The Flow Characteristics of an Evaporating Ethanol Water Mixture Droplet on a Glass Substrate*

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Abstract

Droplet evaporation has attracted much interest recently, being relevant to a wide range of biological and technological applications. The underlying mechanisms for this phenomenon are still poorly understood. We report on experimental results, from micro-Particle Image Velocimetry (μ PIV), of the spatial and temporal velocity field within pure water and ethanol-water mixture droplets evaporating on a glass substrate. The drop profile, evaporation rate and surface temperature were also measured. For pure water droplets, the radial velocity is found to exhibit a maximum spatially towards the three-phase contact line and to increase dramatically towards the end of the drop lifetime. For ethanol-water droplets, three flow phases of (I) vortical flow, (II) transient flow and (III) radial flow were observed. Phase I has vortices, driven, we believe, by concentration differences arising during the preferential evaporation of ethanol. Phase II sees an exponential decay in vorticity with remaining vortices migrating towards the contact line, accompanied by the formation of one large toroidal vortex, possibly due to ethanol depletion at the apex of the drop leading to a surface tension instability. Phase III is characterized by radial flow towards the contact line, matching the evaporative flux and identical to the flow measured for pure water.

Key words: Fluid Flow, Evaporation, Microscale, Sessile Droplets, Velocimetry

1. Introduction

The evaporation and wetting of pure droplets has been extensively studied in the recent years⁽¹⁻⁴⁾. This interest is driven by many technological and biological applications, e.g. the evaporation of blood serum drops has recently been introduced as a diagnostic tool for certain diseases⁽⁵⁾, Craster et al. have proposed the use of drying droplets for nanopatterning deposition⁽⁶⁾ and Dugas et al. have proposed its use in DNA stretching⁽⁷⁾.

The underlying mechanisms for this, seemingly simple, phenomenon are still being debated amongst researchers with many aspects still poorly understood.

For instance, Shahidzadeh-Bonn et al.⁽⁸⁾ have compared evaporation of pure water and pure hexane droplets, noting the variation in radius with time and how this depends on convection within the vapour. Deegan et al.^(9, 10) have studied ring formation from suspension and particle containing water drops, from which they infer that internal flow in the drop is driven by mass conservation to replenish fluid evaporating preferentially at the outer edge of the drop. In contrast, Ghasemi and Ward⁽⁴⁾ report that in a reduced pressure environment,

*Received 16 Dec., 2011 (No. 11-0774)
[DOI: 10.1299/jtst.7.425]

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flow in evaporating water drops is driven by thermocapillary convection, such as was observed by Buffone et al.⁽¹¹⁾ for a meniscus within a capillary.

Over the years many experimental and theoretical studies have been devoted to understanding the dynamics of droplet evaporation including its internal flow. The latter can not only influence the evaporation kinetics but can also affect the ring deposits. The theoretical investigation of Hu and Larson⁽³⁾ has shown that thermocapillary driven flow can be expected within a droplet and that this would change as the droplet profile evolves. The work of Ristenpart et al.⁽¹²⁾ has shown that the relative thermal properties of the substrate and the liquid can affect the direction of flow within evaporating droplets. Xu et al.⁽¹³⁾ revealed, using fluorescent particles as tracers, that there is Marangoni flow in evaporating water droplets, with a stagnation point at the droplet surface, where the surface flow, the surface tension gradient, and the surface temperature gradient change their directions. For water drops⁽¹⁴⁾, we have measured the horizontal component of the velocity within the drop and shown it to be consistent with mass conservation to account for preferential evaporation at the contact line as predicted by Deegan et al.⁽⁹⁾.

In terms of macroscale observation, for pure droplets, the behaviour of the drop depends on the wettability and roughness of the surface. When first formed, the contact angle of the liquid will usually be close to the advancing contact angle. The drop will often remain pinned until the receding contact angle is reached, after which, on smooth surfaces, the contact line will tend to slide with constant contact angle. On rough surfaces the drop usually remains pinned and the contact angle will continue to decrease. Sometimes both the contact angle and drop diameter will decrease simultaneously or the drop will go through a sequence of depinning and pinning such that the drop radius jumps through a number of discrete values.

