On the Pulsed and Transitional Behavior of an Electrified Fluid Interface

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Transient modes of an electrified fluid interface are investigated, specifically, (a) intermittent or pulsed cone-jet mode and (b) smooth and abrupt transitions of the interface in response to a step voltage. These modes were studied experimentally by capturing the motion of the interface and measuring the emitted ion current (via electrospray) as they occur. The observed phenomena are described using an analytical model for the equilibrium of an electrified fluid interface, and the effect of operational parameters on the transient modes is discussed. Pressure, which is related to the supplied flow rate, significantly influences the behavior of the transient modes. It is useful to understand transient modes so they can be avoided in applications that require a stable electrospray. However, with improved knowledge, the modes studied here can assist in the development of specialized applications. [DOI: 10.1115/1.3203203]

1 Introduction

An electrospray will form from an air-fluid interface subject to a large electric field. The interface deforms into a conical shape, and the spray, consisting of highly charged droplets, emits from the apex of the cone. This mechanism is used in electrospray ionization, where compounds are transferred from solution into the gas phase. Electrospray is of great importance for mass spectrometry [1], material deposition [2], and sample synthesis [3].

The shape of an electrified interface, the conditions that lead to the onset of jetting, and the properties of the emitted jet have been studied for decades. Taylor [4] first reported an analytical model for the formation and structure of the electrified cone. Basaran and Scriven [5] and Pantano et al. [6] investigated the shape and stability of droplets in an electric field, and Stone et al. [7] used slender body theory to study drops with conical ends. The “modes” or “regimes” that an electrified interface can exhibit were reported by Cloupeau and Prunet-Foch [8]. Fernandez de la Mora [9] accounted for the effect of space charge in the emitted jet on the cone shape to explain differences in observed cone angles from that predicted by Taylor [4]. Fernandez de la Mora and Loscertales [10] and Ganan-Calvo et al. [11] studied the spray current and emitted droplet size of a conical electrified interface, and introduced scaling laws to predict these two quantities. Chereny [12] used perturbation methods to investigate the structure of the Taylor cone and the emitted jet. For a complete review on the subject of Taylor cones, see Ref. [13].

More recently the dynamic and transient behavior of an electrified interface has received greater attention. Collins et al. [14] reported a simulation of cone and jet formation and droplet breakup. Notz and Basaran [15] investigated drop formation in an electric field, and Reznik et al. [16] investigated the shape evolution of an electrified interface over time, examining isolated droplets and the impact of electrical Bond number on interface evolution.

In this study, two transient modes are examined: (a) intermittent or pulsed cone-jet mode, and (b) smooth and abrupt transitions of the interface in response to a step voltage. These modes are studied by capturing the motion of the interface and measuring the emitted ion current. The observed phenomena are then accounted

for using a recently developed equilibrium model by Gubarenko et al. [17]. The model simplifies the treatment of the complex modes by assuming that the operating point of the interface parameters moves within an operational space and transitions between equilibrium and quasi-equilibrium states. This allows for these phenomena to be understood and predicted, and the impact of operational parameters on the transient behavior is determined.

Several experimental techniques have been used to probe the dynamic behavior of electrified interfaces. Zhang and Basaran [18] used fast imaging to characterize the dynamics of drop formation from a nozzle under electric fields of weak to moderate strengths. Marginean et al. [19] used a combination of fast imaging and current measurements to study the same problem under weak, moderate, and large electric fields. Others used Phase Doppler Anemometry to measure the size and velocity of droplets produced by an electrospray [20,21]. Here, we follow Marginean et al. [19], and use a two pronged approach based on imaging and current measurements.

Typically, a steady cone-jet is of primary importance, especially in applications such as mass spectrometry. Knowledge of the transient modes considered in this study, and the operational parameters that cause them, is useful to avoid the negative aspects of these modes. However, if better understood, the transient modes considered here can assist in the further development of useful applications, such as e-jet printing [22] and material deposition [23].

