Astable regime in electrosprays

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Astable regimes are common in nonlinear systems ranging from electrooptic devices to cardiac rhythms under environmental stress. Electrosprays exhibit three main axial regimes (dripping, pulsating, and cone-jet). It is generally accepted that the transition between the pulsating and cone-jet regimes is sudden, accompanied by an abruptly enhanced spray current. Here we present an alternative to this scenario, in which the electrospray follows a new chaotic astable path to the cone-jet regime. The astable regime could be explained as a result of transitions between a limit cycle (pulsating regime) and a fixed point (cone-jet regime) in a subcritical Andronov-Hopf bifurcation due to small external perturbations (noise). With the introduction of this regime, a broader view of the diverse axial regimes becomes possible based on nonlinear dynamics that enables their consistent classification.

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I. INTRODUCTION

Astable regimes are common in nonlinear systems ranging from electrooptic devices [1] to cardiac rhythms under environmental stress [2]. Many systems in diverse branches of the physical and life sciences exhibit astable behavior including coupled lasers [3], quantum systems [4], and neural networks [5]. Here we demonstrate that a simple electrohydrodynamic arrangement used in electrosprays follows astable behavior during switching between pulsating (limit cycle) and jet ejection modes. We show that unlike the transitions of a dripping faucet between simple dripping and jetting [6], the electrospray may follow an astable path that flip-flops between pulsating and jetting.

After Fenn's landmark discovery of macromolecular ion production through electrosprays [7] the interest in understanding the fundamentals of this process was reinvigorated. Ion production in electrosprays is based on the electrification of a liquid meniscus, which results in the production of finely dispersed charged droplets. The process starts at the emitter-liquid interface, where charge is produced electrochemically. The electric field promotes the charge migration away from the electrode partly through the solution bulk, partly along the liquid surface. Electrified droplets pinch off either from a protruding meniscus or from a jet emerging from a conical meniscus. The increased surface area encourages solvent evaporation, raising the charge density on the droplets. A Rayleigh discharge, i.e., the expulsion of a jet carrying a relatively small amount of liquid and a relatively large amount of charge, occurs when the surface charge density reaches a critical value. Eventually the gas phase ions form by crossing the liquid-gas interface or after all the solvent molecules around them evaporate.

In the first systematic study of the electrospray phenomenon, Zeleny exposed several regimes by running the spray current through a telephone receiver and listening to the individual discharges [8]. He also took the first reported fast images of the liquid meniscus under the influence of electric and hydrodynamic forces at the tip of a glass capillary [9]. One of the earliest spray current measurements can be traced back to Hendricks' efforts to develop space propulsion systems based on electrosprays [10,11].

Taylor systematically characterized a unique electrospray regime, in which the electrified liquid meniscus took the shape of a cone [12]. The term "Taylor cone" was coined to honor his analysis that demonstrated that a stable liquid cone with a semivertical angle of 49.3° could form. Taylor's original model was improved by Fernandez de la Mora [13], who showed that several factors, including liquid loss through the cone and space charge effects, might result in cones established at different semivertical angles [14].

Several research groups tried to establish nomenclature for the diverse variety of observed electrospray regimes. The most commonly cited reviews, written by Cloupeau and Prunet-Foch [15,16], relied on the morphology of the meniscus and the ejected liquid. This classification was followed by a few others taking a similar approach [17,18], or advocating a semiphenomenological perspective [19]. The most insightful classification of axisymmetric regimes was suggested by Juraschek and Röllgen based on current measurements [20]. They placed the pulsating (axial II) and the cone-jet (axial III) regimes in different categories, as opposed to the previous approach in which the former was a variant of the latter. They also described the burst regime (axial I) that typically exhibited two periods. Incidentally, the sequence of regimes they observed did not include the dripping regime prevalent at low voltage values.

