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# On the Effect of Marangoni Flow on Evaporation Rates of Heated Water Drops

F. Girard,<sup>†</sup> M. Antoni,<sup>\*,‡</sup> and K. Sefiane<sup>†</sup>

School of Engineering and Electronics, University of Edinburgh, Kings Buildings, Edinburgh, EH9 3JL, United Kingdom, Aix - Marseille Université - Université Paul Cézanne, UMR - CNRS 6263 ISM2 - Centre St. Jérôme - BP 451, Marseille 13397 Cedex 20, France

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In this letter we show that the Marangoni flow contribution to the evaporation rate of small heated water droplets resting on hot substrates is negligible. We compare data of evaporating droplet experiments with numerical results and assess the effect of Marangoni flow and its contribution to the evaporation process. We demonstrate that heat conduction inside these water droplets is sufficient to give an accurate estimate of evaporation rates. Although convection in evaporating water droplets remains an open problem, our aim in this study is to demonstrate that these effects can be neglected in the investigation of evaporation rate evaluation. It is worth noting that the presented results apply to volatile heated drops which might differ from spontaneously evaporating cases.

The evaporation of sessile droplets is a fundamental phenomenon, pertaining to a wide range of industrial and biological systems. In many of these applications, being able to describe and predict evaporation rates of sessile droplets is of paramount importance. Recent works have demonstrated the complexity of certain aspects of this phenomenon. Despite extensive work on this topic, many aspects associated with this process remain elusive. Understanding the physics of the contact line motion and wetting dynamics as well as surface tension driven and buoyancy convection inside evaporating droplets are examples of outstanding issues still being extensively investigated by many researchers.<sup>1–5</sup>

Xu et al.<sup>6</sup> experimentally investigated internal flow in evaporating water droplets. The authors demonstrated the existence of Marangoni convection in evaporating deionized water droplets seeded with fluorescent particles on glass substrates. They have also shown the existence of a stagnation point on the interface where the surface flow, surface tension, and interfacial temperature gradients change direction. The investigated droplets were at room temperature (28 °C) and have a base radius of 2 mm and 10° of initial contact angle. It is worth noting that Savino et al.<sup>1</sup> have experimentally shown that in the case of pendent drops, the existence of Marangoni flows is observed in organic liquids (*n*-octane) but not in water. Ristenpart et al.<sup>5</sup> argued that, for organic liquids, non-uniform evaporation along the surface induces temperature variations along the droplet interface. These variations are found to generate a thermocapillary flow within the drop. The droplets were deposited on PDMS substrates and have typical initial volume of 2 μL. They were seeded with 1 μm solid particles to reveal Marangoni convection patterns after drying out. Moreover, the authors introduced a criterion to determine the occurrence and direction of Marangoni flow, with

the latter being the ratio of thermal conductivities of the substrate and the liquid. Hu et al.<sup>7</sup> studied both experimentally and theoretically the formation of particles deposits near the edge of a drying droplet on glass substrates. They demonstrated that surface Marangoni flow can redirect evaporation-driven deposition and assembly of suspensions. This will undoubtedly affect pattern formation, resulting from the dryout of droplets containing suspensions. Hu et al.<sup>8</sup> also analyzed the effect of Marangoni stresses on the flow in an evaporating droplet. The authors described the effect of Marangoni stress on the flow of an evaporating droplet using a numerical approach. The temperature field within the droplet was computed and the role of surfactant contamination was also addressed. The authors showed that small contamination tends to prevent Marangoni convection. Moreover, when the contact angle is below a critical value of approximately 14°, Marangoni flow disappears. Girard et al.<sup>9</sup> numerically investigated the evaporation dynamics of small sessile water droplets under microgravity conditions. The numerical analysis revealed temperature gradients on the free interface and as a result, Marangoni convection is generated within the droplet. The authors also found a slowdown in evaporation toward the end of the droplet lifetime. Using a similar approach, Girard et al.<sup>10</sup> investigated water droplets evaporating on heated substrates. The role played by the substrate temperature as well as droplet radius was investigated. The influence of relative humidity was discussed and indicates a strong influence only for low substrate temperatures. An empirical correlation for droplet evaporation time as a function of the basic parameters (ambient and substrate temperatures, humidity) was proposed. David et al.<sup>11</sup> experimentally investigated the effect of thermal properties of the substrate on the wetting and evaporation of sessile drops. The authors measured the temperature field inside millimeter-sized evaporating water and organic liquid droplets using a miniature thermocouple. Substantial evaporative cooling was observed and

\* Corresponding author. m.antoni@univ-cezanne.fr.