2 The Equilibrium Model

A full description of the equilibrium model is given by Gubarenko et al. [17], and the details are briefly summarized here. The model describes the impact of the three dominant stresses—surface tension, electric (Maxwell) stress, and pressure difference—on the equilibrium of an electrified interface (note that the impact of the viscous stress is small and can be neglected). A three dimensional space of the operating parameters is described, and regions or subdomains are defined where equilibrium, quasi-equilibrium, and nonequilibrium conditions exist. These subdomains are explicitly defined below. The surfaces dividing the subdomains are referred to as “critical surfaces,” and represent the boundary of equilibrium (or quasi-equilibrium) and nonequilibrium states. It is convenient to work in a two dimensional operational space, so the electrode separation distance is typically fixed, and the impact of the applied voltage and pressure difference is focused on. In this case, the critical surface is re-

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Fig. 1 Quasi-equilibrium states for the interface. In all cases, the interface emits a spray.

duced to a “critical curve.” The model reveals that the angle at the center of the interface, the apex angle (θ), dramatically affects the location of the critical surface in the operational space.

“Equilibrium” means all forces are balanced on the interface, the apex angle is 0 deg, and the interface does not emit a spray. In “quasi-equilibrium,” all forces are balanced on the interface; however, the apex angle is nonzero and the interface emits a spray (see Fig. 1 for examples of an interface in quasi-equilibrium). Fluids of high conductivity have a small jet formation region located almost entirely at the apex of the cone [8]. This means that an interface in quasi-equilibrium can accurately be described as a continuous function after specifying an apex angle (i.e., the jet formation region can be omitted in the model). Highly conductive fluids are the focus of both this study and the analytical model [17].

An electrified interface has an operating point that is a function of the applied voltage, electrode separation, and pressure difference residing inside the operational space. The location of the operating point defines the important characteristics of the interface. By using the equilibrium model, properties of the interface can be predicted or selected, including the equilibrium status of the interface, the presence of an electrospray, and the shape of the meniscus. The operating point can also move within the operational space and transfer between equilibrium subdomains.

To use the equilibrium model, it is necessary to specify the value of the apex angle and calculate the pressure difference across the interface. The sine of the apex angle defines the location of the critical surface, and the pressure difference dictates (along with the applied voltage and electrode separation distance) the location of the interface operating point in the operational domain. The apex angle term is calculated from the experimental data by fitting a linear function to several points (on the order of 10–20) to a portion of the interface in the vicinity of the apex. It is important to note that the apex angle used here and the classic Taylor angle θ_T [4] are related as $\theta + \theta_T = 90$ deg.

For an interface under pressure, surface tension, and electric stress, the pressure term is found by solving a stress balance for the interface, knowing the curvature of the interface and surface tension coefficient (giving the stress from the surface tension), and the applied voltage and counterelectrode separation (giving the electric stress). Note that the pressure term is the excess internal pressure at the interface that balances the surface tension and electric stress. The position of the interface as a function of pressure difference can be expressed using the stress balance, and compared with the position of the interface at experimentally found points. By minimizing the difference between the measured and calculated points, the pressure difference across the interface can be found [24]. The pressure difference for interfaces not under electric stress can be determined by solving the Young–Laplace equation. Pressure values are gauge pressures.

The equilibrium model accounts for the observed transient phenomena of an electrified interface. The phenomena considered in this study are intermittent or pulsed cone-jet mode and smooth and abrupt transitions of the interface in response to a step voltage. The equilibrium model accounts for these phenomena as movement of the operating point of the interface within the operational domain and the transition between equilibrium and quasi-equilibrium states. This approach simplifies the treatment of these transient phenomena while still accurately describing the observed behavior.

