Negative Droplets from Positive Electrospray

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Image charge detection has been used to measure the charge and velocity of individual electrosprayed water droplets. With a positive bias on the electrospray needle the majority of the droplets are, as expected, positively charged. However, a small fraction, surprisingly, carry a negative charge. Plausible explanations for the presence of the negatively charged droplets are discussed. In particular, we consider the possibility of the negatively charged droplets resulting from a bipolar fission process where the incorporation of a small negatively charged droplet between two larger positively charged droplets lowers the energy barrier for symmetric fission.

Introduction

Charged liquid droplets play an important role in many phenomena, ranging from the charging of thunderstorms1–3 to electrospray ionization.4–8 They become unstable when the electrostatic forces exceed the surface tension. Rayleigh investigated this instability many years ago by considering whether small distortions from spherical were stabilizing or destabilizing.9,10 This analysis led to the now well-known Rayleigh limit for the stability of charged droplets:

\[ q_R = 4\pi[(n + 2)\epsilon_0\gamma r^3]^{1/2} \]  

where \( q_R \) is the charge on the droplet, \( r \) is the radius, \( \gamma \) is the surface energy, and \( n \) indicates the number of lobes in the deformed drop. The quadrupole (prolate/oblate) distortion with \( n = 2 \) becomes unstable at the lowest charge. The unstable droplets may fission into two or more progeny with roughly equal size, explode into many small droplets,11 or discharge by emitting a fine jet of charged nanodroplets.12–16 Such jets have been imaged for levitated microdroplets.13,16–19 While larger charged microdroplets discharge by emitting jets, smaller droplets are expected to undergo a fission process. Explosion into many small progeny appears to be a property of droplets charged substantially above the Rayleigh limit.11,20

Fragmentation is a ubiquitous process, and the ideas developed for the stability of liquid droplets have found applications in related problems including nuclear fission,21,22 the stability of multiply charged metal clusters,23–27 the gas-phase dissociation of protein complexes,28–33 and the expansion of optical molasses.34 In this paper we report results obtained using image charge detection35–40 to examine the droplets generated by electrospraying pure water. Charge and velocity distributions have been recorded for electrosprayed water droplets that are transmitted through a capillary interface into vacuum. Surprisingly, we find that a small fraction of the droplets generated by positive electrospray are negatively charged. Using a simple model we explore the idea that the negatively charged droplets result from a bipolar fission process where a positively charged droplet breaks into two positively charged droplets and a small negatively charged one. The small negatively charged droplet,

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**Introduction**

Charged liquid droplets play an important role in many phenomena, ranging from the charging of thunderstorms\(^1\)\(^{-3}\) to electrospray ionization.\(^4\)\(^{-8}\) They become unstable when the electrostatic forces exceed the surface tension. Rayleigh investigated this instability many years ago by considering whether small distortions from spherical were stabilizing or destabilizing.\(^9\)\(^{-10}\) This analysis led to the now well-known Rayleigh limit for the stability of charged droplets:

\[
q_R = 4\pi[(n + 2)\epsilon_0\gamma r^3]^{1/2} \tag{1}
\]

where \( q_R \) is the charge on the droplet, \( r \) is the radius, \( \gamma \) is the surface energy, and \( n \) indicates the number of lobes in the deformed drop. The quadrupole (prolate/oblate) distortion with \( n = 2 \) becomes unstable at the lowest charge. The unstable droplets may fission into two or more progeny with roughly equal size, explode into many small droplets,\(^11\) or discharge by emitting a fine jet of charged nanodroplets.\(^12\)\(^{-16}\) Such jets have been imaged for levitated microdroplets.\(^13\)\(^{16}^{-19}\) While larger charged microdroplets discharge by emitting jets, smaller droplets are expected to undergo a fission process. Explosion into many small progeny appears to be a property of droplets charged substantially above the Rayleigh limit.\(^11\)\(^{-20}\)

