Scaling Laws for Pulsed Electrohydrodynamic Drop Formation: Supplemental Information

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A1. Experimental Setup

A schematic representation of the experimental setup is shown in Figure 1a of the main text. A thin teflon tube is used as the nozzle to carry liquid for EHD drop generation. The teflon nozzle was 360 µm-OD and 50 µm-ID unless otherwise specified (Upchurch 1930, Oak Harbor, WA). Inner diameters of 75 µm and 100 µm were also used to test the scaling laws. The teflon nozzle was connected to a liquid reservoir through a 0.97 mm-ID polymeric tube (Hamilton 90619, Reno, NV). The working fluid was deionized water and was left to equilibrate in atmospheric condition for 24 h to ensure reproducible conductivity. The conductivity of deionized water equilibrated in atmosphere was measured to be 0.9×10^{-4} S/m. The sealing of liquid path was assisted by a stainless steel union (Upchurch U-437) together with tubing sleeves (F-242) and fittings (F-120). The liquid reservoir was held at a constant height during the experiments (0.05-0.25 m above the nozzle) and was selected to approximately balance surface tension to achieve a 'flat' meniscus, i.e., a condition at which the teflon nozzle remained filled but no liquid protruded from the nozzle by visual inspection. In addition to being thin and insulating which are respectively important for reducing flow rate and preventing corona discharge, the teflon nozzles used here are hydrophobic which restrict liquid wetting to the inner nozzle and ensure a repeatable conical base for reproducible cone-jet transitions.

A high voltage pulse was applied between the teflon nozzle (through the stainless union) and a silicon substrate using a pulse generator (HP 8111A, Palo Alto, CA) and a high voltage amplifier (Trek 20/20C, Medina, NY); each external voltage pulse produced a drop on the substrate. The nozzle was grounded and the silicon substrate negatively electrified. The pulsed jetting process was monitored by a 10,000 fps CCD camera (Redlake MotionPro, San Diego, CA) using a long-distance microscope (Infinity K2, Boulder, CO) at a magnification of 6.6X. The current in the EHD circuit was measured by the voltage drop on an oscilloscope connected between the nozzle and ground. The 300 MHz oscilloscope (Tektronix 2440, Beaverton, OR) has a capacitance of 15 pF and a standard resistance of 1 MΩ.

A2. Empirical Equivalence of Cone and Drop Formation Rates

Figure A1 shows drop volume as a function of pulse duration for the experiment presented in Figure 1b of the main text. The drop volume was calculated by assuming the drop shape to be a spherical cap following Yogi *et al.*[1] The drop volume was a linear function of pulse duration, and a linear extrapolation yielded a drop formation rate of 6.4 nl/s. The intersection of the linear extrapolation with the abscissa, 3.4 ± 0.2 ms, was the delay time for filling the cone. The intersection with the ordinate was the 22 pl, and was close to the measured conical volume of 19 ± 3 pl. Figure A1 also plots the approximately conical volume as a function of time. Within experimental uncertainty, the cone formation rate is equal to the drop formation rate, which means the flow rate is approximately equal before and after the jet is emitted.

The empirical equivalence of the flow rates of drop generation and cone formation is further supported by Figure A2. For a 50 µm-ID nozzle under voltages ranging from 1.1 to 2 kV, the flow rate for drop formation (Q) and the filling rate of the cone (Q_c) are approximately equal. For nozzles with larger inner diameter, the conical base emits a jet before a Taylor cone is completely formed, and it was not possible to accurately measure the cone formation rate. However, the experimental support for the flow rate scaling developed below suggests that this equivalence holds true at larger inner diameter of 75 and 100 µm.