Most applications require transient phenomena to be avoided all together. In mass spectrometry or material deposition, stable cone-jets emitting a steady stream of material are essential. However, other more specialized applications find transient phenomena to be useful. For example, it is possible to use pulsed cone-jet mode to emit discrete packets of droplets through the electrospray mechanism. Rather than having a continuous spray, droplets are emitted intermittently using this mode, and it was proposed to use pulsed cone-jets in printing [22] and material deposition [23] applications. It might also be possible to use this mechanism to mimic the function of an ion gate or shutter. A theoretical understanding of intermittent or pulsed cone-jet mode using the analytical model reported in Ref. [17], combined with the results of this study, will assist in the further development of specialized applications. Application of the equilibrium model to transient phenomena is discussed in Sec. 3.

3 Experimental Investigation of Transient Phenomena

3.1 Materials and Experimental Setup. Testing was performed using metal tubing with a radius of 150 μm . The electrified interface was located at the edge of the metal tubing that was positioned directly in front of the counterelectrode. For the imaging of the interface, the bulk fluid used in this study was a 100 μM solution of Rhodamine B in 70:30 MeOH:H₂O. The surface tension values were determined using Ref. [25]. Rhodamine B is a fluorescent dye and was used to improve the recording, analysis, and display of the interface. For the experiments that involved measuring the emitted ion current, the bulk fluid is a 100 μM solution of sodium iodide (NaI) in 90:10 MeOH:H₂O. For some experiments, the bulk fluid is modified by adding 1% AcOH.

The flow rate was controlled using a syringe pump (Cole Parmer, Montreal, QC, Canada), and the interface was observed and recorded using an inverted fluorescent microscope (Leica, Wetzlar, Germany) and charge-coupled device (CCD) camera (Sony, Tokyo, Japan). Using optical filters and a dichromatic mirror (a filter cube), the microscope can illuminate the interface with light at a wavelength of 515–560 nm, and pass light at a wavelength exceeding 590 nm to the CCD camera. These wavelengths are ideal for the excitation/emission spectrum of Rhodamine B. Voltage is applied to the metal tubing using a high voltage source (Labsmith HVS448) with an operating range 0–3000 V. The radius of the interface in all of the captured images is 150 μm , which is the same as the outer radius of the metal tubing. Images of the interface are captured at a resolution of 640×480 in PNG format and processed using MATLAB [26].

The use of Rhodamine B allows for the interface to be more easily visualized and processed. However, it was typically found that the emitted jet could not be visualized when illuminated by filtered light. This is likely because of the narrow bandwidth applied and the small volume of the jet. The jet was visualized when the full spectrum (bandwidth) of light is applied. All frames are aligned so that the bottom of the image is aligned with the end of the metal tubing. This was confirmed visually and simplifies image processing.

Emitted ion current measurements are made using a current amplifier (Keithley, Cleveland, OH), and the output is monitored using a digital oscilloscope (Agilent, Santa Clara, CA). Ions are emitted from the apex of the Taylor cone and neutralized on the counterelectrode. This current was measured, converted to a voltage, and then amplified for measurement.

3.2 Intermittent or Pulsed Cone-Jet Mode. The intermittent or pulsed cone-jet mode was identified by Cloupeau and Prunet-Foch [8] who reported that this occurs when “the voltage is slightly lower than for which a single permanent jet is obtained,” and this mode is one focus of this study. Marginean et al. [19] studied transitions between the operating regimes of an electrospray in experimental studies, and Li [27] investigated meniscus

Fig. 2 Two images of an electrified interface in “intermittent or pulse cone-jet mode.” The shape of the interface cycles back and forth between (a) and (b) at a frequency of 6 Hz. The apex angle in (b) is 63 deg.

deformation under the influence of a pulsed voltage—in contrast to this work where intermittent or pulsed cone-jet mode is observed for constant voltages.

An example of pulsed cone-jet mode is shown in Fig. 2. The applied voltage was held constant at 3000 V and the flow rate was $0.1 \mu\text{l}/\text{min}$. The time difference between Figs. 2(a) and 2(b) is 165 ms. These two interface shapes repeated cyclically at a constant frequency of 6 Hz, transforming from a rounded apex (slope at the middle equal to zero) to a typical cone-jet configuration, and back again. During the brief cone-jet period, the interface emits a spray, resulting in a pulsed spray being emitted at the same frequency as the interface transition.