Confusing classifications and the lack of consensus on the nomenclature are still major factors undermining the clear understanding of an arguably complex process. We suggest that all observed axial regimes of electrospray could be regimented as dripping, pulsating and cone-jet regimes, or as transitions between them. For example, the burst regime can be viewed as the transition between the dripping and the pulsating regimes. The dripping regime at low electric fields was thoroughly characterized by the Basaran group using fast imaging [21]. We used a combination of current measurements and fast imaging to study the transitions from dripping via the onset of bursts [22] to the pulsating [23,24] regime. This regime change involves period doublings,

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order-chaos-order transitions and logarithmic self-similarity in time [22]. Due to the underlying chemical processes (electrode reactions) the spraying modes also have a profound effect on the nature of the produced ions [25].

While increasing the high voltage, the electrospray exhibits a sequence of regimes, but not necessarily all of them. For example, in the study of Juraschek and Röllgen [20] the electrospray did not exhibit the dripping regime, while in the experiments of Alexander *et al.* [26] the electrospray switched from dripping to pulsating without experiencing the burst regime. Several papers reported [20,27] a direct transition between the pulsating and the cone-jet regimes. Here we describe an astable regime, which is an alternative route an electrospray can follow from the pulsating to the cone-jet regime. We also show that the existence of this regime enables the construction of a self-consistent classification of axial spraying regimes.

II. EXPERIMENTAL METHODS

Since there are no major changes in the experimental setup compared to our latest report [25], only a brief description follows. Solutions were prepared by acidifying 50% methanol with 0.1% (σ=35.87±0.14, pH=3.89±0.02) and 1.0% (σ=100.33±0.4 μS/cm, and pH=3.35±0.01) acetic acid with the measured conductivities and pH values mentioned in parentheses. They were effused by a low noise syringe pump through stainless steel emitters with tapered, od/id=320/100 μm, blunt, od/id=260/130 μm, and 60° oblique-cut od/id=260/130 μm, tips.

High voltage from a regulated power supply was directly applied to the emitter. Translation stages ensured accurate positioning of the emitter against a flat polished stainless steel counterelectrode. The distance d to the counterelectrode was 12 mm unless otherwise specified. The electrospray current was measured on the counterelectrode by a WaveSurfer 452 digital oscilloscope. Images of the liquid meniscus were captured by a fast digital camera through a long-distance microscope. The illumination system was based on fluorescence from a laser dye solution (Coumarin 540A) following excitation with a nitrogen laser. This arrangement helped us to capture images with a 7 ns exposure time, almost four orders of magnitude shorter than the shutter time of the camera (40 μs).

III. RESULTS AND DISCUSSION

It is generally accepted that the transition between the pulsating and the cone-jet regimes is marked by a sudden increase in the spray current. An alternative scenario is presented by the spray current measurement in Fig. 1. The low current level, centered on ~65 nA, corresponds to the pulsating mode. After spending an unpredictable amount of time in this mode, the electrospray suddenly switches to the cone-jet mode. Delivering the increased amount of current (~110 nA) under the conditions of this experiment seems only feasible for a short time interval, thus the spray collapses back to the pulsating mode. It is important to note that these transitions are spontaneous, not induced by an external trigger or event. Considering the electrospray as a system with two states characterized by the spray current levels (low or high), the similarity with an astable oscillator circuit is obvious.