However, whilst there has been significant research into the evaporation of pure fluid drops, much less work has been done on the evaporation of multicomponent droplets.

With droplets formed from binary mixtures of an alcohol (methanol⁽¹⁵⁾, ethanol⁽¹⁶⁻¹⁹⁾ and 1-propanol⁽²⁰⁾) and water the behaviour is generally different from that of pure liquids, particularly for mixtures on the water-rich side of any binary azeotrope⁽²⁰⁾. Depending on the wettability and smoothness of the surface there may be an initial phase during which the drop remains pinned and the contact angle decreases. This is followed on smooth surfaces by a phase in which the contact angle increases, from a value more representative of the alcohol to a value close to that found with pure water drops. Rowan et al.⁽²⁰⁾ found it difficult to take measurements during this phase for propanol/water mixtures on polymethylmethacrylate. During this phase the contact line slides to allow this angle to increase. There may then follow a period where the contact angle remains constant with the contact line sliding or the contact angle will then start to decrease with or without change in the drop radius. For pinned binary drops (as reported here), the contact angle decreases throughout, but the change in characteristics at the contact line is observed in terms of a change in the evaporation rate (Fig. 1).

Fig. 1 Evolution of profile during the evaporation of (a) a pure sessile drop, (b) a binary drop for pinned drops.

It is thought that most of the alcohol evaporates during the first two stages described above, leaving behind a liquid that is almost pure water, so that the final stages of evaporation mirror those of a pure water sessile droplet.

So far, all investigators are agreed that the evaporation can be divided into a period during which the alcohol preferentially evaporates, followed by evaporation of almost pure water. However, as yet no one has studied the interior flow in such drops to gain an understanding of how the fluid mechanics impinge on the evaporation process. We have therefore addressed this issue in an attempt to elucidate the mechanisms governing the various stages outlined above.

In order to address the outstanding issues about the nature and evolution of flow within evaporating droplets, experimental PIV analysis of the full flow field and its evolution in time has been conducted.

We have also investigated the overall drop profile variation and surface temperature map of the evaporating drops to establish whether these correlate with the velocity field within the drop.

2. Experimental Method

2.1 Velocity measurement in a droplet using micro PIV

The apparatus in Fig. 2 was used to obtain velocity information within evaporating sessile drops. $0.12\ \mu\text{l}$ ($\pm 0.03\ \mu\text{l}$) droplets of pure water or 5% vol. ethanol, 95% vol. distilled water, seeded with 0.04% solids of fluorescent micro-spheres ($1\ \mu\text{m}$ diameter, Nile-red, carboxylate modified FluoSphere® beads of density 1.05g/cm^3) were injected onto a clean glass cover slide, sitting on an inverted microscope (Leica DM 5000 M) to yield sessile drops of about 1.25mm diameter (1.15mm for pure water). Due to the presence of particles in the fluid, the contact line remained pinned throughout. A New Wave Pegasus pulse diode laser emitting at 527nm , synchronized with a Dantec Dynamics Nanosense II camera (512×512 pixels) at 20Hz (10Hz in the case of pure water), was used to cause the particles to fluoresce at 575nm and the resulting images captured. The resolution of the images was $320\ \text{pixels/mm}$.

The height, above the base of the drop, of the plane in which the velocities were determined was set by adjusting the focus on the microscope. For all results with mixtures reported here, the height was approximately $10\ \mu\text{m}$ off the base of the drop that is dictated by the resolution of the microscope and the depth of field of the microscope lens was approximately $20\ \mu\text{m}$. For pure water drops, measurements of the velocity distribution were taken in three horizontal planes above the glass cover-slide. The focal plane was centred on three horizontal positions; just above ($1\ \mu\text{m}$) the cover-slide, $30\ \mu\text{m}$ above and $60\ \mu\text{m}$ above. Note that the relative heights off the base are more important here than the absolute values, since the microscope has a depth of field of around $20\text{--}30\ \mu\text{m}$.

