for the pure substances is found to decrease continuously with time, a similar trend is observed for the drop base radius. Cheng et al. [2] studied the evaporation of microdroplets from water-ethanol mixtures on gold surfaces. The substrate used in the investigation was very smooth. Droplets of identical volumes (2 µL) from various compositions (0, 25, 50 and 75% and 100% by volume) were deposited and allowed to evaporate in the air under ambient conditions. The plot of the initial contact angle versus the composition shows an almost linear relationship. The process of evaporation of pure water or ethanol drops could be divided into two phases: pinning and shrinkage. In this investigation, different phases corresponding to different wetting behaviors of the water-ethanol mixtures were identified, the most important is at the beginning, where the water-ethanol mixtures showed an increase in the contact angle and a reduction of
the contact surface area and in the case of pure ethanol the drop volume and the contact angle decreased nonlinearly over time. Seifane et al. [3] studied experimentally the wetting behavior of water, methanol and water-methanol mixture on a smooth substrate. They investigated the influence of methanol concentration variation on wetting dynamics in an environment saturated with water vapor. From the three variables volume, base radius and contact angle \( \theta \), the behavior of the contact angle, \( \theta \), is the most remarkable. Pure water shows first a monotonic decrease of \( \theta \), then it remains constant (in fact, \( \theta \) remains constant for most of the droplet lifetime), whereas methanol exhibits a maximum. Bin et al. [4] carried out an experiment on the evaporating methanol droplet under different horizontal air velocities on Teflon substrate. The droplet shape evolution was investigated using optical techniques (camera) of DSA100 apparatus. The controlled air velocity is at temperature of 22°C (ambient and initial droplet). The contact angle and the base radius were recorded and the volume time evolution is deduced. It was observed that there were three distinct stages for all air velocities: the constant contact angle stage (CA), the constant contact based line stage (CR) corresponding to pinned triple line stage and the transition stage (TS) between CA and CR. In the CA stage, the contact angle is kept at its initial value. In the CR stage, the contact angle decreases from the initial contact angle. In the TS stage, the contact angle first increases to a max value and then decreases to the initial contact angle. Christy et al. [5] analyzed the flow field along the base of water-ethanol binary drops and their time evolution by particle image velocimetry (PIV). They deduced the existence of three distinct regimes. The first is a chaotic regime characterized by vortices that are driven by concentration gradients that occur during the preferential evaporation of ethanol. The second transition regime shows an exponential decay of vorticity with remaining vortices migrating to the triple line, accompanied by a peak of radial velocity along the base of the drop. Lastly, the third step is characterized by a radial flow towards the contact line, which corresponds to the induced evaporation flow, and is identical to the evaporation rate measured for drops of pure water. Zhong and Duan [6] studied the flow regimes and the deposition pattern by changing the concentration of ethanol in a water-ethanol mixture that contains nanoparticles of alumina. To visualize the different flows inside the drops, Particle Image Velocimetry (PIV) was used. Three distinct flow regimes have been revealed. Regime I, where vortices and chaotic flows transport particles in the liquid-vapor interface and promote particle aggregation formation. Regime II, where the aggregates move inward, induced by the Marangoni type flow along the free surface of the droplets. Regime III is dominated by the drying of the remaining water, and the particles circulate radially outwards by capillary flow effect.

It is clear that, besides the limited number of investigations on evaporation and dynamics of wetting of volatile drops, the reported results remain essentially descriptive of the direct observations of the phenomenon. In addition, the reliability of the techniques and instruments used to calculate the velocity field and the temperature profile (PIV, infrared camera) remains largely open to criticism. Further investigations are needed to clarify various aspects of this problem. The aim of this study is to identify accurately and analyze the various evaporation stages of a volatile liquid under the effect of heating the solid substrate. Two experimental techniques are used. One is optical and relies on video recording and image processing and the other one is a thermal technique based on heat flux measurements with a heat flux sensor. The coupling between the thermal and optical method is used to overcome the limit of the optical method in the transient phase where the drop is in the form of a liquid film with an unstable liquid-gas interface.

2. Materials and methods

2.1. Experimental protocol

An experimental apparatus is designed to study the evaporation of sessile drops under controlled operating conditions. The apparatus is instrumented with 2 cameras in order to record the droplet shape evolution from the side view and the top view and then determine the geometrical parameters. A heat flux sensor is also used to assess heat transfer rate between the substrate and the droplet. The apparatus consists of several devices that allow the control of the operating conditions, temperature, pressure and moisture content within a closed test cell represented by a cubic enclosure of 11.5 cm side, made of polyoxymethylene (POM) with Plexiglas walls.