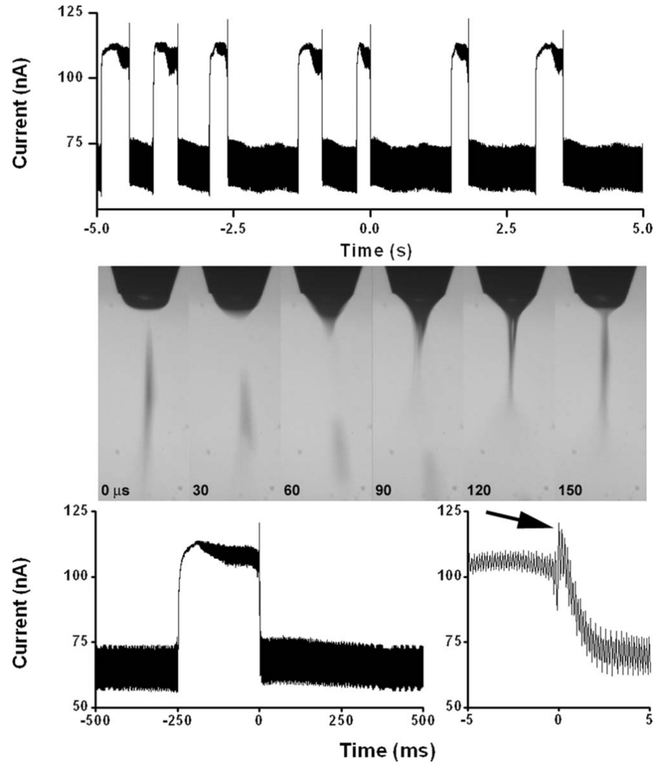

FIG. 1. Astable transitions revealed by spray current measurements for a solution of 50:50 (v/v) methanol:water acidified with 0.1% acetic acid supplied at 1.5 μL/min through a tapered tip emitter (top). Zoomed current waveforms focus on a double (bottom left) and single (bottom right) astable transition. Fast time-lapse images (middle) prove that the current oscillation marked with an arrow is induced by liquid meniscus pulsation.

From this point forward we will make a clear distinction between the terms "regime" and "mode," which were used interchangeably in our previous reports. While operating in the astable regime, the electrospray spontaneously switches between pulsating and cone-jet modes. On the other hand, when increasing the applied voltage, the astable regime may mark the transition between the pulsating and cone-jet regimes.

The bottom part of Fig. 1 expands the spray current waveform showing the transitions in both directions (left) and the transition between the high and low states (right). In these depictions it is clearer that the current has an oscillating component not only in the low state, but also, to a lesser degree, in the high state. While the current oscillations in the low state represent a limit cycle and can be explained by meniscus pulsation [23], it is still unclear if the current oscillations in the high state are induced by fluid motion or charge displacement. We will present more experimental data (see below) that probes whether the high state is a pure cone-jet mode. Time-lapse images in Fig. 1, captured by triggering the camera on the current peak marked with an arrow, prove that the meniscus pulsates after this point; however we could