<sup>†</sup> University of Edinburgh.

<sup>‡</sup> UMR - CNRS 6263 ISM2.

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a strong influence of the substrate thermal properties was demonstrated.

It is clear from the available literature that the evaporation of liquid sessile droplets is accompanied by internal convection. For small droplets, this convection is mainly surface tension driven. The contribution of the latter to the evaporation process is still not clear. The objective of this paper is to quantify the contribution of Marangoni convection to the evaporation process of sessile droplets on heated substrates.

### Model Presentation and Results

The model used in the present investigation is based on classical hydrodynamics. Two main approximations are made: droplets are supposed to be small with a spherical geometry and a fast relaxation of mass flows and temperature profiles inside and in the vicinity of the droplets interface is assumed. As a consequence of the above assumptions, hydrostatic pressure gradients are neglected and quasi-stationary hypothesis is justified. Convection is neglected in the gas phase and assumed to be slow enough inside the droplets for viscous dissipation contributions to be negligible. The liquid phase is described using stationary Navier–Stokes and heat equations

$$(\nu \cdot \text{grad})\nu = \nu \Delta \nu \quad (1)$$

$$(\nu \cdot \text{grad})T = \kappa \Delta T \quad (2)$$

In the above equations,  $\kappa$  is the thermal diffusivity,  $\nu$  is the kinematic viscosity, and  $T$  and  $\nu$  are temperature and velocity, respectively. The Laplace equation is applied for temperature field in the gas phase:

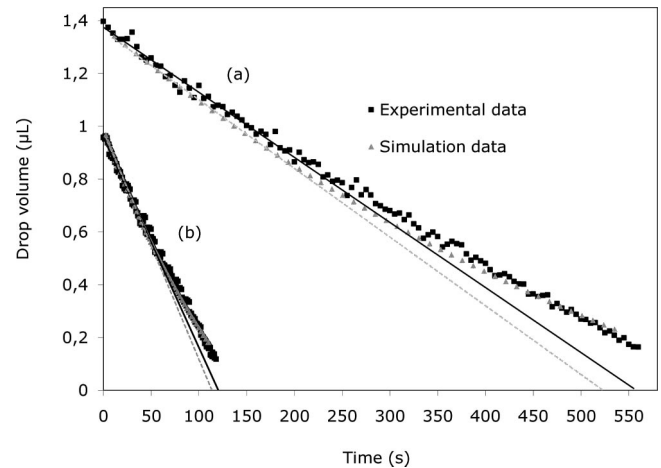
$$\Delta T = 0 \quad (3)$$

A more detailed description of the model could be found in Girard et al.<sup>9,10</sup> Substrate temperature  $T$  is assumed constant (justified for substrates with high thermal conductivity). Far field conditions are given by far field temperature  $T_\infty$  and relative humidity  $H$ . On the droplet's interface, mass velocity is tangential and temperature is a continuous function in the normal direction but varies along the interface. Any thermocapillary stress is hence included in this approach. Temperature dependence of surface tension in particular is carefully treated. The evaporative mass flux is locally computed from temperature gradients across the interface. This is estimated after computation of the temperature profile along the interface. It is worth noting that evaporative cooling is neglected in this approach.<sup>10</sup> Indeed, evaporative cooling is found to generate noticeable temperature gradients in volatile organic droplets but negligible in water droplets.<sup>11</sup> In addition, the temperature gradients resulting from the heated substrate are believed to be dominating compared to evaporative cooling gradients. These boundary conditions are coupled with eqs 1, 2, and 3 to describe the system.