Fig. 2 A photo of the measuring apparatus for flow velocity in a droplet.

Velocities of the particles in the horizontal plane were determined by cross-correlation of successive images^(21, 22), for 16x16 interrogation windows with 50% overlap to yield a 63 by 63 vector array, using Dantec Dynamics Flowmanager 4.71 software. A peak validation algorithm was performed with vectors rejected if the tallest correlation peak was less than 1.2 times the 2nd peak. Typically, up to one quarter of the vectors were rejected at this stage.

Velocity maps were created from image pairs for every 0.5 seconds over the lifetime of the drop and for every 0.05 seconds over the region where the flow pattern was changing. From the velocity map, vorticity around a vertical axis could be evaluated. Prior to calculating the vorticity a moving average filter was applied, substituting vectors by an average based on an 11x11 array centred on the vector position, before a mask was used to exclude any spurious vectors outside the edge of the drop. The vorticity around an axis perpendicular to the image plane at position m, n was calculated from

$$\omega_z = \frac{V_{(m+1,n)y} - V_{(m-1,n)y}}{2\Delta x} - \frac{V_{(m,n+1)x} - V_{(m,n-1)x}}{2\Delta y} \quad (1)$$

where Δx and Δy are the grid spacing.

2.2 Measurement of Shape and Evaporation Rate of a Droplet using Droplet Shape Analyzer (DSA)

A Kruss DSA100™ droplet shape analysis (DSA) system, consisting of a light source, a charge-coupled device CCD camera, a three-axis stage and DSA software was used to analysis the profile of drops of water and of water ethanol mixtures of the same size and concentrations as studied using PIV. The image analysis software enabled measurement of the droplet profile optically. Specifically, the DSA100™ system was used to measure the base radius, maximum height, which is a centre height $h(r, t)$ at $r=0$ of the droplet, contact angle θ and volume V of the droplet with evolution in time, and then the evaporation rate was calculated from the rate of change of the volume of the droplet.

2.3 Measurement of Surface Temperature of a Droplet using Infrared Thermography

A Thermacam™ infra red thermography system (Fig. 3) was used to analyze the surface temperature of droplets of the same size and concentration as for the PIV study. The drop was injected onto a glass coverslide and the camera arranged to observe the drop from vertically above. The spatial and temporal temperature data of the droplet surface field was logged to the PC during the lifetime of evaporation. The air temperature and relative humidity surrounding the slide glass were $21 \pm 1^\circ\text{C}$ and $24 \pm 5\%$ respectively. Each test was performed several times at same condition to examine the reproducibility of the data.

Fig. 3 A schematic diagram of the measuring apparatus for surface temperature of a droplet.

3. Results

3.1 Water Droplets

μ PIV measurements close to the base of a sessile water drop on a glass substrate (Fig. 4) reveal a symmetrical horizontal flow component radially outwards which increases from zero at the centre to a maximum at about 70% of the radius of the drop. The velocity values in Fig. 4 are averages around the drop for each radial position. As expected, the drop remains pinned throughout, due to the presence of deposited particles at the contact line, and the evaporation rate remains constant (Fig. 5 (a)).

Fig. 4 3D Spatio-temporal evolution of the flow field, measured just above the base (within $20\mu\text{m}$) of an evaporating water droplet.

(a) Linear evolution of volume in time, indicating constant evaporation rate.

(b) Contact angle (in the range of 30° - 5°) and height in time.

(c) Shape in time of the droplet. Lines show best-fit lines conforming to a spherical cap.

Fig. 5 Profile of evaporating water droplet on a glass slide from optical measurements (DSA 100).

As evaporation proceeds, two effects are observed (Fig. 4): the radial velocity at each radial position increases, rising dramatically towards the end of the lifetime of the drop; and temporal oscillations are observed in the radial velocities near the outer edge of the drop.

