# How much charge is there on a pulsating Taylor cone?

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The authors show that the capillary wave frequency spectrum of a charged droplet also gives an accurate estimate for the Taylor cone [Proc. R. Soc. London A **280**, 383 (1964)] pulsation frequency. For low conductivity liquids and relatively large radius emitters, this frequency is mainly influenced by the anchoring radius at the emitter tip. For smaller tips the net amount of charge on the Taylor cone becomes increasingly significant. For example, the charge on pulsating Taylor cones with anchoring radii of 65 and 50 $\mu$m increases from 57% to 74%, when expressed as a percentage of the Rayleigh limit [Philos. Mag. **14**, 184 (1882)] of the corresponding droplets with the same radii. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2266889]

The fastest growing applications of electrospray are based on its ability to create gas-phase ions of large biomolecules, i.e., serve as an ion source for mass spectrometry. Other applications include electrospinning, nanoencapsulation for drug delivery, steering of microsatellites in space, and spray painting. The phenomenological richness observed in the nonlinear electrohydrodynamics involved is the subject of active research.

Using perturbation theory, Rayleigh expressed the frequency spectrum for the capillary waves on the surface of a charged droplet,

$$\omega_n^2 \equiv 4\pi^2 f_n^2 = \frac{n(n-1)}{\rho r^3}\left[(n+2)\gamma - \frac{z^2e^2}{16\pi^2\varepsilon_0 r^3}\right], \tag{1}$$

where $\omega_n$ is the angular frequency of $n$th mode, $r$ is the droplet radius, $\rho$ and $\gamma$ are the density and surface tension of the liquid, respectively, $z$ is the number of elementary charges, $e$, and $\varepsilon_0$ is the vacuum permittivity. He has suggested that close to—what is known as—the Rayleigh limit[1] ($z^2e^2=64\pi^2\varepsilon_0\gamma r^3$) the droplet loses its stability and fine jets emerge. The frequency of the lowest excitation mode for a negligible amount of charge, $f_{2,z=0}$, can be expressed as

$$f_{2,z=0}^2 = \frac{\omega_2^2(z=0)}{4\pi^2} = \frac{2}{\pi^2}\frac{\gamma}{\rho r^3}. \tag{2}$$

Rayleigh's prediction on the ejection of fine jets was qualitatively confirmed by Zeleny.[2] He demonstrated the pulsation of the electrified liquid meniscus at the end of a glass capillary and described the complexity of the process in terms of various electrospray regimes.

Taylor thoroughly characterized a steady state spraying mode, in which the liquid takes the shape of a cone and a jet is continuously ejected from its apex.[3] Although under different conditions the observed oscillations in spray current measurements suggested pulsation phenomena,[4] due to its significance most attention was focused on the continuous regime.[5]

With the introduction of electrospray as a source of intact macromolecular ions for mass spectrometry,[6] producing stabile sprays with high ion yields became important. For a given liquid it is straightforward to select a set of parameters that produces a stable Taylor cone regime. In practical applications, however, changes in the liquid composition may occur that lead to instabilities. Regime changes can also be introduced by other factors, such as changes in the electric field[7] or liquid flow rate.

The amount of charge carried by electrosprayed droplets affects their downstream evolution, a phenomenon interesting from both fundamental and practical points of view. For example, if a droplet bears insufficient charge, it may produce a low yield of gas-phase ions. Extensive efforts are directed toward measuring the charge on electrosprayed droplets, especially in the context of Rayleigh discharge phenomena. It is generally accepted that the charge reduction takes place at the Rayleigh limit by the loss of a small droplet mass and comparatively large amount of charge.[8] The sprayed droplets are charged by the electrohydrodynamic entrainment of ions due to incorporation of charges on the Taylor cone. Currently there is no other method available to measure the amount of net charge on an electrified meniscus.

In recent reports we noted a relationship between the position of the contact line at the tip of the capillary and the pulsation frequency of the meniscus reflected by spray current oscillations.[9,10] In this letter a simple approach is described to determine the net charge on the Taylor cone based on measuring the frequency of these oscillations.

The results were obtained using methods similar to what were described in our previous publications.[9,10] Thus, here only the relevant differences are outlined. The physical dimensions of the five blunt tip capillaries (Hamilton Co., Reno, NV) and the tapered tip needle (New Objective, Woburn, MA) are listed in Table I. Each spray current measurement consisted of 250 000 points collected at a 25-kHz sampling rate using a WaveSurfer 452 digital oscilloscope (LeCroy, Chestnut Ridge, NY) at 1 M$\Omega$ input impedance through dc coupling with a bandwidth limit of 20 MHz. The data were processed with the embedded oscilloscope software. The Taylor cone pulsation frequencies and the corresponding standard deviations were extracted from the Fourier transform data through Gaussian fits.

