Marangoni-driven instabilities of an evaporating liquid-vapor interface

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Marangoni-driven instabilities of a liquid-vapor interface of ethanol formed in a horizontally oriented capillary tube of 600 μm diameter are described. Instabilities of the interface are reported as well as instabilities of the liquid flow underneath the meniscus. The experimental results consist of visual observation of the interface, microscale particle image velocimetry measurements of the liquid flow and ir temperature measurements of the interface. The instabilities are found in both the flow structure and the interfacial temperature which present a periodic oscillatory pattern with a characteristic frequency of about 5 Hz. The interface also oscillates periodically, having a characteristic frequency of about 1.4 Hz. The differential evaporative cooling along the extended meniscus in the triple-line region produces a temperature difference which sustains the liquid-thermocapillary Marangoni-driven convection. A linear stability analysis based on a one-sided model, modified to take into account evaporation, is used to show that the self-induced temperature difference at the triple-line region is responsible for the observed interfacial instabilities. The instabilities in the flow pattern are due to competition between the surface tension driving force and gravity and are also found to be influenced by the meniscus instabilities.

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I. INTRODUCTION

It is well established that the role of surface tension becomes important at the microscale [1]. One important parameter characterizing the competition between surface tension and gravitational forces is the capillary length $l_c=\sqrt{\sigma/\rho g}$. Here, l_c is the capillary length, σ the surface tension, ρ the liquid density, and g the gravitational acceleration. When the characteristic dimension of the system drops below 1 mm (typical value for the capillary length of organic liquids) surface tension forces dominate.

Usually thermocapillary driven problems are studied in cases where a temperature gradient along a liquid-vapor interface is created by imposing a lateral temperature difference between the two end walls of a shallow liquid layer [2–4]. The present work is somewhat different as the temperature difference at the interface is self-induced because of differential evaporation.

In a previous work [5] it was demonstrated that for a liquid undergoing evaporation in a horizontally oriented capillary tube the liquid flow pattern is distorted in the vertical diametrical sections of the tube with respect to the axisymetric patterns found in horizontal diametrical sections and it was argued that this is presumably due to the action of gravity. The flow pattern was characterized by the use of microscale particle image velocimetry (μ-PIV), and it was shown that the flow changes periodically. In this work [5] various tube sizes and two liquids are investigated. It is observed that for a particular tube size and using ethanol, the oscillations of the flow pattern are accompanied by macroscopic oscillations of the liquid-vapor interface. In the following we will also refer to the liquid-vapor interface as a meniscus because it is formed in a capillary tube. Buffone *et al.* [5] and Buffone and Sefiane [6] argue that thermocapillary flow is driven by temperature differences established along the meniscus because of differential evaporative cooling. The existence of an operating contact-line region at the tube wall causes the evaporation rate and consequently the heat flux to peak in that region rather than in the meniscus center. This difference in evaporation rate provokes a self-induced temperature difference along the meniscus and consequently of surface tension that drives the observed liquid convection. Buffone and Sefiane [7] also performed temperature measurements using ir measurements to corroborate this idea of temperature differences. This work demonstrated through a systematic investigation involving various capillary tube sizes and different volatile liquids that the evaporative cooling effect near the triple line is higher for the smaller tube size and the use of more volatile liquids. The temperature measurements clearly demonstrated that the liquid-thermocapillary convection is sustained by the heat-transfer mechanism set through the capillary wall allowing heat to come into the system from the external environment surrounding the capillary tube.

Marangoni instabilities arise from temperature variations established towards the liquid-vapor interface that provoke the appearance of waves on the meniscus, ultimately causing the interface to oscillate [8]. Thermocapillary convection instabilities are due to hydrothermal waves appearing on the interface that provoke unsteadiness of the liquid flow as reported by Riley [4], Smith and Davis [9,10] for liquid layers, and Carotenuto *et al.* [11] for liquid bridges. It has been demonstrated in past studies that these oscillations are generated if a temperature threshold is reached. Different cases have been experimentally analyzed for instabilities of evaporating shallow films [12,13] and of heated meniscus in vertically oriented capillary tubes [14]. In the present investiga-