Fragmentation is a ubiquitous process, and the ideas developed for the stability of liquid droplets have found applications in related problems including nuclear fission,\(^21\)\(^{-22}\) the stability of multiply charged metal clusters,\(^23\)\(^{-27}\) the gas-phase dissociation of protein complexes,\(^28\)\(^{-33}\) and the expansion of optical molasses.\(^34\) In this paper we report results obtained using image charge detection\(^35\)\(^{-40}\) to examine the droplets generated by electrospraying pure water. Charge and velocity distributions have been recorded for electrosprayed water droplets that are transmitted through a capillary interface into vacuum. Surprisingly, we find that a small fraction of the droplets generated by positive electrospray are negatively charged. Using a simple model we explore the idea that the negatively charged droplets result from a bipolar fission process where a positively charged droplet breaks into two positively charged droplets and a small negatively charged one. The small negatively charged droplet,
surrounded by a grounded case which has 5 mm diameter entrance and exit apertures which allow droplets to pass through the charge detection cylinder. The charge detection assembly is preceded by a thin plate with a 1 mm aperture which collimates the droplet beam. The signal from the preamplifier is taken out of the vacuum chamber where it is amplified and differentiated (Ortec, 571) and then presented to a transient digitizer (Alazartech, ATS460). The transient digitizer is programmed to trigger on droplet signals above a preset threshold. We typically record 10 000 transients, which are then sorted and analyzed off-line.

Experimental Results

The transient from a single positively charged droplet is shown in Figure 2a. The initial negative-going pulse results from the droplet entering the cylinder, and the subsequent positive-going one results from the droplet leaving. The time between the two pulses (along with the effective length of the cylinder) gives the velocity of the droplet. The area enclosed by the pulses is proportional to the charge. The proportionality constant is determined by applying a small voltage pulse to a known capacitance at the input of the preamplifier.

In addition to traces that show a single droplet, as in Figure 2a, many traces have peaks due to two or more closely spaced droplets, which may result from the breakup of larger droplets upstream from the charge detection cylinder. This breakup could occur as the droplets travel between the electrospray needle and the capillary interface, as they travel through the capillary interface, or after the droplets enter the vacuum chamber. In a vacuum, rapid evaporative cooling will supercool the droplets, and they may subsequently freeze. During evaporative cooling, the droplet diameters will shrink by about 5%, which is probably enough for some droplets to exceed the Rayleigh limit. These droplets may fission or discharge before they dissociate. Once the droplets freeze, dissociation will become much more difficult since it will require the cleavage of a small ice crystal.

The vast majority of the droplets are positively charged. Positive electrospray is expected to yield positively charged droplets. The strong electric field at the end of the electrospray needle polarizes the water and leads to the formation of a Taylor cone which emits positively charged droplets. It is difficult to imagine that a negatively charged droplet could leave the Taylor cone under these circumstances. Despite this we find that a small fraction (typically around 1% under the conditions employed here) of the droplets that pass through the detector are negatively charged. An example of the transient for a negatively charged droplet is shown in Figure 2b. It is similar to Figure 2a except that the polarities of the two peaks are reversed. We stress here that there is no voltage in the experimental apparatus beyond that applied to the electrospray needle. Everything else, including the capillary interface, is grounded. A reviewer suggested the possibility that the negatively charged droplets could arise from discharge events. To address this question we monitored the voltage on the electrospray needle with a fast transient digitizer while another transient digitizer recorded the signal from the droplets. We found that discharge events were rare and not correlated with the negative droplets.

The upper half of Figure 3 shows examples of histograms of the charge and velocity distributions obtained for isolated droplets from a typical data set. The voltage threshold for the transient digitizer was set to a value corresponding to a charge of around 5000 elementary charges (e) (8.0 × 10⁻¹⁶ C) for this data set. The charge distribution for the positively charged droplets appears to be roughly exponential. For the negatively charged droplets, the abundances are scaled up by a factor of 100, only the low charges are observed. The velocity distribution for the positively charged droplets appears to be roughly Gaussian. The distribution is centered around 275 ms⁻¹, and extends from ~150 ms⁻¹ to ~450 ms⁻¹. The velocity distribution for the negatively charged droplets is peaked at a slightly lower velocity than the positively charged ones. The lower half of Figure 3 shows a plot of charge against velocity for the positive (red) and negative (blue) droplets. There is
clearly some correlation between the charge and velocity. The fastest moving droplets all have relatively low charges.