Equations 1–3 are integrated using computational fluid dynamics and the finite element method (FEM) with a meshing that is adapted to the geometry of the system. It is refined at the level of the liquid/gas interface and at the edges of the droplet to avoid any numerical divergences. The spherical geometry of the droplets and the small temperature gradients on the interface make this problem analogous to that of an electrostatic lens.<sup>12</sup> It is then possible to show that the time evolution of the mass,  $m$ , of the droplets is written<sup>12</sup>

$$\frac{dm}{dt} = DR[c(T_s) - Hc(T_\infty)]\varphi(\theta) \quad (4)$$

where  $c(T)$  is the water concentration in air at temperature  $T$ ,  $c(T_\infty)$  is the water concentration in air at temperature  $T_\infty$ ,  $R$  the



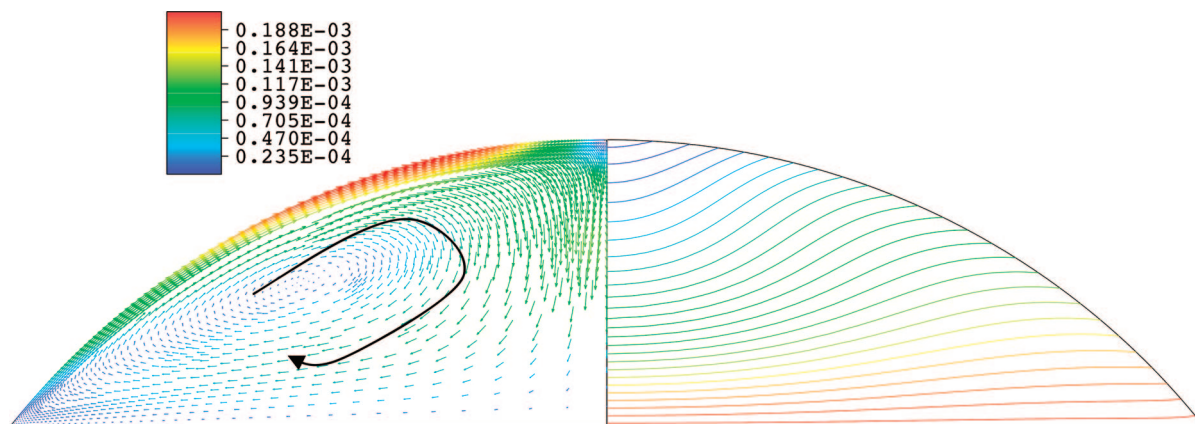
**Figure 1.** Time evolution of droplet volume for  $T_s = 30$  °C (a) and  $T_s = 50$  °C (b). Squares are experimental values, triangles are numerical predictions. Full (respectively, dashed) lines correspond to a linear fittings of the numerical data for  $t < 220$  s (respectively,  $t < 150$  s) (a) and  $t < 50$  s (respectively, 30 s) (b).

droplet contact radius, and  $D$  water vapor diffusivity in air. Function  $\varphi(\theta)$  is the vapor outgoing flow computed from eq 1 to 3 with FEM and  $\theta$  is the contact angle.

It is important to note here that this model includes all convection phenomena in the water droplet as well as thermal Marangoni flow generated by temperature differences along the liquid/gas interface. In the following, convection is neglected in the gas phase. This is justified by the small size of the droplets and by the important difference in the relative viscosities of air and water.

In addition to the numerical model described above, an experimental program was undertaken. A droplet shape analysis instrument (FTA200) is used to measure the evaporation rates as well as the profile of water sessile droplets. Droplets of about 1  $\mu$ L initial volume are deposited on rough aluminum substrates. The temperature of the substrate is controlled using a power heated resistance and a PID controller. Temperature and relative humidity in the room are controlled and monitored. Two temperatures were investigated  $T_s = 30$  °C and  $T_s = 50$  °C with a far field relative humidity of  $H = 50\%$ . Ambient room temperature is maintained at  $T_\infty = 22$  °C.