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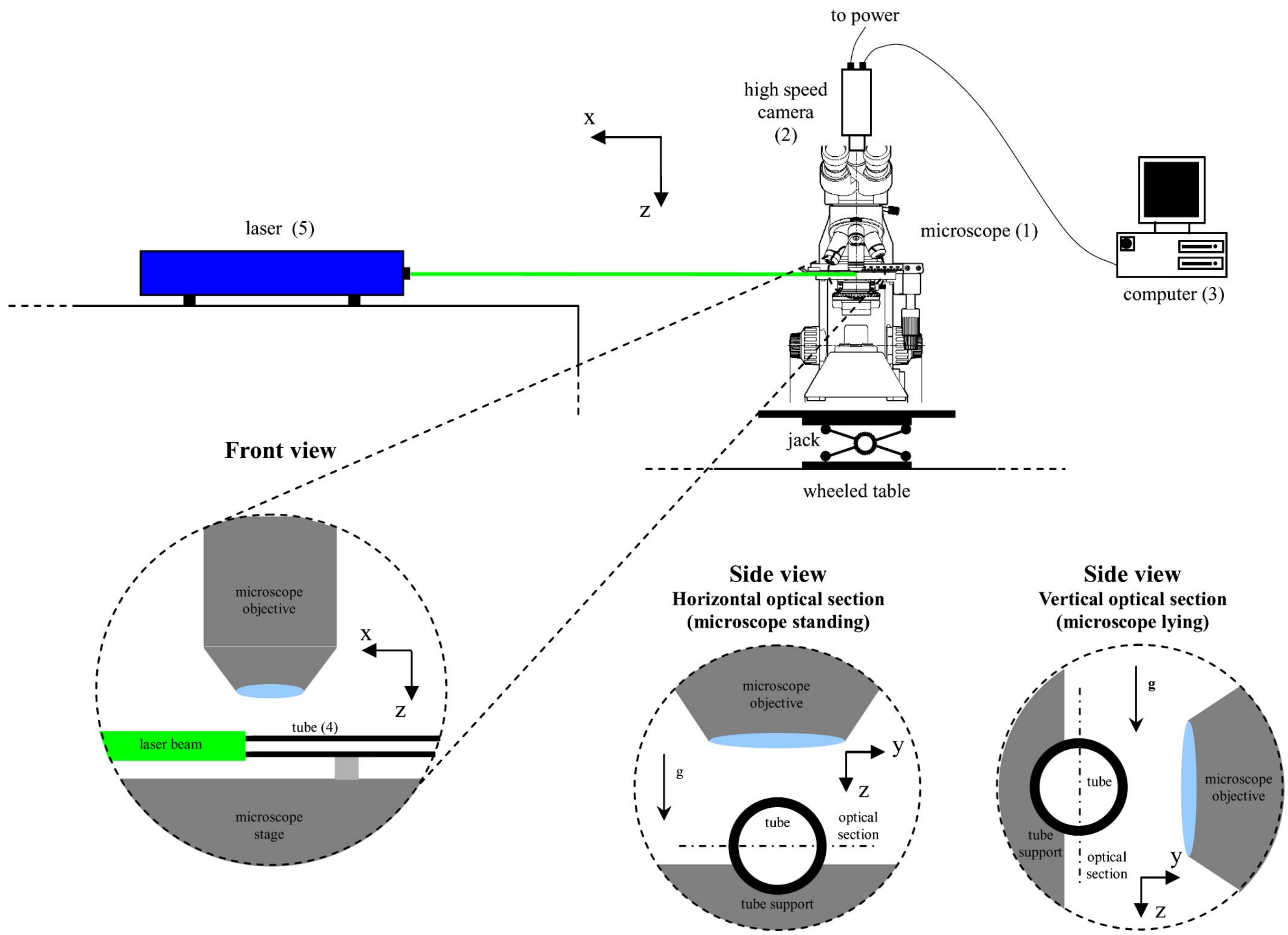

FIG. 1. Schematic of the experimental setup for the meniscus visual observation (without laser) and μ-PIV flow investigation.

tion a capillary tube made of borosilicate glass with an internal diameter of 600 μm (and wall thickness of 100 μm) was partially filled with ethanol, having its axis horizontally oriented; one of the two menisci formed is positioned at one of the two capillary mouths, and the other meniscus is left free to move inside the tube, while evaporation is taking place from both menisci. After initial filling, the tube is no longer refilled to account for the mass lost during evaporation. The attention is focused on the meniscus fixed at the capillary mouth.

The present work is a study investigating further the meniscus oscillations as they are presumably the experimental evidence of what is referred as either Marangoni or hydrothermal instabilities. We wish here to give more insight into the meniscus instabilities and see if there is any coupling effect with the flow instabilities. The characterization of such instabilities is of paramount importance because many industrial applications (heat pipes, porous media, boiling and condensation in microchannels, welding, stem cell culture) rely on the phase change in confined spaces. We will use different techniques for this investigation, starting with the meniscus visual observation by the use of a high-speed charge-coupled-device (CCD) camera. μ-PIV is used to characterize the liquid-flow structure, and the ir technique is employed to map the interfacial temperature. A linear stability analysis, based on the model developed in Pratt *et al.* [14], modified here in order to take into account the evaporation, is also adopted to show that the stability criterion is violated and the meniscus oscillation justified for the present case (600 μm tube and ethanol), but not for the other cases presented in Buffone *et al.* [5].

II. EXPERIMENTAL FACILITIES AND SETUP

Visual observation of the meniscus oscillations is undertaken by the use of a high-speed camera (Phantom camera v.4.3) necessary in order to quantify the fast meniscus movement. The μ-PIV investigation is carried out with the use of a similar setup with the addition of a laser to uniformly illuminate the flow inside the capillary. The experimental setup for visual observation and μ-PIV is outlined in Fig. 1 and comprises the microscope (1), the high-speed camera (2), a PC for data acquisition and storage (3), the sample tube (4), and the argon-ion green light ($\lambda = 532$ nm) laser (5); this latter is used instead of white light for the μ-PIV analysis as the expected scattering from the particles is of a better quality when illumination with coherent light is used. For visual observation of the meniscus oscillations also a different setup was used to prove that the oscillations are not caused by the laser; for this test microscope ordinary light was employed