As shown in the operational domain in Fig. 3, this pulsed cone-jet transition will straddle two critical curves—one corresponding to $\theta=0$ deg and the other corresponding to $\theta=63$ deg (the apex angle in Fig. 2(b)). The operating point of the interface in Fig. 2(a) sits left of the critical curve in equilibrium. As the pressure increases, the operating point moves to the right and crosses the critical curve (to the point marked “●”). The movement is in a straight horizontal line as the voltage is held constant. As the operating point crosses the critical curve to the point marked ●, it smoothly and immediately relocates into the quasi-equilibrium region, left of the critical curve for $\theta=63$ deg, as shown by the broken arrow in Fig. 3. Once in the quasi-equilibrium region, the interface appears as seen in Fig. 2(b).

Once in the quasi-equilibrium region, the pressure increases for a short amount of time until it crosses the critical curve for $\theta=63$ deg to the point marked with a ●. Once it crosses this curve, the interface is in nonequilibrium, and it adjusts to find an equilibrium state.

Fig. 3 Operational domain for an electrode separation distance of 7 mm and surface tension coefficient of 27.48 mN/m. The operating point moves left and right in the domain across the critical curves between equilibrium and quasi-equilibrium.

Fig. 4 Current measurements of emitted ion current. The ion current is collected at the counterelectrode and converted to a voltage. The bulk fluid is a $100 \mu\text{M}$ solution of NaI in 90:10 MeOH:H₂O. The flow rate in (a) is $2 \mu\text{l}/\text{min}$ and in (b) is $0.5 \mu\text{l}/\text{min}$. The current peaks represent the quasi-equilibrium state of the interface.

librium state. Due to the low applied flow rate, the interface collapses and returns to the equilibrium state (shown by the broken arrow). Once back in equilibrium, the pressure builds again and the process repeats itself. This cyclic process is observed to occur at a very regular frequency of approximately 6 Hz.

The question remains as to why the interface in Fig. 2(b), after moving out of the quasi-equilibrium region, collapses to an equilibrium state rather than moving to a second quasi-equilibrium state (as seen for the smooth transition below). This is because of the supplied flow rate. For similar operating conditions at higher flow rates, a stable cone-jet can form [17]. Experimentally, it was found that higher flow rates create larger pressure differences (in the negative direction) across the interface. A similar finding was reported in other electrospray studies [28]. At low flow rates, the pressure difference across the interface remains small, and the operating point of the interface is limited by the amount it can move in the negative pressure direction (to the left in Fig. 3). As a result, the operating point—after crossing into nonequilibrium—must move to the right, back to the equilibrium region. Thus, the contention of Cloupeau and Prunet-Foch [8] that pulsed cone-jet mode occurs at voltages slightly below those required for a stable cone-jet should also include the importance of sufficient pressure (related to flow rate) as well. Fernandez de la Mora and Loscertales [10] and Chen and Pui [29] also reported a required minimum flow rate to achieve a stable electrospray. In their work, scaling laws for the minimum flow rate (Q_{min}) are expressed as a function of the bulk fluid parameters, but they do not specifically address the relationship of flow rate and pulsed mode.

Ion current measurements confirm the regularity of pulsed cone-jet mode and the impact of flow rate (pressure) on the pulse frequency. Figure 4 shows the measured ion current emitted by an interface in pulse cone-jet mode for two different flow rate conditions. Figure 4(a) shows a flow rate of $2 \mu\text{l}/\text{min}$ and Fig. 4(b) shows a flow rate of $0.5 \mu\text{l}/\text{min}$. In both cases, the bulk fluid is a

Fig. 5 Time lapsed images of an interface undergoing an abrupt transition. The pressure difference is smoothly increased in (a) and (b), and a step voltage is discontinuously (abruptly) applied in (c). A loss of mass from the interface can be seen when the voltage is applied. (d) The stable final cone-jet.