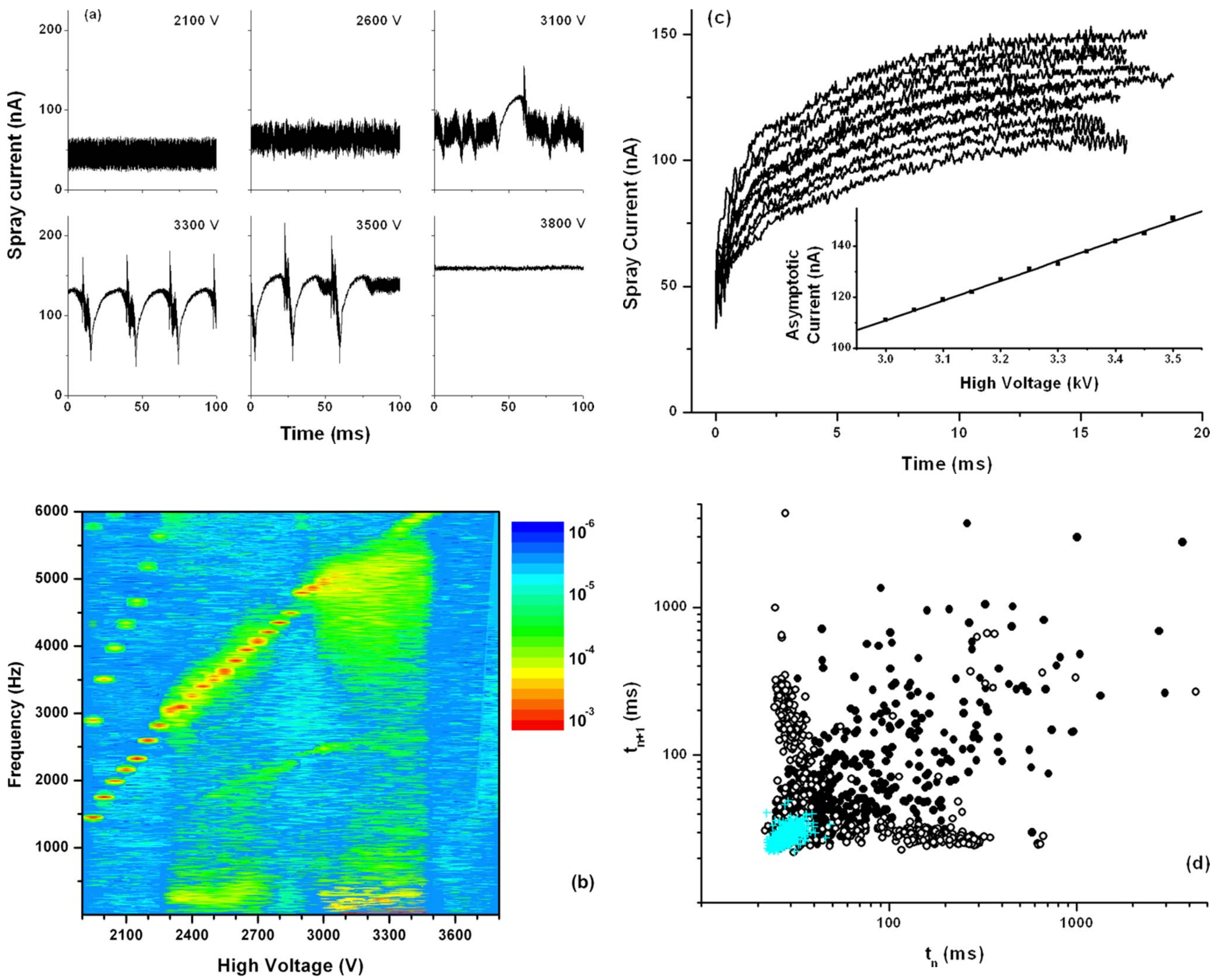

FIG. 2. (Color online) Spray current measurements (a), and Fourier transform map (b) for a solution of 50:50 (v/v) methanol:water acidified with 0.1% acetic acid electrosprayed at 2 μL/min through a blunt tip emitter (d=10 mm). Charging curves during electrospray transition from pulsating to cone-jet modes (c). The inset shows the linear dependence of the asymptotic charging current on the high voltage. Return maps (d) based on the times of collapse from cone-jet to pulsating mode at low (solid circles), intermediate (open circles) and high voltage values (cyan crosses).

not link the previous current oscillations in the high state with any meniscus pulsation.

The astable transient regime is not restricted to tapered-tip emitters only. Figure 2 demonstrates the effect of increasing the high voltage on the working regime of the electrospray established for a blunt-tip emitter. Figure 2(a) focuses on the spray current measured at high voltages at which the spray works in pulsating (2100 and 2600 V), astable (3100, 3300 and 3500 V), and cone-jet (3800 V) regimes. The entire set of spray current measurements corresponding to high voltages between 1900 and 3800 V is represented as a color-coded Fourier transform (FT) map in Fig. 2(b). Below 2250 V the spray works in a very regular pulsating regime, with the pulsation frequency clearly marked in the FT spectra by narrow peaks. Above 2300 V the peak corresponding to the main pulsation frequency broadens and the low frequency region becomes populated, indicating period doubling. An additional weaker period doubling can be observed at ~2500 V. Both of these effects can be identified in the noisier current measurement at 2600 V. The current measurements become even more irregular above 3100 V, reflected in much broader peaks in the FT spectrum. At 3100 V the spray also attempts to switch to the cone-jet mode. With increasing high voltage (see for example the current measurement at 3300 V) these attempts become more frequent and the time the electrospray spends in high state gradually increases. At 3500 V the time the electrospray spends in pulsating mode is minimal, while the duration of the high state increases.