The experiment starts with the alignment of the camera, the substrate and the cold light source on the same horizontal plane and then adjust the optical parameters of the lens for a good image quality. In a second step, we use as a reference a 1 mm diameter ball placed on the heat flow sensor and take a picture of it for a purpose of calibration for length measurements. Then, the ball is removed. After that, we cover the substrate with an aluminum sheet, 70 \( \mu \)m thick, using thermal grease to promote conductive heat exchange between the sensor and the substrate. The enclosure is then closed and the operating conditions inside the cell are controlled with the temperature controllers, the rheostat, the cooling system and the evaporator. It follows the operation of the drop deposition with the injection system. After recording the videos and logging the data.
The aluminum sheet is removed and replaced by a new one for the next experiment. The visualization results are treated with an image-processing tool to measure the dimensions of the drop and the contact angle.

2.2. Heat flux sensor technique

The heat flux measurement system consists mainly of a heating film (Figure 1-A) composed of micro-resistors of diameter 20 mm. Two tangential gradient heat flux meter sensor are stuck on both sides of the heating film (Figure 1-C). Each flux meter sensor has a thickness of 380 μm and a sensitivity of 1.55 μV. W^{-1}. m^2. and it is instrumented at its center by a thermocouple type T. Two thin copper plates with a thickness of 80 μm are used to increase the rigidity of the sensor (Figure 1-D). A thermal grease mixed with a copper powder is used to reduce the thermal resistance between the components of the device (Figure 1-B). This mixture is characterized by a high thermal conductivity.

The last stage, removable, corresponds to the test surface hosting the sessile droplet (Figure 1-F). The contact between the copper sheet (Figure 1 -D) and the solid substrate (Figure 1-F) is carried out with a thin layer of thermal grease with a thickness of about 100 μm ensuring good heat transfer. The test surface completely covers the flux meter. The solid substrate is the aluminum with a thickness of 70 μm. The anisotropy presented by the aluminum film does not translate into a deformation of the drop. Its axisymmetry has been verified. The heat transfer between the solid substrate and the copper sheet is ensured by a thermal grease (Figure 1-E).

2.3. Control of operating conditions

Just after the injection of the droplet, two systematic inspections are carried out. The first on the size of the volume injected and the second on circularity of the triple line at the time of the deposit of the droplet.

In our experiments uncertainties of the operating conditions are (Figure 2): ± 0.5°C for the temperature inside the cell, ± 2% for the humidity, ± 0.5 °C for the temperature of the solid substrate, the pressure inside the test cell ± 10^3 Pa, the volume injected is ± 0.1 μL for a measurement of 1 to 5 μL and ± 0.2 μL for a measurement of 10 μL.
2.4. Validation of thermal method

2.4.1 Droplet lifetime evaporation

The thermal technique is based on heat transfer rate measurement between the substrate and the droplet. Figure 3 shows the response of the heat flux sensor for water and methanol, respectively.

The heat transfer rate obtained from the sensor represents a gain which is the subtraction of the value of the heat transfer rate during each instant of the evaporation period and the density of the heat transfer rate indicated by the sensor when it is empty (without drop on the substrate) for similar operating conditions.

Table 1 summarizes the evaporation lifetime obtained by the two techniques: optical and thermal. The time recorded by the thermal method is slightly higher by 3 to 6s than that deduced by the optical technique. This confirms the ability of the thermal method to predict the end of the evaporation phenomenon where the size of the drop is very small compared to the optical visualization means. It is also from this method that we can determine the total evaporation time used to normalize the plots.