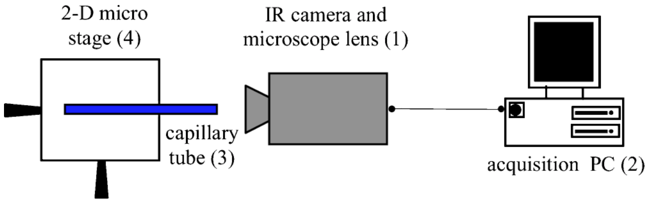

FIG. 2. Sketch of the experimental setup for ir measurements.

and an ir filter was used between the microscope light and condenser to avoid external heating of the system. The experimental setup for the ir investigation is sketched in Fig. 2 and is composed of the ir camera (1), a PC for image acquisition and post-processing (2), the tube sample (3), and the microstage (4). The ir camera is equipped with an ir microscope close-up lens. Both these setups and techniques are extensively explained in two other works [5,7]. The flow and temperature investigations are carried out separately because of the small tube sample involved. In fact, to visualize the liquid flow inside the tube a microscope is required, and because of the microscope design used, no space is left to fit in the ir camera. However, extensive preliminary tests were made to show the experimental reproducibility. A vector spatial resolution of 0.64 μm is obtained for the μ-PIV study and a temperature spatial resolution of 31.25 μm is achieved with the ir camera. The ir camera has a thermal sensitivity of 20 mK at 30 °C and an accuracy of 1% for temperatures up to 150 °C.

III. RESULTS AND DISCUSSION

The meniscus oscillations were analyzed through visual observation. Figure 3 shows an image of the tube next to the interface highlighting the meniscus position with respect to a reference line drawn (*A*-*A*). Note the particles dispersed in the liquid scattering the laser light. It was observed that the meniscus moves and the interface oscillations are clearly brought to light in the next figure, Fig. 4, where the meniscus

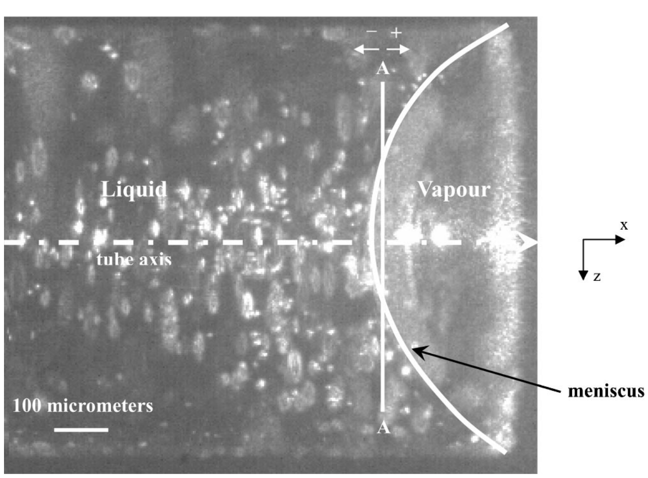

FIG. 3. Visual observation for the meniscus oscillations (meniscus center $z=0$ with respect to line *A*-*A*).

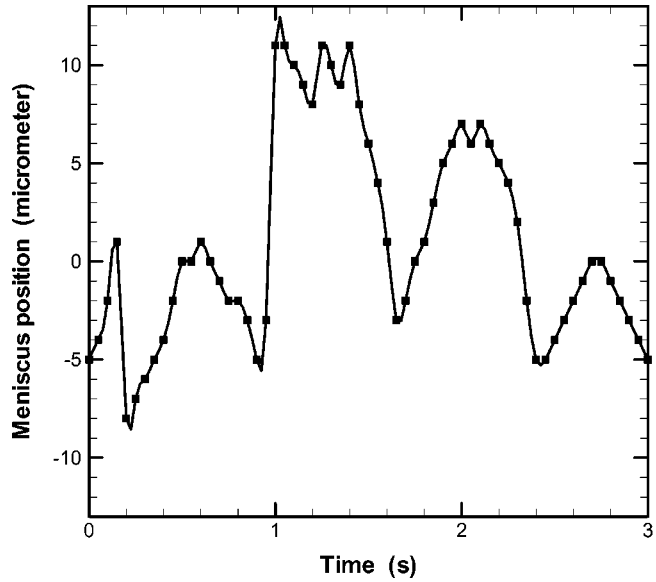

FIG. 4. Meniscus position at $z=0$ with respect to the *A*-*A* reference line of Fig. 3.

distance from the reference line (*A*-*A*) versus time is plotted. Meniscus positions are considered positive at the right-hand side of line *A*-*A* as shown in Fig. 3. The meniscus oscillations appear to have a periodic pattern with an average frequency of about 1.4 Hz ($\Delta t \sim 0.7$ s).