At 3800 V the electrospray operates in cone-jet regime. The difference between the current measurement in this case and the last 20 ms of the 3500 V case is evident. This observation compelled us to describe the phenomenon in terms of low and high states instead of using mode names. Nevertheless, from this point forward we will also refer to the high state as cone-jet mode, even though some differences may exist between them. The tendency of the electrospray to reach the cone-jet mode is suggested by the sudden current

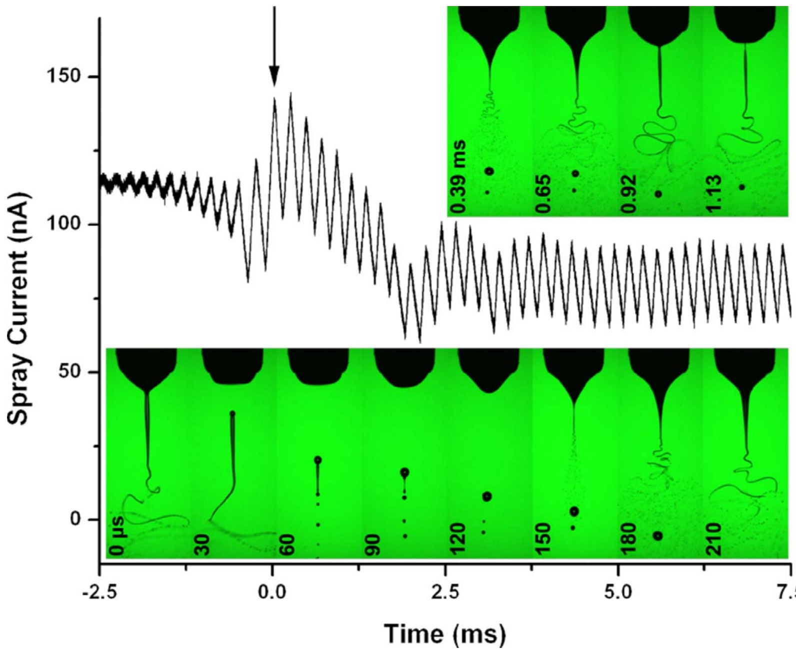

FIG. 3. (Color online) Spray current measurement and corresponding time-lapse images during the high-to-low transition for a solution of 50:50 (v/v) methanol:water acidified with 0.1% acetic acid. The liquid is supplied at 2 μL/min through a blunt tip emitter that is held at 3100 V. Images in the bottom row were captured during an ejection cycle at delay times indicated in the frames. Top-row images show that the small droplets catch up with the relaxed spindle (large drops) from the previous cycle for four different cycles.

jump and by the initial shape of the signal. Immediately after the current jump, the liquid meniscus at the emitter tip is conical and a jet is continuously ejected, as one would expect in the cone-jet regime. We speculate that uneven breakup of the jet induced by fluctuations in the charge density could be responsible for this current oscillation. We were not able to establish with any degree of certainty the real reason; however, the onset of the current oscillations can be seen as the inception of the instability that would eventually lead to the collapse of the electrospray to the pulsating mode.

Although quantitative description of the system is not available at this point, based on the above observations a qualitative picture of the phase portrait emerges. Using the spray voltage as the parameter, Fig. 2(a) depicts the transition from a stable limit cycle (pulsating mode at 2100 V) to a stable fixed point (cone-jet mode at 3800 V), through what appears to be a subcritical Andronov-Hopf bifurcation. The intermediate stages, described as astable regime, exhibited several characteristics of this bifurcation. In this region, the limit cycle and the fixed point coexisted and small external perturbations (noise) could produce the astable behavior. The coexistence of the two states was supported by the observation of hysteresis. By gradually increasing the voltage, the system sometimes remained in pulsating mode even at values typical for the cone-jet regime. Conversely, by slowly lowering the voltage, the system occasionally preserved the cone-jet regime for voltages characteristic of the pulsating mode. Growing (or damped) oscillations, another hallmark of Andronov-Hopf bifurcations, could also be observed in Fig. 2(a) and earlier in Fig. 1 in more detail. Just before the current spike marking the transition from the high to the low state, the oscillations amplified. The system lost stability in the fixed point and swung to the limit cycle, which stabilized the oscillation amplitude.