A3. Pulsation Frequency Measured by EHD Current

Figure 1b in the main text was presented to show the relative steadiness as far as drop generation was concerned. The intrinsic pulsation was not apparent in Figure 1b because the camera shutter was essentially open (except 6 µs necessary for data transfer); as a consequence of the Nyquist criteria, any pulsation at frequency higher than 1.25 kHz could not be captured at 2,500 fps. When the exposure time was reduced to 100 µs or less, pulsations were indeed observed. However, the maximum sampling frequency (10,000 fps) of our camera was inadequate to capture the time-lapsed process. Readers are referred to Marginean *et al.* for a high-speed video of intrinsically pulsating cone-jet captured at more than 100,000 fps.[2]

As a confirmation of the frequency measured by CCD imaging, Figure A3 presents a sample measurement of the intrinsic pulsation frequency through the EHD current signal. The current in the EHD circuit was measured by the voltage drop on a 1 MΩ oscilloscope. At a nominal electric field of 1.0 kV/cm, the Fourier transform of the EHD current peaks at 1.1 kHz, which

corresponds to the frequency of intrinsic pulsation captured by the video imaging. The measured intrinsic pulsation frequency was typically in the lower kilo-Hertz range, comparable to those reported for water-organics mixture.[2,3]

As discussed in the main text, the low-frequency oscillation reported by Juraschek and Rollgen was not observed in our system with self-regulating flow rate. The following calculation further supports that the low-frequency oscillation is related to the externally supplied flow rate: Figure 2 of Juraschek and Rollgen shows a low-frequency pulsation at approximately 30 Hz with a nozzle outer diameter (d_n) of 0.25 mm and a flow rate (Q_e) of 2 µL/min. The time scale to fill the cone scales as $\frac{1}{24}\pi d_n^3 / Q_e$, which is 16 Hz, comparable to the measured low frequency. The outer diameter is used to estimate the conical volume because the metal nozzle is hydrophilic (as opposed to our hydrophobic teflon nozzle).

References

1. O. Yogi, T. Kawakami, M. Yamauchi, J. Y. Ye, and M. Ishikawa, *Anal. Chem.* **73**, 1896-1902 (2001).
2. I. Marginean, L. Parvin, L. Heffernan, and A. Vertes, *Anal. Chem.* **76**, 4202-4207 (2004).
3. R. Juraschek and F. W. Rollgen, *Inter. J. Mass Spec.* **177**, 1-15 (1998).

Figures

Figure A1: Drop volume as a linear function of pulse duration for Figure 1b of main text. Nozzle ID = 50 µm, OD = 360 µm, length = 30 mm; Voltage = 1.6 kV, nozzle-to-substrate separation = 110 µm. Drop volume is assessed from microscopic images assuming a spherical cap. The flow rate from the linear extrapolation is 6.4 nl/s. The intersection of the linear extrapolation with the ordinate is 22 pl, approximately equal to the measured conical volume of 19 ± 3 pl. The error bar is based on uncertainty in conical volume measurement.

Figure A2: Equivalence of flow rates for drop generation and cone formation. Data from two realizations with different pressure heads are presented. ■: voltage = 1.1–1.5 kV; ●: voltage 1.6-2.0 kV. Other conditions are shown in Figure A1. The error bars for drop formation rate are the standard deviation of three independent realizations; those for cone formation are based on the uncertainty in the measurement of conical volume and the time for cone formation.

Figure A3: The Fourier transform of the current in the EHD circuit. Nozzle ID = 50 µm, OD = 360 µm, length = 30 mm; Voltage = 1.6 kV, nozzle-to-substrate separation = 150 µm. The current is measured by an oscilloscope, with 512 data points sampled at 50 kHz. The peak frequency of 1.1 kHz corresponds to the intrinsic pulsation frequency.