HPLC-grade methanol was purchased from Aldrich. Deionized water (18.3 M$\Omega$/cm) was produced using a D4631 E-pure system (Barnstead, Dubuque, IA). The results presented in this letter were obtained with 50:50 (v/v) methanol-water mixture.

Table I summarizes the conditions and the results of our experiments performed with blunt tip, (1)–(6), and tapered

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TABLE I. Spraying conditions and oscillation frequencies for pulsating Taylor cones.

| | Emitter type | OD ($\mu$m) | ID ($\mu$m) | Flow rate ($\mu$L/min) | High voltage (V) | $r_a$ ($\mu$m) | Frequency (kHz) |
|---|---|---|---|---|---|---|---|
| (1) | 90525 | 510 | 260 | 4.0 | 3000 | 205 | $0.953 \pm 0.011$ |
| (2) | 90533 | 460 | 260 | 3.0 | 3000 | 179 | $1.119 \pm 0.013$ |
| (3) | 90539 | 470 | 130 | 8.0 | 3000 | 160 | $1.399 \pm 0.003$ |
| (4) | 90528 | 360 | 180 | 8.0 | 3000 | 159 | $1.353 \pm 0.001$ |
| (5) | 90531 (from Ref. 10) | 260 | 130 | 2.0 | 2900 | 130 | $1.991 \pm 0.011$ |
| (6) | 90531 (from Ref. 10) | 260 | 130 | 2.0 | 2900 | 65 | $4.398 \pm 0.016$ |
| (7) | PicoTip™ Metal TaperTip™ | 320 | 100 | 2.0 | 3000 | 50 | $5.326 \pm 0.020$ |

tip, (7), capillaries. The spray current was measured on a counterelectrode placed 30 mm away from the emitter. To ensure comparable conditions, in all experiments the electrospray was stabilized at the onset of the pulsating Taylor cone mode. This was achieved by adjusting the flow rate for systems (1)–(4) and by changing the high voltage at a fixed flow rate for emitter (7). The results for emitters (5) and (6) were included from our previous report.[10]

Different oscillation frequencies were measured for needles with similar geometries, (1) and (2), whereas similar frequencies were determined for emitters with very different geometries, (3) and (4). This indicated that the oscillation frequencies were not directly correlated with the inner or outer capillary diameters (IDs or ODs). Fast imaging of the meniscus showed that the liquid did not always completely wet the capillary tip, and the contact line could run anywhere between the ID and OD. The anchoring radii, $r_a$, of the menisci (see Table I) were determined during the liquid recoil phase when the boundaries were best defined.

Figure 1 shows the dependence of the squared pulsation frequency on the inverse of the cubed anchoring radius. The dashed line shows the relationship calculated according to Eq. (2). The excellent agreement for systems (1)–(5) (i.e., large anchoring radii) shows that the effect of charge in this region is negligible. As there is no fitting involved, it also indicates that Eq. (2) accurately describes the behavior of the

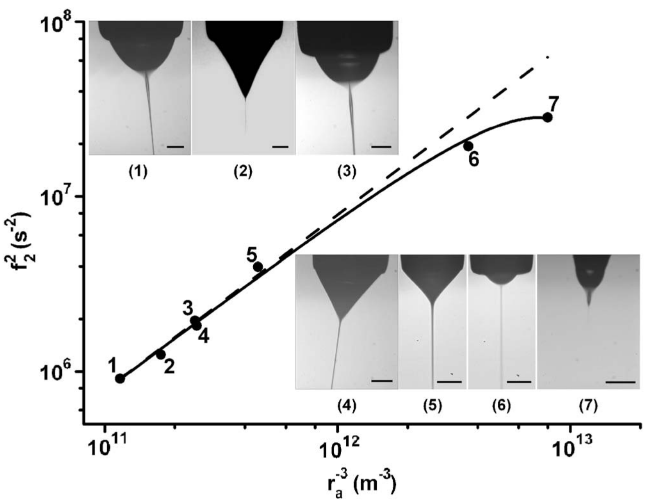


FIG. 1. Squared pulsation frequency is inversely proportional with cubed anchoring radius. For large radii, points (1)–(5), the effect of charge is negligible and Eq. (2) prevails (dashed line). As radii decrease, points (6) and (7), net charge becomes noticeable and Eq. (1) is more accurate (solid line). Data points are accompanied by snapshots of liquid menisci with 100 $\mu$m scale bars. Error bars are within symbols. Numbers correspond to entries in Table I.

meniscus. The close correlation between the frequency and the anchoring radius is surprising because Eq. (1) has been derived for small deformations of spherical droplets. Despite the significantly different boundary conditions for hemispherical liquid volume at the end of the capillary and the large amplitude of the oscillations, Eq. (1) seems to be adequate.[10]

Charge polarization is responsible for liquid ejection from neutral droplets when they are subjected to electric fields.[11] Taylor cones are located in strong electric fields that induce charge polarization along the cone axis. Thus, the charge density in the apex may be high enough to induce divergent short wavelength fluctuations and, consequently, jet ejection. At the same time, the low average net charge density exerts limited influence on the pulsation frequency of the liquid.