Assuming that the droplet is sufficiently small so that the effect of gravity is negligible, the shape of the droplet will be that of a spherical cap. The volume variation is given by: [7]

\[
\frac{dV}{dt} = -\frac{\pi R D (C_{\text{sat}} - C_{\infty})}{\rho} \frac{g(\theta)}{(1 + \cos \theta)^2}
\]

Where \( V \) is the droplet volume, \( R \) is the droplet base radius, \( D \) is the diffusion coefficient of vapour in the air, \( \rho \) is the density of the fluid, \( C_{\text{sat}} \) is the vapour concentration at the interface, \( C_{\infty} \) is the vapour concentration far from the interface, \( \theta \) is the contact angle and the function \( g(\theta) \) is given by: [7]

\[
g(\theta) = (1 + \cos \theta)^2 \left[ \tan \left( \frac{\theta}{2} \right) + 8 \int_0^\infty \frac{\cosh^2 (\theta \tau) \tanh[\tau (\pi - \theta)]} {\sinh(2\pi \tau)} d\tau \right]
\]

The lifetime \( t_{CR} \) of a droplet evaporating in the Constant Radius (CR) mode is given by:

\[
t_{CR} = \left( \frac{2(1 + \cos \theta_0)^2}{\sin \theta_0 (2 + \cos \theta_0)} \right)^{2/3} \int_0^{\theta_0} 2d\theta \frac{g(\theta)}{g(\theta)}
\]

Where \( \theta_0 \) is the initial contact angle.

and the lifetime \( t_{CA} \) of a droplet evaporating in the Constant Angle (CA) mode is given by:

\[
t_{CA} = \left( \frac{2(1 + \cos \theta_0)^2}{\sin \theta_0 (2 + \cos \theta_0)} \right)^{2/3} \frac{\sin \theta_0 (2 + \cos \theta_0)}{g(\theta_0)}
\]
2.4.2. Heat transfer rate

Heat transfer rate calculated by the optical technique is based on the evaporation flux, which is evaluated from time variation of the droplet volume by using a linear second order approximation. The quantity of heat exchanged $Q_1$ between the drop and the solid substrate:

$$Q_1 = \rho \frac{dV}{dt} L_v$$

(5)

$L_v$: The latent heat of evaporation.

The comparison between the optical and thermal techniques of the variation of the heat transfer rate exchanged instantaneously between the drop and the solid substrate for the two liquids water and methanol is represented by the figures 4-a and 4-b, respectively. A 4% mean deviation between the two methods is depicted in the case of water. For the case of methanol, it is observed quite large deviation when the drop shrinks and forms a smaller droplet. The flux sensor measures at the same time the heat transfer induced by the drop and the heat transfer by conduction and convection on the free surface of the flux sensor around the drop. The beginning of the signal corresponds to a stationary mode without drop. Then the drop is deposited on the surface of aluminum. Three stages are observed during all the phase of evaporation. The first stage is transient and it is presented on the curve by an abrupt increase in the heat transfer rate and it justified by the warming of the drop. The second stage is characterized by a horizontal plateau of the heat flux, which corresponds to a constant kinetics of evaporation. In the third stage, the heat flux decreases sharply until reaching the initial value. This last stage corresponds to the evaporation of the last traces of liquid present on the surface. Unlike optical measurements, which are not possible until the last traces of liquid.

Figure 4-b shows a comparison of the heat transfer rate assessed by the two techniques for an initial volume of a drop of water varied from 1 to 10 μL. The heat transfer rate presented is the average flux recorded by the flux sensor in stage 2 (horizontal plateau) multiplied by the exchange section between the drop and the solid substrate. In terms of appearance, a linear dependence is observed as a function of the wetting radius deduced and a very good agreement is registered between the two techniques.

For the case of methanol, the variation of the volume in figure 3-b is not governed by a linear law, which makes the accurate computation of the heat transfer rate between the drop and the substrate by means of the optical method difficult (Figure 4-c) and especially in the presence of an instability of the liquid-gas interface (hypothesis of the symmetry of the drop is not verified).

**Table 1: Comparison between the two optical and thermal techniques of the droplet lifetime, Substrate temperature =25°C.**

<table>
<thead>
<tr>
<th>Volume (μL)</th>
<th>Water</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>lifetime by optical method (s)</td>
<td>817</td>
<td>94.5</td>
</tr>
<tr>
<td>lifetime by thermal method (s)</td>
<td>820</td>
<td>97</td>
</tr>
<tr>
<td>lifetime by the model of Stauber et al. (s) [7]</td>
<td>752</td>
<td>82</td>
</tr>
</tbody>
</table>

**Fig. 3:** Lifetime of evaporating droplets, Substrate temperature =25°C, $V_{\text{initial}}=1\mu$L, (a) Water, (b) Methanol.
3. Results and discussion

Results are presented for a pure methanol droplet of 1 µL initial volume deposited on Aluminum substrate under cell temperature of 25 °C, atmospheric pressure of 1 atm and a relative humidity of 50%.

