Hydrothermal waves on ethanol droplets evaporating under terrestrial and reduced gravity levels

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This experimental study, performed under microgravity conditions, focuses on the evaporation dynamics of ethanol drops and the formation and behaviour of the hydrothermal waves that spontaneously develop on the drop surfaces. The aim of this study is to compare our results to a similar study performed under normal gravity conditions to confirm the purely thermocapillary origin of these instabilities. A scaling law predicts with good agreement the number of instabilities that form, regardless of the gravity level.

Key words: capillary flows, interfacial flows, Marangoni convection

1. Introduction

Thermocapillary instabilities, also known as Marangoni instabilities, develop during the evaporation of volatile fluids when the surface tension gradient is sufficiently strong. When the surface of the fluid is static, instabilities are created as a response to the temperature gradients because of the relationship between temperature and surface tension. These instabilities were first observed by Bénard (1900) by optical methods on liquid sheets and were studied by Pearson (1958) in a theoretical work that pointed to the role of surface tension in this phenomenon.

Smith & Davis (1983) were the first to theoretically predict a new type of instability called hydrothermal waves (HTWs) and to theorize that HTWs depend on the Prandtl number (Smith 1986). For low Prandtl numbers, the instabilities run in the same direction as the horizontal temperature gradients, and for high Prandtl numbers, they run perpendicular. These Prandtl-number-based models fit the experimental studies previously performed by Pearson (1958). Riley & Neitzel (1998) succeeded in experimentally demonstrating the existence of HTWs in a layer of silicone oil and created a transition map for the different types of instability depending on the Marangoni and the dynamic Bond numbers.

Garnier & Chiffaudel (2001) experimentally studied the criteria for the formation of HTWs and their behaviour. They investigated these instabilities inside a two-dimensional circular vat with different configurations and a temperature gradient from the inside to the outside. The geometric characteristics of the system (depth and width of the fluid, characteristic length of the vat) have a strong influence on the nature of

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the instabilities. If the depth of the fluid is greater than the capillary length, stationary rolls will form instead of HTWs. Moreover, in a vat with a rectangular configuration, the HTWs move from the cold to the hot spots with a constant angle of propagation (type HTW$_1$) whereas if the configuration allows the HTWs to propagate in every direction (as typically occurs in vats with cylindrical configurations), the angle of propagation will change as a function of the gradient temperature (type HTW$_2$). The theoretical work of Garnier, Chiffaudel & Daviaud (2006) allows the prediction of different regimes of the instabilities depending on the height and physical properties of the fluid, using dimensionless numbers (Rayleigh number, $Ra$; Marangoni number, $Ma$; static and dynamic Bond number, respectively $Bo$ and $Bd$, definitions in table 1).

HTWs develop in configurations in which the characteristic length is less than or equal to the capillary length, revealing the thermocapillary nature of the instabilities. Nevertheless, gravitational forces are not null when the experiment is performed under normal gravity. During their experiments in a vat with a cylindrical configuration, Garnier et al. (2006) observed a vertical temperature gradient from the bottom of the vat to the free surface of the fluid near the location at which the HTW$_2$ formed. This gradient, as a result of the cooling caused by the evaporation of the fluid, distorts the horizontal temperature profile to form gravitational convection rolls.

HTWs were also studied in the evaporation of sessile drops. This configuration is reminiscent of the configuration used by Garnier et al. but is three-dimensional with a free, curved surface. Moreover, the larger temperature gradient is not horizontal (from the centre of the pool to its edge) but is vertical (larger temperature difference between the apex (top of the drop) and the substrate). Sefiane, Steinchen & Moffat (2010) and Brutin et al. (2011) studied this type of configuration, among others, using infrared visualization at room temperature and on heated substrates, respectively. Different fluids were used, including water, fluorinert electronic liquid (FC-72), ethanol and methanol. The instabilities develop spontaneously during the evaporation. Sefiane et al. reveal the effect of the volatility of the fluid and the conductivity of the substrate on the appearance and number of HTWs. Sobac & Brutin (2012) studied the influence of the substrate temperature and the volume of the drops on the dynamic of the number of instabilities during the evaporation.