Measurements of the radial velocity with time and radial position (Fig. 6) at three different heights did not reveal any significant variation with height.

Fig. 6 Vertical distribution of radial velocity and its variation with time for 3 different radial positions for pure water drop.

3.2 Ethanol-Water Mixtures

The vorticity is shown in terms of colour coding on the velocity vector maps in Fig. 7.

Three distinct phases of flow behaviour were observed, as depicted in Figs 7, 8 and 9. In the first stage (I), a number of vortices are present in the fluid, which appear to have random orientation and number (up to eight distinct vortices were observed), though the spatial average vorticity remains roughly constant at about 0.35 s^{-1} . There is some evidence of oscillation of these vortices, revealed also in fluctuation of the average intensity. In the third stage (III), the flow is radially outwards, with virtually zero vorticity around the vertical axis, and the velocity increases rapidly towards the end of the lifetime of the drop. Comparison of Figs 4 and 8 shows clearly how the early flow behaviour is radically different for pure water drops and ethanol water mixture drops.

Fig. 7 PIV results showing flow field in terms of velocity vectors and vorticity for the three identified evaporation stages.

Fig. 8 3D map showing the evolution of averaged velocity in time along the radial position, the three phases are clearly identified.

Fig. 9 Spatially averaged vorticity versus time.

Between stages I and III, we have a transition stage (II), in which the vorticity decays exponentially towards zero with time (Fig. 10). During this transition stage, we also observed a remarkable spike in the radial velocity (Fig. 8) as the vorticity was undergoing its exponential decay.

The radial flow in stage III shows exactly the same characteristics as that measured by us for pure water. The flow is radially outwards and there is both a rise in radial velocity spatially towards the contact line and a dramatic rise in the radial velocity temporally towards the end of the drop lifetime. The magnitude of the velocities is also similar, being consistent with mass conservation to match the evaporative flux near the contact line.

From the Fig. 10 it is clear that there are two distinct exponential decay curves. The first has a slope of 0.78 s^{-1} and the second a slope of 4.3 s^{-1} . From these slopes we can calculate diffusion times of 1.3 s and 0.23 s respectively, which with a diffusion constant for ethanol in water of $1.5 \times 10^{-9} \text{ m}^2/\text{s}$ leads to diffusion lengths ($= (D\tau)^{0.5}$) of $4 \times 10^{-5} \text{ m}$ and $2 \times 10^{-5} \text{ m}$ respectively. There is a clear discontinuity between these curves. This discontinuity occurs at the same time as the spike in velocity.

Fig. 10 Semi-log plot of the averaged vorticity in time for the transition stage (stage II).

Fig. 11 Temperature maps, both taken 10 seconds after the start of evaporation.

Comparison of the surface temperature maps (Fig. 11) for pure water and a 5% ethanol/water mixture in the early stages of evaporation (stage I) do not show significant differences in local temperature gradients, even though evaporation in the case of ethanol/water is greater than that in the case of pure water.

4. Discussion

4.1 Water Droplets

As outlined previously by us⁽¹⁴⁾, we explain the increase in velocity towards the end of the lifetime of the drop, for pure water drops, in terms of mass conservation. The evaporation rate was constant at about 0.0014 $\mu\text{l/s}$ throughout and the height of the droplet decreases with time (Fig. 5), so for preferential evaporation near the contact line, the velocity at any radial position must increase as the evaporation proceeds.