**Discussion**

The droplets are accelerated as they travel through the capillary interface and in the expansion at the end of the capillary. The average flow velocity in the capillary is in excess of 180 m s⁻¹ (based on the gas flow through the capillary). The terminal flow velocity for a perfect isentropic expansion of air at 300 K is 780 m s⁻¹. However, the expansion at the end of the capillary is relatively mild, and the terminal flow velocity will not be this high. The droplet velocities range from 150 to 450 m s⁻¹. Some of this distribution probably results from velocity slip within the expansion. Heavier molecules in a seeded supersonic expansion are often not accelerated to the full velocity of the carrier. Since the droplets studied here probably have diameters that range up to several micrometers, some velocity slip is expected. The correlation between the charge on the droplets and their velocity supports this interpretation.

The more highly charged droplets (which are presumably also the larger droplets) have velocities at the low end of the distribution (200–300 m s⁻¹), while those with low charge and high velocities (350–450 m s⁻¹) are probably the smaller droplets.

The most intriguing result reported here is the observation that around 1% of the droplets passing through the detector are negatively charged when the electrospray needle is at +4.5 kV. It is difficult to imagine a negatively charged droplet leaving the electrospray needle when it is biased at such a large positive voltage. Negatively charged droplets would be attracted back to the electrospray needle by the very strong electric field around the needle. Thus the negatively charged droplets must result from the positively charged droplets after they enter the capillary interface.

To a first approximation, the energy of a charged, conducting, spherical droplet can be thought of as being composed of the electrostatic energy and the surface energy:

\[ E = \frac{\varepsilon^2 e^2}{8\pi\varepsilon_0 r} + 4\pi r^2 \gamma \]  

where \( r \) is the radius, \( \varepsilon \) the charge, and \( \gamma \) the surface energy. The energies of possible fragmentation pathways can be obtained by summing the energies of the progeny, subject to the constraints of conservation of charge and volume. At low charge, the parent droplet is stable (because both symmetric and asymmetric fission increase the surface energy), but with increasing charge the parent becomes unstable toward asymmetric fission (the products of asymmetric fission become lower in energy than the parent). This occurs at around 50% of the Rayleigh limit. At around 70% of the Rayleigh limit the products of symmetric fission become lower in energy than those of asymmetric fission. With increasing charge it becomes energetically more favorable to break apart into three equal-sized progeny rather than two, and then, at the Rayleigh limit, four.

Ultimately, as the charge is raised further and further above the Rayleigh limit, explosion into many small progeny becomes the most energetically favored fragmentation route.

In experimental studies, however, the droplets do not fission into a few roughly equal-sized progeny or even explode into many roughly equal-sized progeny. Instead, they discharge at close to the Rayleigh limit by emitting a jet of charged nanodroplets. In this process the charge is substantially reduced (by around 10–25%) with only a small decrease in the mass.

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The result of minimizing \( \Delta E \) as a function of the progeny relative volume, subject to the constraints mentioned above, is shown as the solid red line in Figure 4. The results shown in the figure are for a droplet with \( r_p = 4.0 \) μm at the Rayleigh limit (\( \varepsilon_p = 10^9 \) e). Symmetric fission into two equally sized progeny droplets is the lowest energy fragmentation process. The dashed line in Figure 4 shows the result of adding repulsion between the progeny droplets to give the energy barrier according to eq 3. Symmetric fission has the highest energy barrier, while the barrier vanishes in the asymmetric fission limit (i.e., fragmentation into one very large and one very small droplet). The products generated by this process are not as low in energy as in symmetric fission. However, the energy barrier is lower and sequential loss of many small droplets will discharge the parent droplet because the charge-to-volume ratio of the small droplets is much greater than for the large one. This is equivalent to the jetting process that has been observed for large microdroplets. The substantial energy barrier to

\[ \Delta E_B = \Delta E + \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 (r_1 + r_2)} \]  

where \( \Delta E \) is the energy difference between a parent and two progeny droplets as a function of the relative volume of the progeny. The energy difference was obtained by minimizing eq 4 in the text subject to conservation of volume and charge. The dashed line shows the result of incorporating the energy barrier according to eq 3 in the text. The results are for a parent droplet with \( r_p = 4.0 \) μm at the Rayleigh limit (\( \varepsilon_p = 10^9 \) e).
between the droplet at the Rayleigh limit, the electrostatic interactions of a parent droplet with are equal to each other. The results are plotted in Figure 5 for charge and volume of the central droplet, assuming that the situation, we minimized the energy barrier as a function of the two positively charged droplets. To identify the most favorable energy barrier is decreased compared to that for fission into +− system and the corresponding energy barrier. The energy barrier is significantly lowered by fission into three +− droplets instead of two positively charged droplets. The lower half of Figure 5 shows a plot of the optimized −fractional charge (solid line) and fractional volume (dashed line) for the middle of the three +− droplets. A fractional charge of −0.02 on the middle droplet indicates fractional charges of +0.51, −0.02, and +0.51 on the droplets, relative to the charge of 106 e on the parent droplet. Within the framework of the simple model employed here the energy barrier at the Rayleigh limit is minimized with a fractional charge of around 0.03 and a fractional volume for the middle droplet of around 0.01.