The two-dimensional (2D) μ-PIV measurements are performed on a horizontal and vertical diametrical section of the meniscus as shown in the insets of Fig. 1. We have shown in a previous work [5] that the flow pattern in horizontal sections of the meniscus is closer to what one would expect for purely thermocapillary driven flows. In fact, the toroidal-shaped Marangoni cell appearing in the liquid phase of the meniscus should have a symmetric pattern with respect to the tube axis. However, what the horizontal and vertical diametrical sections show is slightly different. In particular, the horizontal section (Fig. 5, frame 1) shows a symmetrical flow pattern, whereas the vertical one (Fig. 6, frame 1) is not. We have concluded [5] that the flow asymmetry in the vertical diametrical sections could be due to the action of gravity. Figures 5 and 6 are two time sequences of velocity vector maps with superimposed vorticity map and streamlines. The tube walls and axis and the meniscus are also drawn as indicated in frame 1 of Fig. 5. In what follows, we will assume as a measure of flow strength the vorticity value defined as the curl of velocity; vorticity is assumed positive for an anticlockwise vortex. Note that the vorticity in Figs. 5 and 6 is scaled with the extreme values of each frame. Figure 7 reproduces the peak vorticity values for both horizontal and vertical diametrical sections versus time. A portion of Fig. 4 is included in Fig. 7 to show the meniscus oscillations. It is evident from Fig. 7 that the flow strength also varies periodically with a average mean frequency of 5 Hz ($\Delta t \sim 0.2$ s). From this figure it is also evident when the meniscus oscillations take place (the vorticity suddenly peaks just before these events). In fact, the tracers are first attracted towards the meniscus, producing a compression of the roll structure, and consequently the vorticity strengthens (see Fig. 5, frames

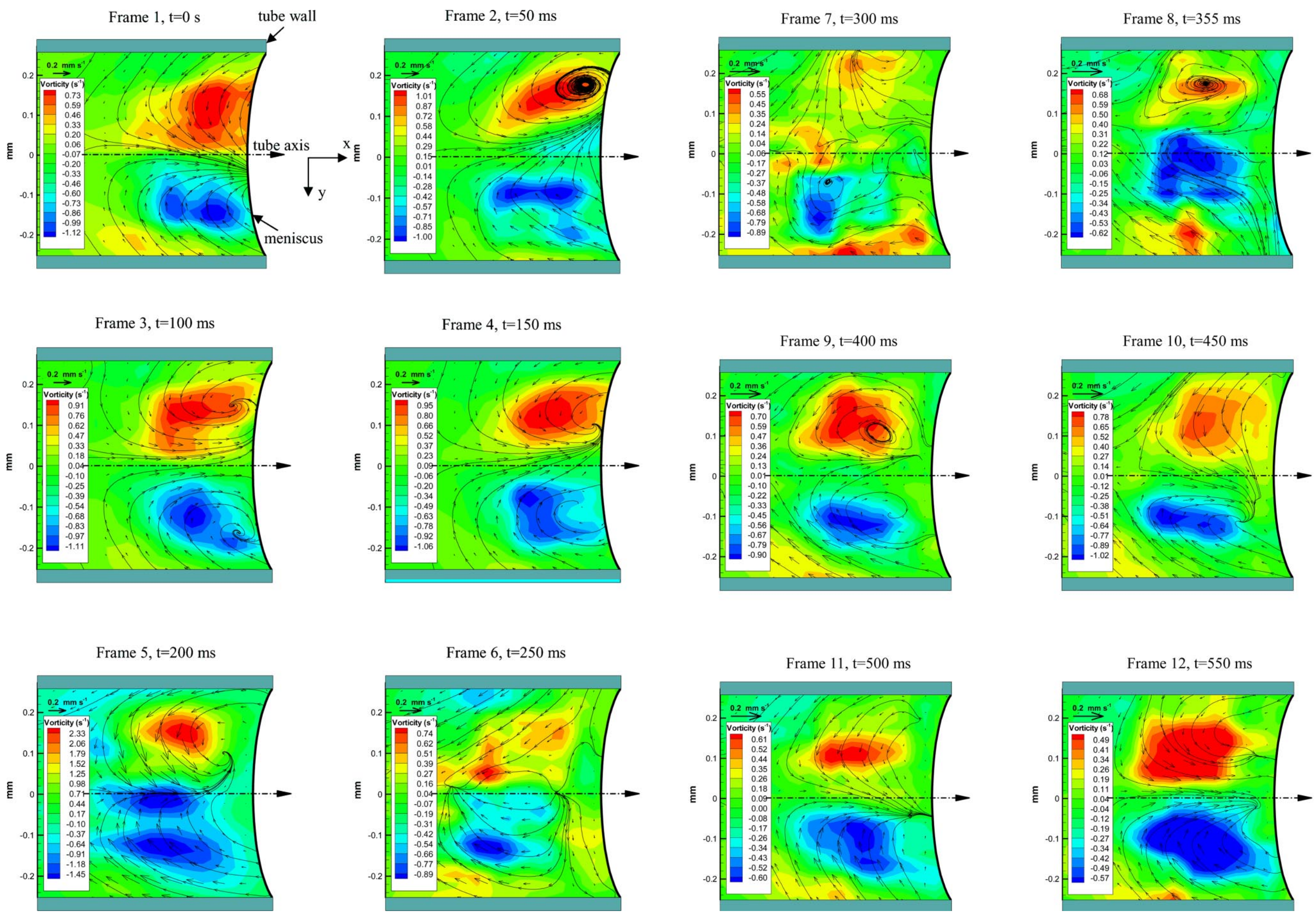

FIG. 5. Time sequence of 12 PIV analysis frames (horizontal diametrical tube section).