Our first aim is to validate the numerical model against the obtained experimental data. Experimental data were compared to numerical results considering time evolution of the droplet volume,  $V$ . It is worth mentioning that the numerical model does not include any fitting parameters apart from the parameter related to the size  $L_s$  of the heating substrate. For the best agreement with experiments, this parameter is set as  $L_s = 1.5R$ , which is a realistic value considering the experimental conditions. The comparison between experiments and numerical results gives a good agreement. This is illustrated in Figure 1 where the time evolution of the droplet volume is plotted at two different temperatures. Figure 1 shows that there is a good agreement as long as the contact line radius remains pinned. When contact line depins ( $t > 550$  s for  $T_s = 30$  °C and  $t > 130$  s for  $T_s = 50$  °C), a discrepancy is then clearly noticeable due to the fact that the model is no longer valid. Note, however, that there is a significant deviation of the initial linear trend of the droplet volume as time progresses, even for pinned droplets ( $t < 550$  s for  $T_s = 30$  °C and  $t < 130$  s for  $T_s = 50$  °C). This effect has already been observed in previous works<sup>7,8</sup> and indicates a slowing down of evaporative flux for pinned heated droplets toward the end of droplet lifetime. This suggests that the evaporative regime could



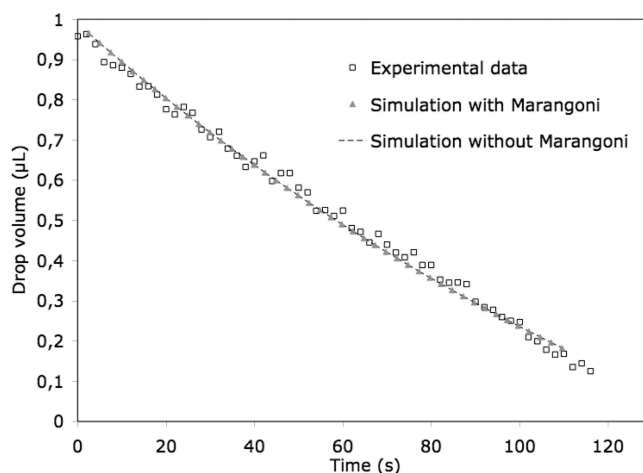
**Figure 2.** Velocities (left) and isotherms (right) in the droplet for  $T_s = 50\text{ }^{\circ}\text{C}$  and  $\theta = 50^{\circ}$ . Black thick lines illustrate the course of the velocity field. The color coding on the left indicates the values of the velocities. These velocities are normalized here by the characteristic velocity  $U$  with  $U = 14.6\text{ m/s}$ .

be at some point of the droplet lifetime controlled by the surface of the water/air interface. Because of evaporation, the latter decreases with time and so does the evaporative flux. The reduction in the evaporation surface and the area accessible for molecules to diffuse in the gas phase is thought to be the cause of the slowdown. This effect does not seem to be balanced by the increasing temperature of the droplets due to increasing proximity to the heated substrate.

The results presented above include Marangoni convection contributions in the model. Temperature profile indicates a temperature at the apex of the droplet which is cooler than the one at its edge. The so-generated Marangoni convection flows from the contact line region down to the apex of the droplet along the interface. The results from the model giving velocity field and isotherms are displayed in Figure 2. Due to continuity, the shear due to the Marangoni flow will generate a convective roll inside the droplet volume. This convective roll in 3D has the shape of a flattened torus. In 2D, two contrarotating rolls are observed. The isotherms show a distorted shape with the apex of the droplet being cooler than the edge. Temperature gradients along the interface depend on the substrate, far field temperatures, as well as contact angle.

Convection is one of the mechanisms contributing to enhance transport phenomena. Marangoni convection in the investigated system is expected to enhance the transport of heat from the substrate to the interface and hence should increase the evaporation rate. As far as we know, this general idea has not yet been assessed in the case of evaporating droplets.

In what follows, we set about to investigate the precise role of Marangoni flow in the kinetics of evaporation. Indeed, in the validated numerical model the Marangoni effect can be switched on and off at will by neglecting convection contribution to the Navier–Stokes equation for the liquid phase. We performed a simulation campaign neglecting this contribution and compared the findings to both the experiments and the case where convection is accounted for. It must be pointed out that simulation conditions and meshing of the system are identical to those already described in refs 9, 10 but with the important difference that eq 2 is now replaced by a Laplace equation for the liquid phase. It is interesting to note that the results from the simulations with and without Marangoni effect both show a rather good agreement with experimental data. Time evolution of the volume in both cases is illustrated in Figure 3. Surprisingly, the results from the simulations with no Marangoni effect show no difference whatsoever from those taking into account Marangoni flow. This is a fundamental finding which indicates that the contribution of