Our work supports the prediction of Deegan et al.⁽¹⁰⁾ that the flow within the droplet arises from mass conservation, since Marangoni convection from the contact line to the apex would lead to higher velocities along the base of the drop than those required to satisfy mass conservation due to evaporation. At first sight it contradicts that of Ghasemi and Ward⁽⁴⁾. However, it is important that the relative importance of the Marangoni effect is evaluated for our experiments. It is worth noting that the experimental results in Ref. (4) are for an enhanced evaporation rate in a reduced pressure environment. This might point to the fact that Marangoni flow contribution becomes a more significant energy transport mechanism as evaporation rate increases. In these experiments, the contact angle varied between about 30° and 5° as shown in Fig. 5. Under these conditions, the influence of Marangoni flow may be assumed to be negligible, as the variation in drop height with radius and hence thermal conduction from the solid substrate to the surface of the drop is small. Indeed, Infra Red measurements (Fig. 11) suggest less than 0.3K of a temperature difference between the contact line and the apex of the drop. As the drop evaporates the conduction length decreases, so that variations in temperature along the interface must also decrease. If the flow were influenced by Marangoni convection, we would therefore expect the velocities measured to decrease with time. The fact that the velocity increases is therefore supporting evidence for mass conservation being the driving force for the measured velocities in this study.

Figure 6 shows the velocity distribution in each plane over the evaporation life time. There is no significant difference in velocity with distance from the cover-slide, suggesting an approximately uniform flow distribution in the vertical direction at each radial position. This is in agreement with the velocity profiles predicted by Hu and Larson⁽²³⁾ for low contact angles, where Marangoni convection has little influence. Indeed, the order of magnitude of the velocities predicted by Hu and Larson (10^{-5} m/s) is in agreement with those measured in our study.

Additionally, in the experimental condition, we discuss the velocity closest to the substrate. It should be noted that the resolution of our system did not permit measurements to be resolved within the boundary layer.

We have calculated the velocity variation with radial position represented by the mass conservation flow resulting if the majority of the evaporation occurs at the outer edge of the drop reported in Ref. (14).

We used normal glass microscope slides as substrates. The glass was wiped with acetone to remove grease and/or oily contaminants. Following this, the substrate was rinsed with pure ethanol, and finally it was washed with distilled water and dried with air.

4.2 Drops Containing Ethanol Water Mixtures

The presence of multiple vortices in the first phase suggests that the internal flow at this

stage is driven either by concentration or temperature gradients and not simply by evaporative flux, since evaporation is known to be greatest in the region of the contact line, which would lead to a radially outward flow, as for pure water drops. Cheng et al.⁽¹⁷⁾, although unable to take measurements during this phase because of the instabilities in contact line behaviour, postulate that the instabilities are driven by temperature gradients, citing the work of Hopkins and Reid⁽²⁴⁾ on temperature variations in evaporating aerosol drops of alcohol/water mixtures. We have used Infra-red thermography on our sessile drops (Fig. 11) and observed very little temperature difference at the surface of the drop, so believe that these vortices must be driven by concentration gradients, most likely through the effect of concentration on the local surface tension, though it is possible that even small variations in temperature, perhaps themselves the result of differential evaporation due to concentration variation, may also lead to surface tension gradients. Dehaeck et al.⁽²⁵⁾ have demonstrated how concentration gradients in evaporation of ethanol/water mixtures can lead to buoyancy-driven convection in a Hele-Shaw cell. It should be noted, however, that the length scales over which initial gradients were measured in their experiment were larger than the size of our drops. For our experiments, surface tension effects arising from concentration gradients are likely to dominate buoyancy effects.

The radial flow in stage III shows exactly the same characteristics as that measured by us for pure water⁽¹⁴⁾. The flow is radially outwards and there is both a rise in radial velocity spatially towards the contact line and a dramatic rise in the radial velocity temporally towards the end of the drop lifetime. The magnitude of the velocities is also similar, being consistent with mass conservation to match the evaporative flux near the contact line. Our experiments therefore confirm the observations made previously that the majority of the alcohol evaporates in the early stages of the evaporation process.

Stage II is of most interest, revealing for the first time details of the transition between the highly disturbed ethanol evaporation regime and that of the evaporation of residual water. Here there are two hitherto unseen characteristics, which shed some light on the mechanisms of transfer within the drop. The first is an exponential decay in the vorticity with time, accompanied by a migration of the remaining vorticity towards the outer edge of the drop and the second is a truly remarkable spike in the radial flow, much too large to be explained by evaporative flux alone, just before the flow settles down to that of a pure water drop.