All of these studies were limited by the height or depth of the fluid being less than the capillary length ($Lc = \sqrt{\sigma/\rho g}$ where $\sigma$ is the fluid surface tension, $\rho$ the density and $g$ the gravity level) to reduce the influence of gravity. Under normal gravity conditions, the capillary length of ethanol is 1.69 mm whereas under

<table>
<thead>
<tr>
<th>Number</th>
<th>$Ra$</th>
<th>$Ma$</th>
<th>$Bo$</th>
<th>$Bd$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta g \Delta T h^4$</td>
<td>$-\frac{d\sigma}{dT} \Delta T h^2$</td>
<td>$\rho gh^2$</td>
<td>$Ra$</td>
<td>$Ma$</td>
</tr>
<tr>
<td>Gravity level</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 g</td>
<td>100.7</td>
<td>1278</td>
<td>0.105</td>
<td>0.078</td>
</tr>
<tr>
<td>$\mu$g</td>
<td>1.23</td>
<td>1161</td>
<td>0.00093</td>
<td>0.00106</td>
</tr>
</tbody>
</table>

**Table 1.** Characteristic dimensionless numbers for two droplets of ethanol under two levels of gravity: normal gravity ($T_s = 35 \degree C, P = 1013.25$ mbar, $R_{1g} = 2.81$ mm), and reduced gravity ($T_s = 35 \degree C, P = 835$ mbar, $R_{\mu g} = 2.77$ mm).
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reduced gravity conditions, the capillary length is 7.46 mm. Even under this limit, the gravitational effects cannot be entirely avoided. Chan & Chen (2010) extended Smith & Davis’ linear stability analysis to include the effect of gravity. It turns out that gravity increases the potential energy of the fluid layer in their energy balance analysis and changes the type of propagation of the instabilities (they will tend to have a transverse mode instead of an oblique mode as the effect of gravity increases). Microgravity experiments are the only way to completely rule out gravity. Several studies of oscillatory thermocapillary flows in silicone oil performed under microgravity conditions can be found in the literature (Kamotani, Ostrach & Masud 2000; Schwabe, Zebib & Sim 2003), but these studies were only performed in open-annuli configurations. Studying drop evaporation under microgravity could confirm the thermocapillary origin of HTWs and demonstrate experimentally that gravity does not affect the development of the instabilities. In this study, an experimental set-up has been designed to compare the evaporation of drops of ethanol on a substrate heater under two gravitational conditions (normal gravity on Earth and microgravity during parabolic flights).

2. Experimental set-up

The experimental set-up enables the creation of a 99.9% pure ethanol droplet on a heated substrate and the monitoring of its evolution with an infrared camera, a high-definition (HD) camera and a heat flux meter (Brutin et al. 2010). The infrared camera (Variocam High Resolution Head, 640 × 480 pixels of 40 µm) images the top of the droplet to record the thermal motion on the droplet. The HD camera (Canon EOS-7D), laterally positioned, follows the evolution of the geometric parameters (radius, contact angle and height of the drop). The substrate temperature \( T_s \) is measured with a type-K thermocouple and the heat flux absorbed by the droplet by a heat flux meter using a large number of thermocouples connected in series circuit (figure 1). The heat flux meter has a diameter of 15 mm and a thickness of 0.6 mm and is made out of copper, which makes the heat resistance from the heater (spherical polyimide thermofoil heater regulated by a PT-100 sensor with a PID regulator at ±0.1 °C) to the droplet negligible thanks to its good conductivity. A 3 mm thick Nuflon substrate enables the droplet to maintain contact angles \( \theta_i \) less than 40°. A 1.74 µm roughness allows the substrate to pin the contact line during the major part of the evaporation process. A range of temperatures between room temperature and 55 °C is investigated. Ethanol is injected through a thin 0.7 mm pipe at the centre of the substrate, and the droplet is allowed to evaporate in an atmosphere composed of air at a temperature \( T_a \) of 20 ± 1 °C and a pressure \( p_a \) of 835 ± 2 mbar (cabin pressure during flight). The experimental conditions of the cell are recorded using a pressure sensor and a thermocouple of type K.