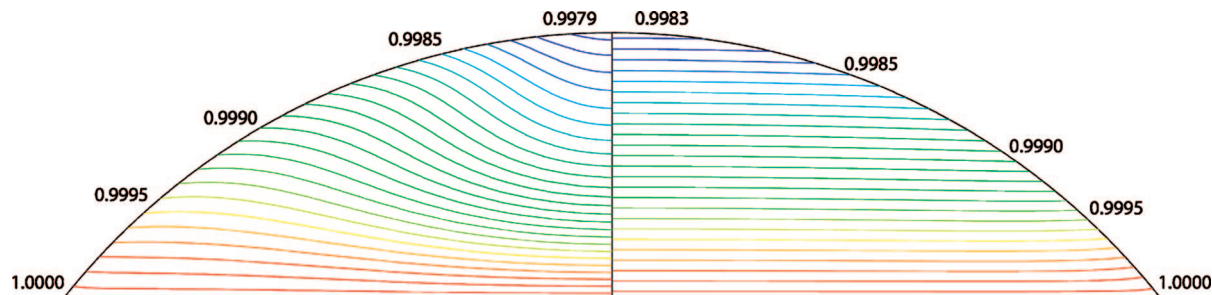
**Figure 3.** Time evolution of the droplet volume with convective contributions included in the model (triangles) at  $T_s = 50\text{ }^{\circ}\text{C}$ , without convective contributions (dashed lines). Squares are the same data as the values already plotted in Figure 1.

Marangoni flow to the overall evaporation is negligible. Hence, a detailed study of the hydrodynamics occurring in the droplet is not necessary to accurately estimate evaporation rates of sessile pinned droplets. A purely diffusive model for heat transfer inside the drop is sufficient.

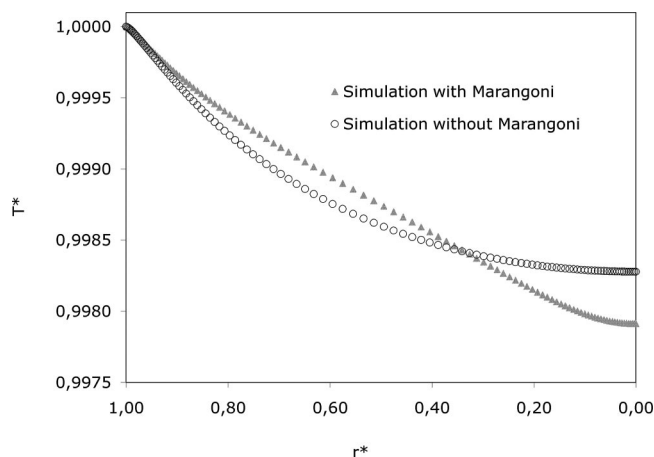
Marangoni flow is likely to affect the temperature field within the drop. The temperature profile inside the droplet is displayed in Figure 4 for both convective and nonconvective models. As already mentioned, isotherms are distorted in the convective situation due to the appearance of a convective roll in the droplet. In the nonconvective model, typical diffusive profiles are found. The values of temperatures indicated in this figure show very small differences between the apex of the droplet and the substrate. This is due to the value of the contact angle  $\theta = 50^{\circ}$  for this specific case. Larger differences would result for larger values of the contact angle.<sup>10</sup> Due to continuity, temperature in the gas phase immediately above the droplet shows identical small gradients when moving along the interface. However, in the normal direction to the interface very steep gradients are found due to the small thermal conductivity of air. It also appears in Figure 4 that temperatures inside the droplet are quantitatively very similar for both models.