The exponential decay in the second phase may be explained as follows: During the first phase the intense vorticity leads to uniformity of ethanol concentration throughout the drop, with convective transfer of ethanol to the drop surface, where it preferentially evaporates. We believe that the vortices are fed by local surface tension gradients induced by gradients in the ethanol concentration at the surface. As we noted earlier, Infra-Red Thermography did not reveal significant temperature variations that might also lead to surface tension gradients.

As discussed in (Ref. 26), we believe that concentration gradients at the surface, lead to surface tension variations that cause vortices to form in the liquid (phase I). As ethanol evaporates the bulk ethanol concentration will drop. As it drops the mechanism for transfer of ethanol to the surface will shift from being driven by convection to a diffusion dominated regime. Diffusion of the remaining limited ethanol in the bulk will lead to an exponential decay in the maximum concentration on the surface and hence in the local concentration gradients. Since these gradients drive the vortices, we expect an exponential decay in vorticity, as is observed in Fig. 10.

The sudden spike in radial velocity, observed in our velocity map as a symmetrical radial flow towards the contact line, may be associated with the formation of a single toroidal vortex. The velocity is more than an order of magnitude higher than that associated with the velocity expected due to fluid evaporation at the contact line, so mass conservation would require an associated inward flow in the upper region of the drop, such as would occur if the surface tension near the apex became significantly greater than that near the contact line.

Such a situation could arise if the apex of the drop became almost totally depleted of ethanol, whilst the surface in the outer region of the drop continues to have ethanol present. Since our observation is that vortices die out first near the apex, this may explain how such a situation could arise. Without vortices close to the apex, replenishment of ethanol at the surface following local evaporation would be by molecular diffusion, whereas vortices will continue to ensure that ethanol is convected to the surface near the contact line. This difference in efficiency of transfer of ethanol to the surface could lead to a significant concentration gradient and the resultant peeling back of the surface.

Following the proposed scenario, we speculate on the existence of a zero-concentration wave which starts at the apex of the drop and propagates toward the edge. Indeed the total depletion of ethanol must start somewhere in the drop, it is likely that the last ethanol molecules will be concentrated near the interface, the zero-concentration wave propagation would correspond to the total depletion of ethanol which seems to start at the apex of the drop.

We speculate that the second, more rapid decay in vorticity is driven by viscosity in the absence of ethanol diffusion to the surface to sustain concentration gradients, occurring once the ethanol runs out. These figures for the diffusion length are consistent in magnitude with those observed by Dehaeck et al.⁽²⁵⁾ during their experiments.

Future work can explore the effect of seeding particles on the contact line dynamics and evaporation kinetics, Sefiane and Tadrist⁽²⁷⁾.

5. Conclusions

For pure water the velocity profile along the radius of the droplet is found to exhibit a maximum towards the three phase contact line, with a dramatic increase in the velocity towards the end of the droplet lifetime. An analysis of the potential mechanisms responsible for the flow within the droplet demonstrated that these observations can be accounted for by mass conservation alone.

For evaporating binary mixture droplets the velocity field has three distinct stages. The first is a chaotic regime characterised by vortices. Thermographic measurements suggest that the difference in initial behaviour between that of pure water and of water ethanol mixture droplets is not dictated by surface temperature variations, since the temperature field is similar for both. The vortices formed in the mixture are therefore most likely to be caused by surface tension gradients driven by concentration variations due to the preferential evaporation of ethanol. The second, transition regime, sees an exponential decay in the vorticity with the remaining vortices migrating towards the contact line, accompanied by a spike in the radial velocity along the base of the drop, perhaps due to depletion of ethanol in the drop surface close to the apex of the drop leading to surface tension instability. The third stage is characterised by radial flow towards the contact line to match the evaporative flux and is identical to the flow measured by us for pure water drops.

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