Measuring the local and global evaporation rate of fast evaporating droplets with interferometry

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Abstract In the current work, digital holographic interferometry is used to measure the refractive index field surrounding evaporating droplets. From this measurement, several key quantities can be extracted. These are the vapour mole fraction distribution surrounding the droplet, the temperature and local evaporation rate all along the interface of the droplet and finally, the global evaporation rate. All these measurements can be extracted from a single image. This novel technique is applied to an evaporating pending droplet deposited on a silicon wafer. As the chosen liquid (HFE-7000) has a very heavy vapour, the resulting vapour plume is shown to be heavily modified due to natural diffusion. This convectional motion is here shown to boost the total evaporation rate by a factor 4. This work was recently published in Langmuir [6].

1. Introduction

Evaporating sessile droplets occur in many industrial applications such as inkjet printing, DNA handling [9] or spray cooling [8]. What is often of interest for these applications is the so-called ‘coffee-stain’ effect which was described in detail by Deegan et al. [5]. They showed that the origin of the effect is due to the non-uniformity of the local evaporation rate along the droplet interface. In fact, this quantity was theoretically found to diverge close to the contact line (e.g. [5,15,22]). This crucial parameter was also used in order to assess the dominant direction of the Marangoni flow inside the droplet [23].

However, up to this point, only three papers (using three different experimental methods) have appeared to our knowledge that have measured the local evaporation rate experimentally. Dhavaleswarapu et al. [7] used micro-piv to measure the mass loss when approaching the contact line following the measurement at a couple of different heights and several points along the interface. As this approach is very time-intensive, only very slowly evaporating drops were investigated. In addition, they did not obtain the local evaporation rate along the entire interface. As a result, they did not integrate the local evaporation rates to obtain the global evaporation rate and validate this with an independent measurement. Ghasemi and Ward [11] used micro-thermocouples to measure the temperature gradients on both sides of the interface at several locations. Solving a heat balance at the interface then allows to extract the local evaporation rate. However, this approach is very intrusive which can possibly affect the measurements and again only allows to study very slow processes. Finally, Girard et al. [12] used a regular infrared camera to extract interfacial temperatures. Solving a simplified heat balance taking into account only heat conduction in the liquid phase and neglecting temperature effects in the solid, then allowed extraction of the local evaporation rates. As will be shown, such stringent restrictions are not necessary for the experimental procedure presented here.

Measuring the vapour concentration field surrounding evaporating droplets has been performed with several different techniques in the past. Laser induced fluorescence and phosphorescence is a tested technique (e.g. [1,3,13]) and also Fourier Transform Infrared Absorption (FTIR) has been used to that end [18]. However, these techniques have not yet been able to yield the required resolution near the liquid interface so as to yield a measurement of the local evaporation rate. Previously, interferometry was also used to measure the vapour concentration field surrounding an evaporating droplet [25] and here also interfacial temperatures could be extracted from the measurement of the vapour concentration at the interface. However, the authors did not continue to measure the local evaporation rate nor extract the global evaporation rate from these measurements. In the present contribution, we will revisit this technique and show that it is now capable of delivering much more information about the evaporating drop.
2. Experimental Setup and Image Processing

For the experiment, a simple Mach-Zehnder interferometer is used such as the one shown in Figure 1. A droplet of 3M™ Novocur™ HFE-7000 is deposited underneath a silicon wafer. This hanging droplet (the black object in the shown raw image) is left to evaporate in the ambient air, while shielding it from draughts. Before the deposition of the drop, the interferometer is set to generate a homogeneous system of vertical fringes. At this time a first image is acquired, which is used as a pixel-wise calibration for which the refractive index is known to be homogeneous and equal to that of pure air. Then the drop is deposited and the fringes are distorted by the presence of the vapour cloud surrounding the droplet, which itself appears black in the image. This image is analysed to yield the phase shift at each pixel by the Fourier Transform Profilometry algorithm described by Takeda in [24]. This phase is then compared to the reference phase obtained for that pixel in the previously mentioned reference/calibration image (as in [19]). This then yields the total phase shift for that pixel. However, the information obtained in this way is 'wrapped', which means that the phase shift image ranges from 0 to 2\( \pi \). Next step is the so-called 'unwrapping' of this image by the algorithm described by Herraez et al. [14] resulting in a map of the total phase shift for each pixel.

This phase map is proportional to the optical path length difference between the object and the reference beam. In order to convert this into a refractive index field, a tomographic reconstruction step is required as our measurement has integrated the local refractive index field along a line of sight. As the present subject is axisymmetric, this reconstruction can be done based on a single image and using the inverse Abel transform (e.g. [4]). Inherent to this transform is a certain augmentation of the noise, especially near the symmetry axis. As such, many of the algorithms proposed over the years (such as in [20]) add a certain filtering capability to alleviate these problems. We have implemented three different algorithms in order to ascertain which one could give the best results in our particular case: the three-point Abel transform method by [4], the Modified Fourier-Hankel (MFH) method by [20] and the Even-Power (EP) method by [10]. The preliminary scan of these three algorithms has shown that all methods give essentially the same results. However, with the aim of extracting local gradients, the smooth result from the EP-method is preferred for the present work.