At their Rayleigh limits ($z_R^2 e^2 = 64\pi^2 \varepsilon_0 \gamma r^3$), small liquid volumes, $V$, are able to sustain higher charge densities than larger liquid volumes ($z_R / V \propto r^{-3/2}$). The deviation from linearity with decreasing anchoring radius [points (6) and (7)] in Fig. 1 shows that higher charge density on a smaller Taylor cone affects the fluid dynamics for a nanospray more significantly than for a regular electrospray. This can be explained by the increased relative effect of the net charge on the Taylor cone. The ratio of the charge on the Taylor cone and the charge on a droplet with the same radius at the Rayleigh limit can be expressed from Eq. (1) as

$$z/z_R = \sqrt{1 - \pi^2 \rho f_2^2 r^3 / (2\gamma)}. \tag{3}$$

For 50% methanol with $\gamma = 0.0356$ N/m and $\rho = 920$ kg/m$^3$ from Eq. (1), the amount of charge on the Taylor cone can be evaluated as $z_{r=65\ \mu\mathrm{m}} = (2.62 \pm 0.02) \times 10^7$ and $z_{r=50\ \mu\mathrm{m}} = (2.30 \pm 0.01) \times 10^7$ elementary charges. From Eq. (3) these values are 57% and 74% of the Rayleigh limits corresponding to droplets of radii 65 $\mu$m ($z_{R,r=65\ \mu\mathrm{m}} = 4.61 \times 10^7$) and 50 $\mu$m ($z_{R,r=50\ \mu\mathrm{m}} = 3.11 \times 10^7$).

Increasing the spray voltage in the pulsating Taylor cone mode leads to an increase in the oscillation frequency [see Fig. 4(a) in Ref. 10]. Since the amount of charge on the Taylor cone is not expected to decrease with increasing high voltage, the increasing frequency can be explained by a decrease in the amount of liquid pulsating at the end of the needle. This is quite difficult to observe in the pulsating cone regime, but a decrease in the cone base angle with increasing high voltage has been reported.[12] The declining frequencies with increasing flow rates [Fig. 4(b) in Ref. 10] can be explained similarly by an increase in the liquid volume. Even with constant high voltage and flow rate, the amount of pulsating liquid may fluctuate, inducing slight changes in the pulsation frequency, reflected by peak broadening and/or the presence of a low frequency component in the Fourier spectra of the spray current. Thus, an important necessary condition for the validity of Eq. (1) and the above analysis is the presence of a sharp high frequency peak and the absence of low frequency components in the Fourier spectra. These conditions are typically satisfied at the onset of the pulsating cone mode.

In addition to the determination of the net charge accumulated on the Taylor cone, spray current oscillation frequency measurements can also be used to determine the surface tension of different liquids. Using nonwetting liquids with known properties, radii of relatively small orifices can also be measured.

Based on the behavior of spontaneous pulsation for electrostatic sprays outlined above, some literature data on forced pulsation induced by ac high voltage can also be rationalized. As in the case of dc electrospray, increasing the amplitude for a given ac frequency leads to transitions between different electrospray regimes.[13] Sung and Lee determined the necessary spray voltage amplitudes, $U_{sp}$, for these transitions as a function of the forcing ac frequency, $f_{ac}$. All $U_{sp}=U(f_{ac})$ mode change curves showed minima for the transitions, such as the dripping to spindle mode, spindle to varicose instability, and varicose to kink instability, at approximately the same frequency. Spraying distilled water ($\rho=1000$ kg/m$^3$ and $\gamma=0.073$ N/m) through a capillary with OD=420 $\mu$m, the lowest high voltage for all three mode change curves was at 450 Hz. Droplet size measurements also showed a minimum very close to the same frequency.

Using Eq. (2) the calculated pulsation frequency for this system is 447 Hz. This agreement is interesting because it indicates that the resonant excitation of capillary waves not only governs transitions closely associated with the meniscus (dripping to spindle) but also influences the breakup of the liquid filament (varicose to kink). This observation has implications for the optimization of ac electrospray droplet generators with predictable droplet sizes, as well.

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