Videos are recorded for each droplet. Then, an image-processing tool is used to capture the shape of the droplet at different instants. Figure 5 illustrates the evolution of the droplet shape for both 25°C (a) and 40 °C (b). Figure 6 exhibits the evolution of the geometrical parameters: contact angle and base radius (a), droplet height (b) and volume (c), for methanol droplet, the transition period is evidenced by the sharp increase of the contact angle (Figure 6a) and the drop height (Figure 6a), and an abrupt decrease of the contact radius (Figure 6b).

The case of methanol seems to be complex as it is shown and the evaporation of methanol can be divided into two stages according to the variation of the volume (Figure 6-c):
- The first stage is characterized by a fairly fast kinetics that lasts 61% of the life of the drop where 96% of the volume has evaporated, while the contact angle and the height of the drops decrease and then increase sharply to form a peak.
- The second stages is characterized by slower kinetics than the first phase, it lasts 39% of the time and only 4% of the volume evaporates.

The evaporation dynamics is characterized by the presence of three phases according to the variation of the contact angle:
- The first stage occupies about 40% of the life of the droplet with a pinned contact line and decreasing contact angle until the drop takes the shape of a liquid film. During this first period, 81% of the volume of the drop evaporates.
- The second stage is characterized by the flattening of part of the droplet or all of it to form a liquid film.
- The third stage begins with a sudden contraction of the drop to form a small droplet with an increase in its height and contact angle of an order almost equal to the initial contact angle. The evaporation kinetics of the new droplet is much slower since it lasts for nearly 39% of the droplet lifetime despite its low volume. The new droplet, representing 4% of the initial volume, evaporates at slightly decreasing radius and diminishing contact angle.

The effect of heating of the solid substrate is characterized by the figures 6 for two temperatures of heating (25 and 40°C) and an initial volume of 1 µL. No considerable change in the behavior of the methanol except that with 40°C the kinetics of evaporation is 4.7 times faster than the case tested at 25 °C and the initial height of the new drop created after the contraction of the drop of methanol at 40 °C is lower than that created at 25 °C. The estimation of the volume variation in the transient phase of figure 6-c by the optical method is very difficult in the presence of instability of the liquid-gas interface and the flattening of the drop to form a very thin liquid film. In this case the thermal method will find its place by the following relation:

\[
\frac{dV}{dt} = \frac{Q_2}{\rho L_v}
\]  

Fig. 4: Heat transfer rate transmitted between the drop and the solid substrate measured by the two methods (thermal and optical), Tsubstrate = 25°C.
Where $Q_2$ is the heat transfer rate measured by the thermal method.

Analysis of the behavior of methanol for a Bond number greater than 1 (volume of 10 µL) and less than 1 (volume of 1 µL) shows the same trend for both volumes with a transition zone led to significant instabilities (Figure 7). On the other hand, the study of the evolution of the h / 2R ratio (height / 2x base radius) seems more significant where the beginning of the transitional phase; between the pinned phase of droplet and the phase of contraction; begins for the two volumes studied by an almost constant h / 2R ratio of 0.03 ± 0.01 (Figure 8).

![Figure 6: Influence of the solid substrate temperature on the geometrical properties of a Methanol, V_{initial}= 1µL.](image)

![Figure 7: Substrate temperature effect on the evolution of the Bond number, V_{initial}= 1µL.](image)

![Figure 8: Substrate temperature effect on the evolution of h/2r ratio, V_{initial}= 1µL.](image)

**4. Conclusion**

Experiments were performed for studying the kinetics and the dynamics of methanol droplet evaporation in a well-controlled environment with respect to temperature, pressure and humidity. Experimental results obtained with optical and thermal methods showing the dynamic wetting behaviour of the methanol drop are presented.

The kinetics of evaporation of methanol is summarized in two stages: the first is fast where almost the totality of the volume evaporates, while the second phase is slow for a very small volume of the drop.

According to the variation of the contact angle, the dynamics of evaporation is summarized in three stages.
- The first stage is characterized by a pinned contact line with a decrease in the contact angle.
- The second stage is characterized by the creation of a liquid film in the presence of instabilities of the interface liquid-gas.
- The third stage starts with the contraction of the drop to form a small droplet.

The coupling between the thermal method and optics enabled us to calculate with more precision the droplet lifetime and allowed us to follow the kinetics of evaporation where the drop is almost invisible in the third phase of evaporation.
References