The microgravity experiments took place aboard Novespace’s A300-ZeroG aircraft in Bordeaux (France). This aircraft is dedicated to parabolic flights and creates 22 s of microgravity (0.01 ± 0.05 g) framed by two stages of hypergravity. For each parabola, a sessile ethanol droplet is created on a substrate at constant temperature and left to evaporate. After the microgravity, the cell is connected to the plane vent-line to flush the ethanol vapour. Once the pressure drop has removed the remaining liquid, ethanol-vapour-free air at room temperature is injected inside the cell to start a new experiment.

The microgravity results are compared with results obtained under normal gravity using the same experimental protocol (Sobac & Brutin 2011). The normal gravity
Figure 1. (Colour online) Confined volume and the equipment used for the ethanol sessile droplet injection and evaporation on a Nuflon substrate: a test cell that contains a heated substrate and a heat flux meter, a one-way syringe pump and high-definition and infrared cameras.

The experiment differs from this work in the pressure conditions (atmospheric pressure) and radii of wetting of the drops (smaller than those used in this study, typically \( R_{\text{drop}} = 1.5 \pm 0.5 \text{ mm} \), to avoid distortions due to gravity). On Earth, a more efficient infrared camera (resolution of 640 × 512 pixels of 10 \( \mu \text{m} \)) can be used to obtain a more precise measurement of the flow motion. These two differences are not believed to affect the flow motion or the internal heat transfer mechanisms in the droplet. Consequently, the quantitative comparison between the terrestrial and microgravity results is valid.

3. Heat transfer and flow motion

3.1. Description of a typical experiment under microgravity

Figure 2 shows the evolution of the heat flux absorbed by the droplet and the temperature of the substrate in one flight parabola. This detailed case was performed under the following conditions: \( T_\text{s} = 50 ^\circ \text{C}, T_\text{a} = 21 ^\circ \text{C}, p_\text{a} = 834 \text{ mbar}, \) Volume = 14.1 \( \mu \text{l}, R_{\text{drop}} = 4.35 \text{ mm}, \) height of the drop = 0.56 mm, \( \theta_i = 23.2^\circ \). Similar trends are observed regardless of the experimental conditions tested.

The first phase (\( a \)) of the experiment is a phase of hypergravity at 1.8 g. The substrate is dry at the set temperature. The flux measured by the heat flux meter during this phase corresponds to the loss by natural convection from a horizontal...
flat plate at 1.8 g (approximately 200 W m\(^{-2}\)). A microgravity phase follows this hypergravity phase.

At \(t = 0\) s, a droplet is created by the injection of the fluid, and a transition regime is observed. The substrate temperature decreases rapidly by approximately 2 °C, and the heat flux increases to 1500 W m\(^{-2}\) (phase \(b\)). These changes are caused by the warming of the droplet coupled with the spreading of the liquid on the substrate. This transitional phase lasts between 5 and 8 s. After the quasi-stationary regime is reached (phase \(c\)), we observe that these two variables (temperature and heat flux) remain constant. The limiting phenomenon of evaporation, for a conductive substrate, is the vapour diffusion into the atmosphere (David, Sefiane & Tadrist 2007). The evolution of the evaporation mass flow rate is consistent with the theoretical model of quasi-steady diffusion-driven evaporation implemented with the temperature variation. This model assumes an isothermal droplet at the temperature of the substrate. The rate of evaporation is then expressed by (Hu & Larson 2002)

\[
-\frac{dm}{dt} = \pi RD\Delta C_v f(\theta),
\]

where \(R\) is the radius of the droplet, \(D\) the diffusion coefficient (for ethanol evaporating into an air at 835 mbar and 25 °C, this coefficient is \(1.5 \times 10^{-5}\) m\(^2\) s\(^{-1}\)), \(\Delta C_v = C_0 - C_\infty\), with \(C_0\) the vapour concentration at the liquid–vapour interface calculated by \(C_v(T_S)\) (concentration of saturated vapour at the substrate surface temperature), assuming that the interface temperature is almost equal to the substrate temperature in first approximation, and \(C_\infty\) the vapour concentration far from the droplet, considered null because of the large characteristic length of the cell compared to the droplet characteristic length. Finally, \(f(\theta) = 1.3 + 0.27\theta^2\) is a function that depends on the contact angle, taken according to the approximation of Hu & Larson (2002) (valid for angles between 0 and 90°). For angles below 40°, we note that \(f(\theta)\) is almost constant at approximately 1.3 (Sobac & Brutin 2011). Expression (3.1) is
then simplified to
\[-\frac{dm}{dt} \approx 4RD\Delta C_V. \quad (3.2)\]