1–5). In the subsequent frame 6 the tracers are pushed away from the interface as the meniscus moves deeper inside the tube and the roll structure is almost destroyed (frames 6–7). In the subsequent frames the roll structure is rebuilt as the meniscus moves back. In a previous work [5], through a systematic study involving various tube sizes and two evaporating liquids, we had clearly shown that the flow pattern in vertical diametrical sections of the meniscus is oscillatory. However, the flow in horizontal diametrical sections was found to be almost steady. The case being investigated here is more interesting as the meniscus is also oscillating and the flow in the horizontal diametrical section is greatly affected. In addition, there is an important coupling between flow and temperature fields because the Prandtl number expressing the ratio of kinematics to thermal diffusivity is of the order of ~ 16. The large flow-temperature coupling is therefore thought to be responsible for the oscillatory flow pattern experienced also in the horizontal diametrical section because of the flow oscillations taking place in the vertical diametrical section. The oscillatory pattern in the vertical diametrical section is a direct consequence of the competition between the surface tension driving force and gravity as explained in detail in Buffone *et al.* [5].

The ir results are presented in Figs. 8 and 9. Figure 8 is an ir image of the meniscus surface showing the temperature map. The tube walls are clearly marked with dashed lines. Note the axisymmetric temperature map with respect to the vertical diametrical section (*C*-*C*) and the asymmetric temperature map with respect to the horizontal diametrical section (*D*-*D*). As explained in detail in Buffone and Sefiane [7], this is a consequence of the flow field structure (see also Figs. 5 and 6). The ir system used allows for movie storage with a maximum time resolution of 750 Hz. It is worth mentioning that not the whole curved meniscus lies in the ir camera depth of focus [7]. We have seen from Fig. 4 that the meniscus movement is limited to ± 12 μm; therefore, we can assume that the points of interest close to the tube internal wall lie in the ir camera depth of focus (100 μm) at all times. The temperature of point *B* in Fig. 8 is reported versus time in Fig. 9. Again, an oscillatory periodic pattern is present also for temperature. The average main frequency is about 5 Hz ($\Delta t \sim 0.2$ s); again, the meniscus oscillations can be clearly spotted (1, 2, and 3 events marked in Fig. 9) with a frequency of about 1.4 Hz ($\Delta t \sim 0.7$ s). These values of frequency are close to both the meniscus oscillation and flow pattern oscillation frequency values found in Figs. 4 and 7.

We have mentioned earlier that the present case can be characterized as either a hydrothermal or Marangoni instability. In the past many researchers [4,9,10] have predicted and reported the existence of hydrothermal waves propagating on the surface of shallow liquid films experiencing thermocapillary effects. However, the present case is somewhat different from those. In fact, here the meniscus is not flat and it is also oscillating. In addition, the heat constraint imposed in