The final step is then to transform this 3D refractive index field into the vapour concentration field \( \chi \). From the Lorentz-Lorenz equation (e.g. [2,21]) and the analysis in [6], we can find that

\[
\chi = \frac{1}{(n_{\text{HFE}}-n_{\text{air}})_{\text{air}}} \frac{T}{T_{\text{amb}}} \left[ \Delta n - \left( n_{\text{air,amb}} - 1 \right) \left( \frac{T_{\text{amb}}}{T} - 1 \right) \right],
\]

where now \( \chi \) is the mole fraction of HFE-7000 vapour in the gas mixture, \((n_{\text{HFE}}-n_{\text{air}})_{\text{air}}\) is the difference in refractive index of pure HFE-7000 vapour and of pure air both at ambient temperatures (or more specifically at the initial temperature) and \( \Delta n \) is exactly the refractive index difference field obtained from the inverse Abel transform detailed above. In general, there are 2 unknowns in this single formula: the local temperature \( T \) and the local vapour concentration \( \chi \) and there is no additional relation between these two variables that allows us to close the system and obtain both variables in the entire vapour cloud. However, because the impact of concentration changes on the refractive index field is more pronounced than of the smaller temperature variations, we simply put \( T/T_{\text{amb}}=1 \) in the above formula. In this way, we find a simple proportionality relationship between \( \Delta n \) and \( \chi \). A posteriori we have calculated that neglecting the temperature influence introduces at most an error of 3% in the present vapour mole fraction fields.

However, at the droplet interface there is a second relation between mole fraction and temperature when assuming chemical equilibrium, this is the known saturation-pressure data (or simply the Clausius-Clapeyron relation). Therefore, at the liquid interface, the effect of temperature variations on the refractive index field...
does not need to be neglected but can be determined simultaneously with the interfacial mole fraction. These measurements of interfacial temperature will also be shown in the next section.

Next step in the processing of the data is the extraction of the local evaporation rate. To this end, one also needs to calculate the local gradient of the mole fraction along a normal to the droplet interface so as to be able to measure the local evaporation rate $J_{surf}$ through the following formula:

$$J_{surf} = -\frac{M_v P_{sat} D_v}{RT(1-\chi_\sigma)} \frac{\partial \chi_\sigma}{\partial n}$$

with $M_v$ the molar weight of the vapour (0.2 kg/mol), $P_{sat}$ the total (atmospheric) pressure, $D_v$ the diffusion coefficient of the vapour-air mixture ($8.11 \times 10^{-6}$ m$^2$/s) obtained by independent Stefan-tube experiments, $R$ the universal gas constant (8.31 J/molK), $T$ the temperature, $\chi_\sigma$ the mole fraction at the interface (see above) and $\frac{\partial \chi_\sigma}{\partial n}$ the normal mole fraction gradient at the interface. As spatial variations of the gas pressure are expected to be thermodynamically negligible, we take $P_{sat}=P_{amb}$ and $T=T_{amb}$.

Finally, from our images there are three ways to determine the global evaporation rate. The simplest one is simply measuring the evolution in time of the droplet interface from its shadow. As this is a standard way of measuring the global evaporation rate, it will be used as the validating measurement here. The second approach is by integrating the above-determined local evaporation rates over the surface of the drop. As the normal gradient at the contact line is eventually infinite and because the profile fitting of the drop is subject to some uncertainty, a third method using the iso-concentration lines was also developed to avoid this source of imprecision. Although the derivation of the formula is not performed here (this is done in [6]), it turns out that the integration of a pseudo-local evaporation rate along an iso-concentration line also leads to the correct global evaporation rate (but not to a correct local evaporation rate, mind you). In essence, the above-formula for $J_{surf}$ is calculated now along an iso-concentration contour and integrated. A clear advantage of this approach is that the estimation can be performed at multiple iso-concentration lines and averaged in order to obtain a more accurate measurement. Additionally, this approach can even be performed when the liquid interface is not clearly visible (too small or too flat) or when the resolution/precision near the interface is not large enough (such as is the case for PLIF measurements due to the halation effect). An advantage of both vapour-based techniques with respect to traditional measurement techniques based on backlighting or gravimetric methods is that both of the vapour-based global evaporation rate measurement techniques are instantaneous and do not require time-differentiation.