The transition from the pulsating to the cone-jet mode is accompanied by a rise in the current resembling the charging of a capacitor [Fig. 2(c)]. Indeed, in a simple equivalent circuit, the electrospray can be viewed as a gap characterized by a resistor-capacitor (RC) circuit. The data for low to high transitions measured at high voltages between 3000 and 3500 V was used to determine the parameters for the time dependence of the spray current $i=i_0-b\exp(-t/\mathrm{RC})$ by nonlinear regression. The time constant $\mathrm{RC}=4.4\pm0.5$ ms was very similar for all cases. The inset of Fig. 2(c) shows that the asymptotic current i_0 flowing through the equivalent circuit had a linear dependence on the applied high voltage. From the slope of this representation we estimated an effective gap resistance of $R=12.9\pm0.2$ GΩ. The corresponding gap capacitance was $C=0.35\pm0.03$ pF. The charging process captured in these transitions should be related to the charge reorganization on the liquid surface due to the transition from pulsating to cone-jet mode.

During the reverse transition, a similar fit would be prone to increased error due to the oscillatory nature of the data; however, the faster current drop suggests a smaller time constant. The equivalent astable circuit should also include two nonlinear components (transistors) that do not have an effect on the time constants as those are dictated by the passive components. The time constants mentioned above do not completely characterize the electrospray in the astable regime. The time spent by the spray in the two modes cannot be predicted due to the chaotic nature of this regime.

The current spikes marking the transitions to the pulsating mode in Fig. 2(a) were used to plot the return maps shown in Fig. 2(d). Because they only mark one type of transition (high to low), scrutiny of the current measurements is required to reach consistent conclusions. At low voltages the points show up erratically on the return map (dark circles). The current measurements show that the spray spends an unpredictable and a minimum amount of time in the pulsating and cone-jet modes, respectively. With increasing voltage, the points cluster into the attractor in the lower left corner (cyan crosses) showing a relatively periodic process for a range of high voltages. Under these conditions the

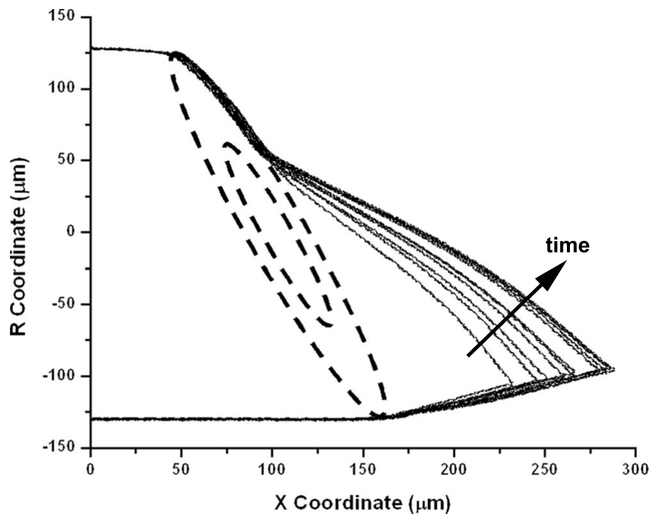

FIG. 4. Growth of liquid cone, shown for an oblique-cut emitter tip, after the onset of cone-jet mode may explain instability during an astable regime. There was a small angle between camera axis and the normal to the emitter symmetry plane. Dashed lines in the image, suggesting the emitter profile, clarify that the liquid was anchored to the inner wall of the emitter, which could not be observed in the shadowgraphs. The experiment was conducted at 3200 V with a 50:50 (v/v) methanol-water mixture acidified with 1% acetic acid and supplied at 2 μL/min.