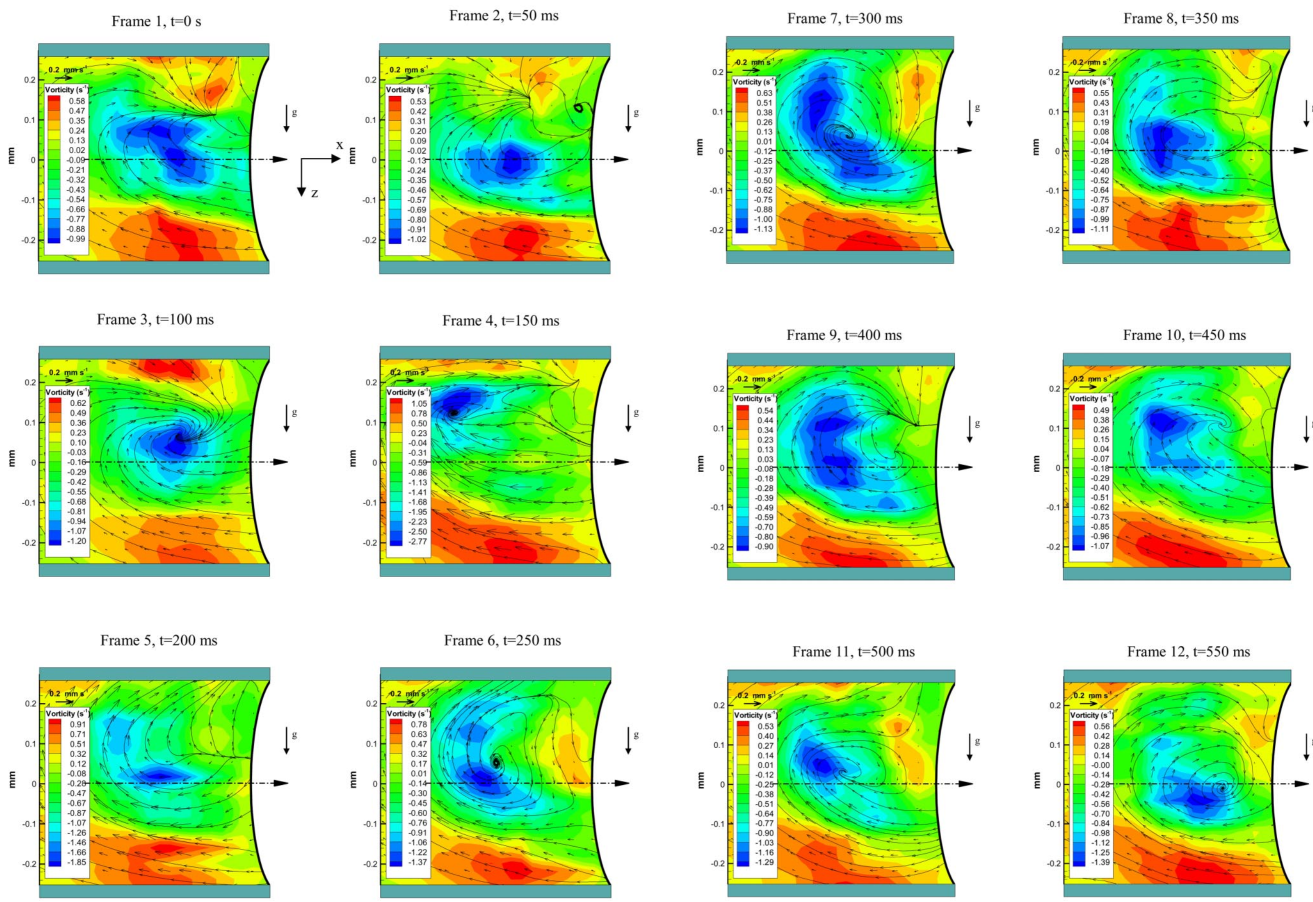

FIG. 6. Time sequence of 12 PIV analysis frames (vertical diametrical tube section).

those studies is replaced here by the self-created temperature difference because the interface is undergoing evaporation. As discussed in Buffone and Sefiane [6], this self-induced temperature difference is due to the stronger evaporation close to the meniscus triple line with respect to the meniscus center that experiences a lower evaporation. This leads to a strong nonlinear variation of temperature along the interface as reported by previous ir measurements [7]. All these practical difficulties make it difficult for the present case to show if there are hydrothermal waves traveling along the meniscus surface from the cold region at the meniscus wedge to the hot region at the meniscus center. For an evaporating drop as shown by Kavehpour *et al.* [8], when the drop height has fallen below a certain value Marangoni instabilities arise

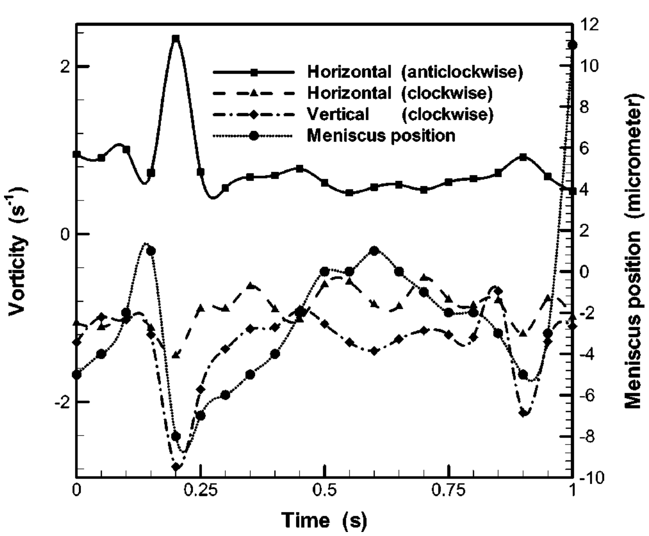

FIG. 7. Vorticity values for horizontal and vertical diametrical sections and meniscus position (this latter reproduced from Fig. 4).

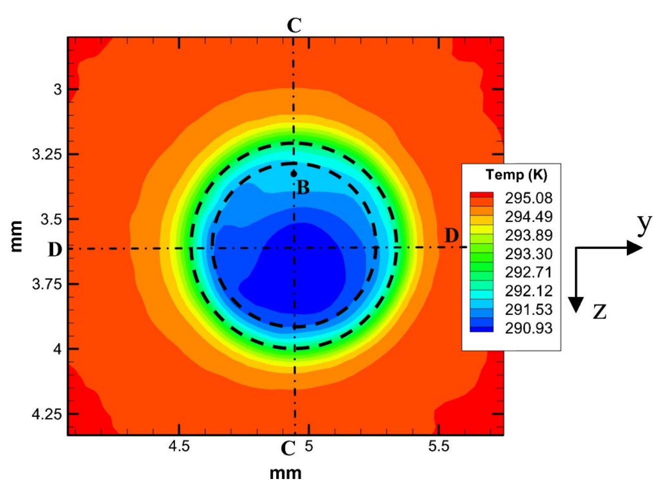

FIG. 8. ir image of capillary tube mouth cross section (the two dashed circles are the tube walls).