We do not pretend that this model gives an accurate quantitative description, but we believe that it captures the essential physics of the problem. It shows that the energy barrier for symmetric fission can be substantially reduced by incorporating a small negatively charged droplet between the two larger positively charged progeny. However, while this bipolar fission process lowers the activation barrier for symmetric fission, asymmetric fission still has a lower activation barrier at the Rayleigh limit. The barrier for asymmetric fission (to produce two positively charged progeny) approaches zero as the smaller droplet becomes vanishingly small. For bipolar fission the energy barrier vanishes (and becomes <0) for droplets charged to less than 10% over the Rayleigh limit, compared to more than 50% over the Rayleigh limit for symmetric fission into two positively charged droplets. So bipolar fission becomes competitive with asymmetric fission for droplets charged to less than 10% over the Rayleigh limit. The rapid evaporative cooling that occurs for droplets in a vacuum could drive some of them to more than 10% over the Rayleigh limit. So it is plausible that bipolar fission can account for the negative droplets found here. The crude model used here almost certainly overestimates the energy barriers for symmetric fission because we do not consider the polarization of the progeny droplets (where one droplet polarizes the other).

In the experiments, the negatively charged droplets have charges of around {\(2(\pm 3) \times 10^4\) e. If this corresponds to around 3% of the total charge, then the parent droplet charge must be around 106 e. The next obvious question is where does the negative charge arise from? The excess positive charge on the droplet is presumably due to H3O+. The H3O+ is expected to lie on the surface of the droplet, leaving the core uncharged. The water in the core of the droplet will self-ionize according to

\[
\text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \quad (5)
\]

and the resulting OH− could be the source of the negative charge. Using the ionization constant of water (\(K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}\) at STP) there are expected to be around \(1.6 \times 10^4\) H3O+/OH− pairs in a droplet with a radius of

Figure 5. The upper plot shows the energies of the fission fragments from a parent droplet with \(r_p = 4 \mu m\) plotted against the total charge. The Rayleigh limit is at \(10^6\) e. The solid black line shows the energy change for symmetric fission. The dashed black line shows the energy barrier for symmetric fission obtained by incorporating the electrostatic repulsion (see text). The solid red and dashed red lines show the energy difference and energy barrier, respectively, for the optimized three droplet +− system. The lower plot shows the charge and volume of the central droplet of the optimized three droplet system. The solid red line shows −fractional charge plotted against the charge on the parent droplet, and the dashed red line shows the relative volume.
4 μm. Thus if there is no further ionization during the dissociation process, virtually all of the OH− generated by self-ionization must be localized in the negatively charged droplet. The driving force for this charge localization is the lowering of the energy barrier to fission. A bipolar fission process where the incorporation of a small negatively charged droplet between two larger positively charged fission fragments lowers the energy barrier to fission. According to the model, bipolar fission becomes competitive with asymmetric fission for droplets charged to less than 10% over the Rayleigh limit. More sophisticated simulations, that include polarization, are required to fully evaluate the feasibility of this process. We also consider the possibility of the negatively charged droplets resulting from field induced polarity changes, from high energy collisions of the droplets with metal surfaces, and from turbulence within the capillary interface.

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References and Notes


(41) The effective length of the charge detection cylinder was determined using two identical detectors separated by 11.1 cm. For individual droplets that passed through both detectors we determined the times spent in both detectors (i.e. the times between the centers of the entrance and exit pulses) along with the time spent traveling between the detectors (i.e. the time between the centers of the entrance pulses for both detectors). With this information, and knowledge of the geometry, the effective length can be determined.


(43) Based on a rough estimate using the bulk heat capacity of water, the latent heat of evaporation, and a freezing temperature of 200 K (from ref 40).