3 Results and discussion

3.1 Global vapour cloud configuration

In Figure 2, the measured concentration field surrounding the evaporating droplet is shown together with two iso-concentration lines. This configuration is completely different from the pure diffusional field anticipated which would yield circular isoconcentration lines centred on the droplet centre. This is due to the presence of natural convection which makes the heavy vapour mixture at the interface (approximately 4 times heavier than regular air) fall down in a plume. While the presence of such convection in the vapour phase could be neglected in many of the papers dealing with evaporating droplets (e.g. [5]), it nevertheless is important for droplets with heavy vapours ([16-17]) where it can significantly enhance the global evaporation rate. In the present configuration, we have also found that the global evaporation rate is increased by a factor 4 for a droplet of 2mm radius and we will show for the first time what the influence is on the local evaporation rate distribution.
Figure 2: Vapour mole fraction field surrounding the droplet. This figure is adapted from [6].

3.2 Interfacial temperature

Figure 3: Measured interfacial temperature as a function of non-dimensional radial position.

In Figure 3, the measured interfacial temperature is shown as a function of the non-dimensional location $r$ for a droplet with radius 1.81mm. This goes from the center of the drop ($r=0$) up to the contact line ($r=1$). Error estimations are coming from repetitions and denote a 95% confidence interval. This shows that the temperature is much smaller in the center of the drop than at the contact line. At the contact line this temperature should in theory go back to the ambient temperature (i.e. 24°C) due to the good conductivity of the substrate but experimentally this is not recovered. However, as is demonstrated in [6], this is probably a limitation of our tomographic reconstruction technique which smooths out the large gradients present at the contact line and is hence underestimating the concentration at the contact line. When going further away from the contact line, the interfacial temperature drops sharply due to the fact that the necessary heat supply through the liquid phase becomes more difficult.
This sharp drop in interfacial temperature leads to a very intense change in interfacial tension along the droplet interface. This creates a so-called Marangoni flow inside the droplet. Numerical simulations not shown here, have demonstrated that this Marangoni flow can reach velocities inside the droplet of up to 5 cm/s. This speed is so large, it even has a marked impact on the convection of the vapour cloud. As the interfacial motion is directed towards the cold point (i.e. the centre) and the general motion in the vapour cloud is also in this direction, the Marangoni flow leads to an acceleration of the vapour evacuation and hence an intensification of the evaporation rate, which numerically was shown to be up to 30%.

### 3.3 Local evaporation rate

![Graph showing local evaporation rate as a function of non-dimensional radial position.](image)

**Figure 4:** Measured local evaporation rate as a function of non-dimensional radial position.

The local evaporation rate measurement is shown in Figure 4. This shows indeed that the local evaporation rate increases dramatically when approaching the contact line. This together with the larger area associated with the contact line with respect to the centre of the drop, leads to a significantly larger evaporation rate for the contact line region than for the centre of the drop. We remark here that the local evaporation rate is not seen to diverge for $r$ going to 1 as is theoretically the case for the pure diffusion regime (see e.g. [5,22]). But again this is expected, due to the tomographic reconstruction step which smooths out the large gradients expected in that case. Note that this measurement can also easily be transformed into a local heat removal rate by multiplying with the latent heat. Possibly neglecting the heat supply through the vapour, it is then possible to simulate numerically the mass and heat transport inside the droplet. This is important in order to estimate the deposition pattern present inside the droplet, or the thermal load on the substrate.

### 3.4 Global evaporation rate

Ideally, we would like to validate directly the local evaporation rates measured above. However, the three techniques discussed in the introduction which have previously been used to measure these rates are difficult to implement and require set-up modifications and expensive equipment. As a result, the only validation that could be obtained in the present framework is by comparison of the measured global evaporation rates with respect to an independent measurement of the evolution of the projected shadow of the droplet $J_{g,shadow}$. This comparison is shown in Figure 5. For the side view shadow measurement, the derivative with respect to time was taken and averaged over multiple images (up to 30). Nevertheless, this side view measurement remains very noisy. As mentioned before, $J_{g,surf}$ is obtained from the integration of the local evaporation rate over the droplet interface and $J_{g,int}$ is obtained from the integration of the pseudo-local evaporation rate over any
closed iso-concentration contour. These vapour-based measurements are instantaneous and are clearly also less noisy. Overall a very satisfactory agreement is obtained thus validating in some sense our local evaporation rates extracted previously.

![Image]

**Figure 5**: Global evaporation versus droplet radius obtained in three different ways.

4 Conclusions

As the results have shown, digital holographic interferometry is capable of measuring a precise vapour concentration field surrounding evaporating droplets. From these measurements, one can also obtain absolute interfacial temperature fields, the local evaporation rate distribution and finally also at least two different instantaneous global evaporation rate measurements. Essentially all the critical parameters governing the evaporation process can be obtained from a single laser and camera set-up. All of these measurements are obtained from a single image, meaning that very transient processes such as the present droplet can be tracked in time (here at 30 fps). Applied to the present set-up with hanging droplets of HFE-7000, it was shown how convection can have a dramatic impact on the local and global evaporation rate of droplets.

References

[7] Dhavaleswarapu HK, Migliaccio CP, Garimella SV and Murthy JY, "Experimental investigation of evaporation...