Equation (3.2) demonstrates that the relationship between the evaporation flow rate and the contact angle becomes null, and the radius of the droplet is the only parameter that plays a role under similar atmospheric conditions. Because the radius of the droplet is constant throughout phase (c) (triple line pinned onto the substrate), the flow rate of evaporation is constant during this period. With a power balance, one can find the evaporation rate from the heat flux density, $Q$:

\[-\frac{dm}{dt} = \frac{QS}{L_V}, \quad (3.3)\]

where $L_V$ is the latent heat of vaporization, and $S$ is the wetting surface of the droplet with the substrate. Almost all of the droplets created have a diameter smaller than 8 mm and therefore leave a major part (at least 46%) of the heat flux meter dry. For the most disadvantageous case (smallest droplet: 6 mm and highest substrate temperature: 55 °C) the radiation exchange with this region represents almost 23% of the power used by the droplet to warm up and evaporate. Therefore, for the rest of the study, the radiative part has been subtracted from the heat-flux-meter signal so as to only consider the energy needed to evaporate the droplet. Moreover, under microgravity, because the buoyancy forces are null, the heat flux measured by the heat flux meter is the energy transferred to the droplet without any need for correction to account for the natural convection on the dry regions of the substrate. The heat flux applied to the drop is constant over time in phase (c). During the evaporation, we observe the systematic development of HTWs at the surface of the droplet. The next section is devoted to the study of these HTWs under microgravity and the comparison of their dynamics with those observed under normal gravity.

3.2. Comparison of fluid motion under normal and reduced gravity conditions

During the evaporation, thermocapillary instabilities develop. Figure 3 shows the HTWs on two droplets with a similar diameter ($R_{1g} = 2.81$ mm and $R_{\mu g} = 2.77$ mm) that are evaporating on equally heated substrates ($T_S = 35$ °C) under two levels of gravity. In both cases, the droplets of ethanol are hemispherical, and the initial contact angles ($\theta_i$) are less than 40°.

Utilizing the work by Garnier et al. (2006), the two cases can be compared using characteristic dimensionless numbers (table 1). The Rayleigh number, representing the buoyancy forces, is compared to the Marangoni number, representing the thermocapillary forces. In both cases shown, buoyancy forces are quite small, allowing thermocapillarity to dominate. In this configuration, the instabilities that develop are of type HTW$_2$.

The use of a microgravity environment induces a 113-fold decrease of the static Bond number ($Bo = \rho gh^2/\sigma$) and a 74-fold decrease of the dynamic Bond number. Under normal gravity, the thermoconvective effects are dominated by the thermocapillary ones but are not negligible ($Bd_{1g} = Ra/Ma \sim 0.08$) whereas under microgravity, only the thermocapillary effects exist ($Bd_{\mu g} \sim 0.001$).

Under normal gravity, a temperature gradient develops during the evaporation from the apex of the droplet and the contact line, resulting in a gradient of surface tension. This gradient then generates the thermocapillary instabilities. These HTWs propagate radially around the apex, where most of the evaporation occurs. The HTWs are spaced
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Figure 3. (Colour online) Infrared visualization of ethanol droplets presented in table 1 under normal gravity (a) and reduced gravity (b) (see movie 1 online available at journals.cambridge.org/flm).

by an almost constant angle along the axial symmetry of the triple line. Two different spatial dynamics were observed. The HTWs were found to run ortho-radially around the edge of the droplet either from a source point where they are established to a well where they collapse or all in the same direction but with no preferred direction (clockwise or anticlockwise), depending on the temperature of the substrate and the height of the droplet (Sobac & Brutin 2011).

Under microgravity, the temperature gradient is not as well defined as it is under normal gravity, but the apex maintains a temperature below the temperature of the triple line. In this configuration, HTWs have the same trend, but their movements are not as systematic as they are under normal gravity. The instabilities develop during the transitional phase (figure 2, phase b). During the quasi-stationary regime (phase c), the HTWs propagate from a source point to a well. These instabilities also propagate on the edge of the droplet, but the angle of propagation is not as constant as it is under normal gravity. This change in propagation could be caused by the vibrations of the aircraft, which cause significant fluctuations in the level of microgravity. Despite this lack of stability, the evolution of the number of HTWs is similar under both gravitational conditions.