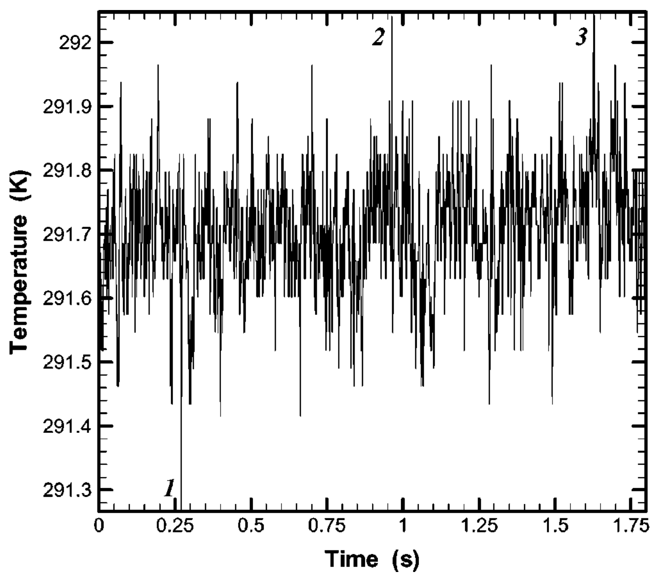

FIG. 9. Temperature evolution of point *B* in Fig. 8.

from temperature variations established normal to the liquid-vapor interface that provoke the appearance of waves on the liquid surface, eventually causing the interface to oscillate. Kavehpour *et al.* [8] show that these instabilities are not present in droplets of nonvolatile liquids. Therefore, for the time being we conclude that the present study is a case of Marangoni-driven instabilities, although we cannot rule out the existence of hydrothermal waves, and refer to this as a case of evaporative-driven hydrothermal instability convection. More experimental work is certainly needed to clarify this point.

IV. LINEAR STABILITY ANALYSIS

A linear stability analysis based on the model developed by Pratt *et al.* [14] is employed here to describe the meniscus oscillations observed experimentally. Their stability analysis has been developed for a heated meniscus formed in vertically oriented capillary tubes. Although that case seems to be different from the present one where a horizontally oriented tube was investigated, the model can still be applied because it concerns only the meniscus region close to the contact line (what Pratt [15] calls the extended meniscus). As pointed out by Buffone *et al.* [5], Pratt [15], Potash and Wayner [16], and Swanson and Herdt [17], the meniscus region close to the triple line is of paramount importance to describe the heat and mass transfer from a curved liquid-vapor interface. In fact, most of the evaporation takes place in this region of the meniscus where the disjoining forces are balanced by the thermocapillary ones. In order to describe the stability of an evaporating meniscus formed in capillary tubes, again this region becomes the focus of attention. As shown by many authors [15,16], the gravitational forces in this region of the meniscus can be neglected; therefore, the same analysis performed by Pratt *et al.* [14] for a vertically oriented tube can be applied to the present case where the tube was horizontally oriented.

Another important difference between the case of Pratt *et al.* [14] and the present one is that the meaning of meniscus instability in their study is different from ours. In Pratt *et al.* [14] the meniscus becomes unstable when it is pushed down the tube beyond a threshold of an imposed temperature gradient. In the present case we regard as instabilities the meniscus oscillations.

The stability analysis developed in Pratt [15] starts from the conservation equations of mass, momentum, and energy. The system of governing equations with relevant boundary conditions is transformed in a dimensionless system which is then expanded in terms of the meniscus slope and a linearization method is employed. The resulting system is then combined to get an evolution equation for the meniscus film thickness which depends on both time and position, this latter in the direction of the tube axis. Upon some assumptions this evolution equation is then perturbed and a stability condition is obtained. Details can be found in Pratt [15]. Here, we will summarize the procedure and focus on the conclusions. For the system under investigation, we can concentrate on the liquid side only (one-side model) as the physical parameters for thermocapillary driven phenomena lead to the following [15,18]:

$$\frac{\rho_v}{\rho_l}, \frac{\mu_v}{\mu_l}, \frac{k_v}{k_l} \cong 0. \tag{1}$$

Here, ρ stands for density, μ for dynamic viscosity, and k for thermal conductivity, and the subscripts ν and l stand for vapor and liquid, respectively.

Without reproducing all the calculations shown in Pratt [15] we report here only their conclusions. Basically, Pratt [15] concludes that the stability criterion for an evaporating meniscus lying on a temperature gradient is expressed as

$$\frac{\mathrm{Ma}}{4\,\mathrm{Pr}} \geqslant \Pi^*, \tag{2}$$

where Ma is the Marangoni number, Pr the Prandtl number, and Π the disjoining pressure.

Equation (2) says that the system becomes unstable when the thermocapillary effects overcome the disjoining ones. Pratt [15] also suggests rewriting the above inequality in terms of the physical variables, obtaining the following stability condition:

$$\Delta T \geqslant \frac{2}{\left(\frac{\partial \sigma}{\partial T}\right)} \left(\frac{2\overline{A}^{1/2}\sigma}{r}\right)^{2/3}, \tag{3}$$

where T is temperature, A the Hamaker constant, σ the surface tension, and r the tube radius.

The above inequality suggests that the meniscus is more stable at smaller tube sizes and at lower temperatures—this latter because for the majority of liquids, surface tension increases decreasing the temperature. The above inequality gives us a criterion to evaluate the stability of the evaporating meniscus lying in a self-induced temperature gradient.

TABLE I. Experimental, stability, and modified stability temperature gradients.