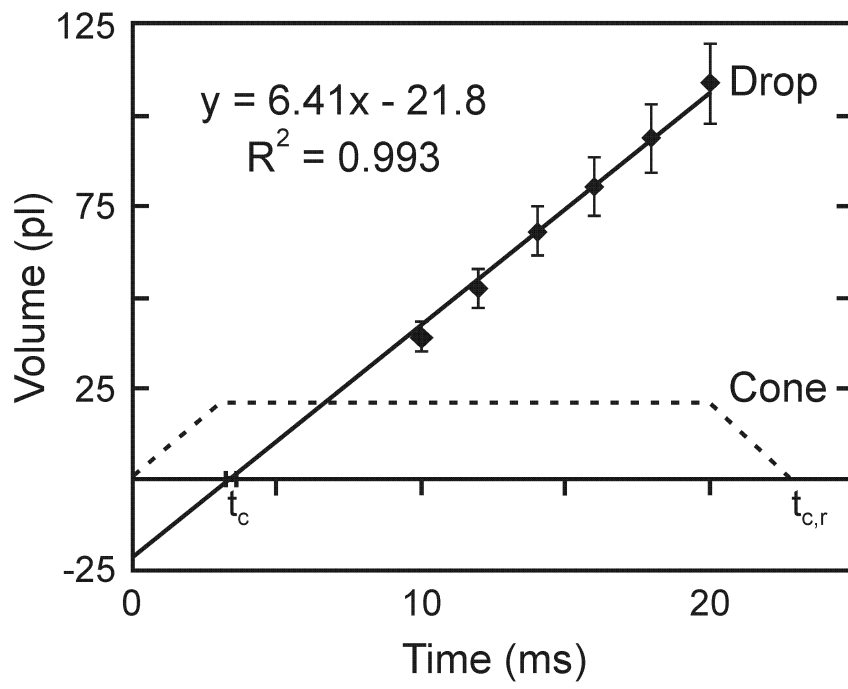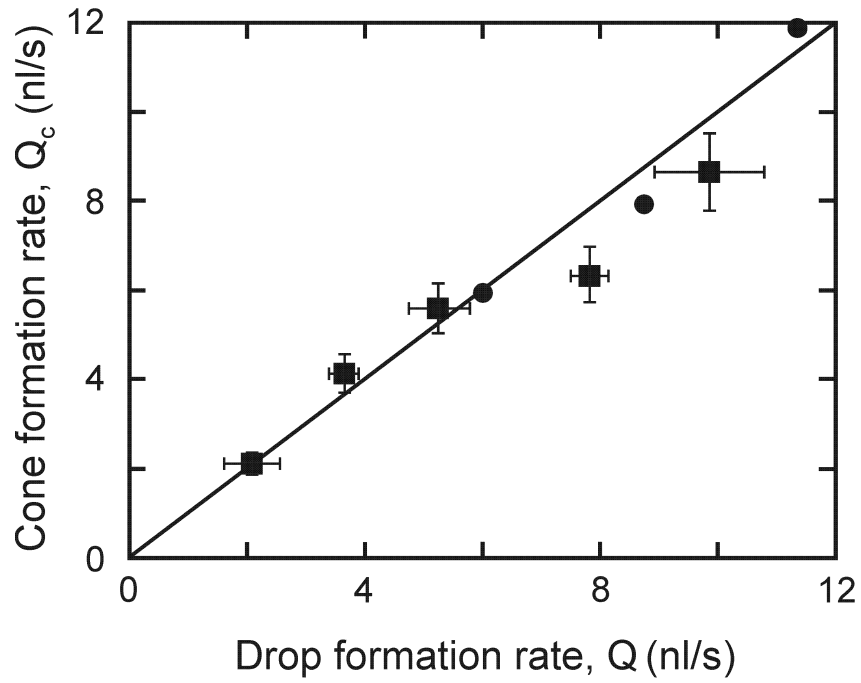$$y = 6.41x - 21.8$$
$$R^2 = 0.993$$

Drop

Cone

t_c

$t_{c,r}$

Volume (pl)

Time (ms)

Cone formation rate, Q_c (nl/s)

Drop formation rate, Q (nl/s)

x 10⁻³

Frequency, f (kHz)