100 μM solution of NaI in 90:10 MeOH:H₂O. The current between pulses is primarily attributed to external electrical noise. In Fig. 4, the current peaks correspond to a quasi-equilibrium state of the interface (i.e., Fig. 2(b)), and the zero current condition corresponds to the equilibrium state (i.e., Fig. 2(a)). The pulsed mode seen in Fig. 4 is the low frequency component of what Juraschek and Rollgen [28] identified as “axial spray mode I.” The low frequency oscillation of the spraying jet corresponds to the jumping (i.e., movement) of the operating point in the parameter space between equilibrium and quasi-equilibrium subdomains. This measurement shows that the magnitude of the emitted current remains constant despite changes in the pulse frequency, and that the pulse frequency (the emitted ions) can be controlled via the pressure difference across the interface (i.e., the supplied flow rate).

3.3 Smooth and Abrupt Transitions in Response to a Step Voltage. Experimental evidence reveals that it is possible to have both smooth and abrupt transitions from equilibrium to final quasi-equilibrium state. The type of transition (for fixed electrode separation) depends on how smoothly the pressure difference and voltage are applied to the interface. Smoothly applying an increasing pressure difference across the interface is done by operating the syringe pump at a constant flow rate. Smoothly applying the voltage is more difficult, as most high voltage supplies (including the unit used in the study) do not allow gradual transitions over a wide operating range, instead, allowing only finite steps. Nevertheless, the impact of varying the spray voltage, as well as the resultant response of the interface, was previously addressed by Marginean et al. [19].

Examples of transitions are shown in Figs. 5 and 6. Figure 5 represents an abrupt transition where pressure is smoothly applied, and the voltage is abruptly applied (a voltage step) from 0 V up to 3000 V. Figure 6 represents a smooth transition where the voltage is applied before any fluid is present (at 3000 V), and then pressure is smoothly applied. The time delay between each frame is shown in each figure.

The transition of the interface in Figs. 5 and 6 can be tracked using the operational domains shown in Figs. 7 and 8, respectively. The solid and dashed arrows represent smooth transitions

Fig. 6 Time lapsed images of an interface undergoing a smooth transition. The voltage is applied in (a) before any fluid is present. The pressure difference smoothly changes from (b) to (d). The interface in (d) has been steady for hundreds of milliseconds. No abrupt loss of mass is seen for this smooth transition compared with the abrupt transition.

Fig. 7 Operational domain for an electrode separation distance of 10 mm and surface tension coefficient of 27.48 mN/m. The solid arrow represents the smoothly increasing pressure difference, and the dotted arrow represents a discontinuous or abrupt increase in voltage. The application of voltage is discontinuous and not smooth. The pressures at (a), (b), and (d) are known exactly. There is no pressure to report for (c) since the interface has ruptured.

and the dotted arrow represents an abrupt change in voltage. For both cases, the electrode separation is fixed.

The operating point of the interface shown in Fig. 5 on the domain shown in Fig. 7 starts with a zero pressure difference and zero applied voltage (*S* in Fig. 7). As fluid is infused with the syringe pump, the operating point moves smoothly to the right (increasing positive pressure), up to the point shown in Fig. 5(a). The pressure difference across the interface in Fig. 5(a) can be found by measuring the height of the interface [17]. Mass is continually infused until nearly the boundary of equilibrium shown in Fig. 5(b). At this point, a step voltage of 3000 V is applied, and an image was taken (Fig. 5(c)) showing the interface undergoing an abrupt transition. As the interface completely ruptures, a substan-

Fig. 8 Operational domain for an electrode separation distance of 10 mm and surface tension coefficient of 27.48 mN/m. The solid arrow represents smoothly increasing pressure difference, and the dashed arrow represents smooth relocations of the operating points. The transition is smooth; therefore there is no abrupt loss of mass, as seen in Fig. 5.

tial mass of fluid is ejected. Since the interface loses mass, the pressure difference across the interface moves in the negative direction. The operating point after transition (Fig. 5(d)) is to the left of the critical curve for $\theta=50$ deg in a quasi-equilibrium state, since the interface emits a spray after the voltage is applied.