As the droplet evaporates, the behaviour of the HTWs evolves. Because the formation of HTWs has been found to depend on the length of the apex–triple line interface of the droplet, a parameter that evolves over time, the number of HTWs decreases as the droplet evaporates. Figure 4(a) shows the evolution of the HTWs (number of HTWs ($N_W$) as a function of the normalized time) at different substrate temperatures and levels of gravity. Under the normal gravity condition, since the time available for evaporation is not limited, normalized time is obtained by dividing the time by the time of total evaporation of the droplet (approximately 240 s for a substrate at 55 °C). Unfortunately, under microgravity conditions, the time for total evaporation cannot be measured (only 22 s of evaporation is available under microgravity conditions). An estimation can be obtained by

$$t_{evap} = \frac{\rho V}{dmdt}.$$ (3.4)
The measurement errors on the microgravity points are more important than those on the normal gravity points because of this estimation calculated from the evaporation flux rate. This value is time-dependent but, since the allocated time is short, the evaporation flux rate is measured during the stationary part of the evaporation (phase $c$ on figure 2) when the triple line is pinned onto the substrate.

Sobac & Brutin (2012) observed a power-law decay in the number of HTWs, which depends on the substrate temperature and the volume of the droplet. These microgravity experiments show the same power-law evolution. To compare the decay for the two levels of gravity, the measurements were rescaled using relevant dimensionless numbers:

\[
\frac{N^*_w}{N_w} = \left( \frac{Bo}{Bd} \right) = \frac{\rho gh^2/\sigma}{Ra/Ma} = \frac{-d\sigma/dT}{\sigma \beta}.
\]
Since we are comparing the competition between gravitational and capillary forces the static Bond number will be used. Furthermore, the observed HTWs are thermocapillary-force originated. Consequently, the dynamic Bond number is involved since it compares the ratio of Rayleigh and Marangoni numbers.

Equation (3.5) shows that the dimensionless number of waves is not a function of any characteristic dimension but involves only the surface tension, its variation with temperature, and density. The quantity \( N_{W}^* \) is shown in figure 4(b) for the same series of experiments. A grouping of values on the line \( y = a x^b \) with \( a = 10.0 \pm 0.5 \) and \( b = -0.26 \pm 0.02 \) (black dashed line) is observed. The errors bars have not been displayed in the figure because of their exaggerated spreading on the logarithmic scale (approximately 10% error for points in normal gravity versus 25% error for the microgravity points). We demonstrate a very good agreement between the results with and without gravity. The dimensionless analysis enables all the data to be scaled whatever the substrate temperatures, the droplet sizes and the gravity levels are. The history of the substrate (wear of the substrate) or the imperfect reproducibility of droplet formation could explain the slight scatter of the data. The atmospheric working pressure could also play a role.

4. Concluding remarks

The resources employed in this experimental study allow the comparison of two droplets of ethanol evaporating from a heated substrate under two levels of gravity. The results obtained under microgravity confirm those obtained on Earth. The weakness of gravitational forces in the microgravity conditions confirms that the development of HTWs is purely due to the thermocapillary forces.

During the quasi-stationary regime, the HTWs have the same behaviour under microgravity as under normal gravity with a motion around the apex of the droplet from the source point to the well. The differences in shapes, sizes and movements of the HTWs have been eliminated by the use of dimensionless numbers that take into account the temperature gradient of the substrate and the radius of the droplet for the different gravitational conditions. The temporal evolution of the HTWs is similar regardless of the gravity level and follows a power-law decay.

We propose a scaling law based on both Bond numbers, static and dynamic, to scale our results. A very good agreement is observed and confirms the capillary-driven nature of the HTWs. To obtain more details and to complete these results, this experiment will be performed in a scientific satellite to monitor the total evaporation of a droplet with gravity levels thousands of times lower than those obtained in parabolic flight with a longer range of effective working times.

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Supplementary movies

Supplementary movies are available at journals.cambridge.org/flm.
REFERENCES