spray is unstable in both modes and keeps switching back and forth between them, behaving similar to a deterministic astable circuit. At even higher voltages, as the electrospray becomes more stable in the cone-jet mode and spends minimal time in the pulsating mode, the single attractor grows into an L-shaped attractor (open circles). This shows that switching between the stable cone-jet and unstable pulsating modes takes place at least twice. The shorter time period spent in the pulsating mode is better defined, whereas the longer time spent in the cone-jet mode varies in a wide range. The open circles that do not belong to the L-shaped attractor correspond to the measurement at a high voltage of 3500 V, where the electrospray stability in the pulsating mode is almost completely compromised.

Figure 3 shows a spray current measurement during an astable high to low transition along with time-lapse images of the meniscus pulsation triggered by the current peak indicated by the arrow. Images of the meniscus deformation and liquid ejection during the first pulsation cycle, with a period of ~240 μs, is presented below the data, with the delay time indicated in each image. It is clear that different mechanisms are responsible for droplet formation at different phases during the pulsation cycle. The initial small droplets form by the breakup of the filament distorted by kink instabilities (frames 0 and 30 μs), while the last droplet forms by the relaxation of the ejected spindle (frames 60, 90, and 120 μs). Since the mobility of the droplets depends on their size and charge, larger droplets could eventually fall behind the smaller ones created during the following pulsation. Indeed, this can be observed in the 150 and 180 μs frames. The images in the top row show the same scenario repeating itself during the next four pulsation cycles.

We have recently started to characterize the dynamics of the electrified fluid surface at the tip of oblique-cut emitters to assess the effect of the boundary condition at the emitter tip on the spraying regimes (data not shown). Here we discuss only one result, which may point to a possible explanation for the collapse from the cone-jet to the pulsating mode and thus is relevant to this study. Figure 4 presents contours of the emitter tip and the asymmetric liquid cone for an electrospray operating in the astable regime, which were obtained by processing fast time-lapse images of the cone during its ~50 ms existence in the cone-jet mode. The asymmetry of the emitter is most likely responsible for the liquid anchoring on its sharper side, where the higher electric field better assists the spray. The constant increase in the cone volume, which levels off during the last 15 ms indicates that the removal of the liquid through jet ejection is not sufficient to balance its influx. Thus, the cone grows until its stability in the cone-jet mode depreciates and the electrospray collapses into the pulsating mode. While in the pulsating mode, the excess liquid must be ejected before the cone-jet mode can be reestablished. Inconsistency in the time spent in the cone-jet regime may be related to the initial size of the liquid cone and/or to the amount of time the cone-jet mode lasts in the final phase of cone growth.

IV. CONCLUSIONS

The description of the astable axial electrospray regime, which can be viewed as a chaotic transition between the pulsating and the cone-jet regimes, completes the classification of axial electrospray regimes based on nonlinear dynamics. In this broader context, the dripping faucet is the low electric field limiting case of the electrospray. With the electric field turned on, the electrospray exhibits three axial regimes, dripping, pulsating, and cone-jet, potentially separated by two chaotic regimes, burst and astable, respectively. The dripping and pulsating regimes represent stable limit cycles. For certain values of the flow rate and the voltage the system settles into one of these limit cycles. Changes in flowrate or voltage in the dripping regime can result in converting to the burst mode and chaotic behavior. Further increase of these parameters produces a new limit cycle known as the pulsating regime. As we have shown in this paper, elevating the voltage even more can result in a heretoforeunknown astable regime. The conditions that favor the astable instead of the sudden switch between the pulsating and cone-jet electrospray regimes still need to be clarified. Although electrospray formation is a complex process, based on spray current and image analysis a unified view of the axial regimes can be constructed that is far simpler than suggested by previous studies.

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