Liquid	Tube size i.d. (μm)	∇T_{expt} (K m^{-1})	∇T_{stab} (K m^{-1})	∇T^{*}_{stab} (K m^{-1})
Ethanol	600	4965	1370	4495
	900	2046	693	1516
	1630	164	256	309
Methanol	600	7447	1390	9709
	900	2983	705	3283
	1630	298	260	668

Applying the above criterion to the present case gives a temperature gradient of 1370 K m^{-1} above which Marangoni instabilities set in. From the ir measurements performed it is possible to evaluate the temperature gradient close to the meniscus triple line to be 4965 K m^{-1}. This value is more than 3 and 1/2 times greater than the one given by the stability criterion; therefore, meniscus instabilities set in. Because of the ir systematic study involving various tube sizes and two liquids previously undertaken [7], it is possible to compare the stability criterion with the measured temperature gradients. Table I reports the temperature gradient experienced during experiments and the one given by the stability criterion. It appears evident that most of the cases investigated in Buffone and Sefiane [7] are supercritical apart from the largest tube size. Therefore, all these cases should present interfacial instabilities. However, this is not the case as shown in the flow-field investigation presented in Buffone and Sefiane [6].

It is evident that some new parameters must act to allow supercritical conditions to be kept without exhibiting interfacial instabilities. In addition, why does methanol, having a larger $\nabla T_{expt}/\nabla T_{stab}$ ratio, not show interfacial instabilities? It is worth remembering that as evaporation takes place at the interface, a Poiseuille flow towards the interface is established inside the tube to supply the liquid evaporated. This flow is thought to have a stabilizing effect. The evaporation mass flux is larger for an increased liquid volatility and reduced tube size [5]. Therefore, the stabilizing effect of the Poiseuille flow is larger for methanol and smaller diameters. In order to take into account these effects we introduce a dimensionless vapor pressure $P^{*}=P_{\nu}/\rho g r$, which is the ratio between the saturated vapor pressure (P_{ν}) and a hydrostatic pressure. P_{ν} takes into account the fact that more volatile liquids have larger vapor pressure, and r takes into account that, as we have demonstrated in a previous work [6], the evaporation mass flux is larger for smaller diameters. If we multiply this dimensionless vapor pressure divided for an accommodating coefficient of 1000, we get a new stability limit value (∇T^{*}_{stab}) also reported in Table I. It is clear now that methanol is undercritical for all tube sizes and ethanol is supercritical at 600–900 μm. This may explain the meniscus instabilities experimentally observed in the present work for 600-μm tubes.

V. CONCLUSIONS

This work shows an experimental study of Marangoni-driven instabilities arising from differential evaporative cooling effects along the liquid-vapor interface of ethanol formed in a horizontally oriented capillary tube of 600 μm diameter. Instabilities of the interface are accompanied by instabilities of the liquid flow underneath the meniscus. Visual observation of the interface along with μ-PIV measurements of the liquid flow and ir temperature measurements of the interface are presented and discussed. Instabilities are found in both the flow structure and the interfacial temperature which present a periodic oscillatory pattern with a frequency of about 5 Hz. In addition, meniscus instabilities presenting an oscillatory behavior with a characteristic frequency of about 1.4 Hz are observed. A standard linear stability analysis shows that in the present case the meniscus is unstable but fails to demonstrate why other cases investigated in Buffone *et al.* [5] are stable instead. A modified linear stability analysis taking into account evaporation (through the introduction of a dimensionless vapor pressure) is applied to show that the temperature difference—self-induced because of differential evaporative cooling along the extended meniscus in the triple-line region—is responsible for the observed meniscus instabilities. This modification clearly predicts that the present case should be unstable whereas the others presented in Buffone *et al.* [5] are stable.

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[1] V. G. Levich and V. S. Krylov, Annu. Rev. Fluid Mech. **1**, 293 (1969).
[2] D. Villers and J. K. Platten, J. Fluid Mech. **234**, 487 (1992).
[3] A. G. Kirdyashkin, Int. J. Heat Mass Transfer **27**, 1205 (1984).
[4] R. J. Riley, Ph.D. thesis, Georgia Institute of Technology, 1996.
[5] C. Buffone, *et al.*,Fluid Phys. (to be published).
[6] C. Buffone and K. Sefiane, Int. J. Multiphase Flow (to be published).
[7] C. Buffone and K. Sefiane, Exp. Thermal Fluid Sci. (to be published).
[8] P. Kavehpour, B. Ovryn, and G. K. McKinley, Colloids Surf., A **206**, 409 (2002).
[9] M. K. Smith and S. H. Davis, J. Fluid Mech. **132**, 119 (1983).
[10] M. K. Smith and S. H. Davis, J. Fluid Mech. **132**, 145 (1983).
[11] L. Carotenuto, D. Castagnolo, C. Albanese, and R. Monti, Phys. Fluids **10**, 555 (1998).
[12] J. P. Burelbach, S. G. Bankoff, and S. H. Davis, J. Fluid Mech. **195**, 463 (1988).

[13] S. G. Bankoff (unpublished).
[14] D. M. Pratt, J. Brown, and K. P. Hallinan, J. Heat Transfer **120**, No. 1, 220 (1998).
[15] D. M. Pratt, Ph.D. thesis, University of Dayton, 1996.
[16] J. M. Potash and J. P. Wayner, Int. J. Heat Mass Transfer **15**, 1851 (1972).
[17] L. W. Swanson and G. C. Herdt, J. Heat Transfer **114**, 434 (1992).
[18] S. H. Davis, Annu. Rev. Fluid Mech. **19**, 403 (1987).