This can be verified in Figure 5 where numerical calculation of the temperature profile along the interface is displayed for both convective and nonconvective models. As in Figure 4,





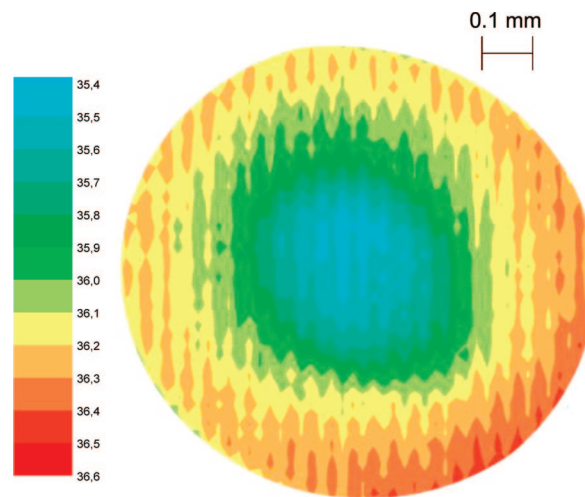
**Figure 4.** Isotherms inside the droplet for  $T_s = 50\text{ }^{\circ}\text{C}$  at time  $t = 24\text{ s}$  ( $\theta = 50^{\circ}$ ) with convective contributions (left) and without (right). Some values of  $T^* = (T - T_{\infty})/(T_s - T_{\infty})$  are plotted.



**Figure 5.** Normalized temperature  $T^*$  along the interface for  $T_s = 50\text{ }^{\circ}\text{C}$  at time  $t = 24\text{ s}$  ( $\theta = 50^{\circ}$ ) with (triangles) convective contributions and without (circles). Apex of the droplet corresponds to dimensionless radial coordinate  $r^* = 0$  and contact line location is  $r^* = 1$  where  $r^* = r/R$  and  $R = 1.08\text{ mm}$ .

temperatures again show qualitative differences but with numerical values that are almost identical. We can hence notice here that convection inside the droplet generates qualitative differences in the general shape of isotherms but numerical values of temperatures remain of the same order of magnitude; hence, no major difference of the overall evaporation rate is expected.

Temperature gradients along the liquid–vapor interface are indeed the driving force behind Marangoni flow within drops. In order to investigate the interfacial temperature, we set about to explore the temperature profile along the surface using the infrared (IR) technique. A FLIR ThermoCAM SC3000 IR camera was used; it has a thermal sensitivity of 20 mK and an accuracy of 1% up to 150 °C. The camera's detector has a spectral range 8–9  $\mu\text{m}$  with a resolution of  $320 \times 240$  pixels. The field of view at minimum focus distance (26 mm) is  $10 \times 7.5\text{ mm}^2$  and the system can acquire images in real time at speeds up to 750 Hz. The acquired images are transferred to a PC with a ThermoCAM specialized software. The emissivity of distilled water (0.96) is a stored parameter to accurately measure the surface temperature. A water sessile drop of about 1  $\mu\text{L}$  of initial volume was deposited on aluminum substrate at 40 °C. An interfacial temperature map of the drop is obtained with the IR camera and shown on Figure 6. It can be clearly seen that a temperature gradient on the surface exists between the apex and the edge of the drop. The drop is cooler on the apex; a temperature gradient of about  $\sim 0.8\text{ }^{\circ}\text{C}$  is



**Figure 6.** Infrared image of evaporating sessile drop on aluminum substrate at 40 °C. The color coding on the left indicates the values of the actual temperatures in  $^{\circ}\text{C}$ . Note the cold cap in the center of the drop.

noticeable. This result confirms the qualitative predictions of the model for interfacial temperature variation. It also indicates that there must be thermocapillary flows within the droplet, flowing from the edge (hot) to the apex (cold). This is the first time, to our knowledge, such temperature gradients have been experimentally revealed. The experimental value of the temperature gradients is, however, larger than the value predicted by the model on Figure 5. This difference is due to the difference of substrate temperature, to the initial condition problem (in particular to the initial temperature of the droplet), and to uncontrolled contact angle. Still, this preliminary finding could contribute to further understanding of the evaporation process of droplets on heated substrates. Detailed investigations of the interfacial temperature using an IR camera are underway.

The present investigations studied experimentally and numerically the evaporation of pinned sessile water droplets on heated substrates. The contribution of Marangoni flow to the evaporation of the drop was assessed and found to be negligible. Therefore, a simple approach based on heat diffusion is sufficient to estimate evaporation rates. The conclusions reached in this study may help to alleviate the complexity in studying and modeling the evaporation of drops which has a wide range of application.

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