Reznik et al. [16] also found a total rupturing of the interface, as in Fig. 5(c) (they defined this as droplets “jumping off”), but only for large contact angles in excess of 0.8π . Here, rupturing occurs at much smaller angles. Reznik et al. [16] dealt with isolated droplets—while here droplets are infused with mass from the syringe pump.

Qualitatively, it has been observed that when the pressure difference across the interface is large before an abrupt transition, the sudden loss of mass from the interface in transition is large. As seen in Fig. 5, when the applied pressure before transition is near the equilibrium limit, the mass lost when the voltage is applied was large. For smaller pressure differences before abrupt transition, the amount of mass lost from the interface was observed to be comparatively less.

For the smoothly transitioning interface in Fig. 6, the operating point starts at zero pressure difference but at an applied voltage of 3000 V (the step voltage is applied before any fluid is present). Mass is continually infused with the syringe pump, and the pressure difference smoothly increases in the positive direction, causing the operating point on the domain in Fig. 8 to start at *S* and move to the right. After crossing the critical curve for $\theta=0$ deg, the operating point immediately relocates to the quasi-equilibrium region, where the pressure increases again. Here the operating point moves to the right, crossing into nonequilibrium, and adjusts to find equilibrium. The flow rate in this case is sufficiently high; therefore the operating point can move to the left (for decreasing pressure, as also noted in Ref. [28]), and the interface moves into a second quasi-equilibrium state. This process repeats until the interface reaches a final steady operating location.

For the operating domain in Fig. 8, only three discrete transitions into three different quasi-equilibrium regions are shown and correspond to the three time delays of the interface shown in Fig. 6. It is possible to take more intermediate images of the interface and plot additional operating points. This would show a series of transitions between quasi-equilibrium states until reaching the steady configuration shown in Fig. 6(d), and would mean that the transitional operating points and critical curves would get increasingly closer together.

Overall, the interface in Fig. 6 smoothly transitions to a final quasi-equilibrium state: cone-jet mode. On the operating domain, the operating point moves in a smooth manner. Most notably, there is no dramatic rupture of the interface that is found for the abrupt transition found in Fig. 5, just a smooth transition to an interface in cone-jet mode.

The smooth transition can be compared with the pulsed cone-jet configuration considered in Sec. 3.2. In this case, the interface does not collapse and is able to return to a quasi-equilibrium state after a critical curve is crossed. The most notable difference in operating conditions is the supplied flow rate, where the smooth transition in Fig. 6 is an order of magnitude larger than the conditions in Fig. 2. With adequate flow rate, the pressure difference can decrease sufficiently, such that the operating point can move to the left. The operating point will relocate in a smooth manner between quasi-equilibrium regions, until a steady value for pressure difference is reached.

4 Summary

Two transient modes of operation for an electrified interface, intermittent or pulsed cone-jet mode and the smooth and abrupt transitions of the interface in response to a step voltage, have been investigated. Using an analytical model [17], the behavior was simplified by assuming that the operating point of the interface parameters moves within an operational domain and transitions between equilibrium and quasi-equilibrium states. The experimen-

tally measured interface motion and emitted ion current confirmed this and revealed the impact of the operational parameters on the transient modes. It was found that pulsed cone-jet mode is not only influenced by the applied voltage—pressure (related to the supplied flow rate) also plays a role in its formation and behavior.

When applying a step voltage, it is important to avoid an abrupt transition in most applications. When forming an electrospray for use in mass spectrometry, a dramatic loss of mass, as the voltage is first applied, could result in significant sample loss (contained in the solvent). For material deposition, an abrupt emission of mass affects the uniformity of the film being applied. The amount of mass ejected during the abrupt transition is unpredictable, and a good way to avoid abrupt transitions is to smoothly vary the pressure difference (from zero) after the step voltage is applied.

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