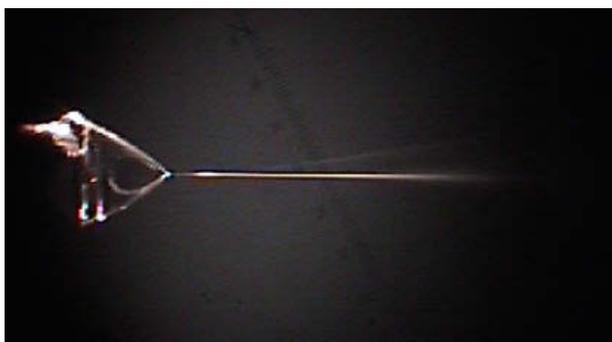


Session 44/45 : Cone-jet Electrosprays, or Colloid Thrusters

Once the electric traction overcomes surface tension, a Taylor Cone-like liquid structure could appear. It is clear that a Taylor Cone is a highly idealized situation in which no flow and perfect electric relaxation are assumed. Under those conditions, the electric field will simply intensify towards the tip until becoming infinitely large at the infinitesimally small apex. In reality, however, full relaxation cannot continue if there is non-zero liquid flow, and a departure from an ideal Taylor Cone is expected. As the photograph below shows, a jet is seen to issue from the cone's tip, implying the need for a flow rate, say Q (m^3/s). Since the surface being ejected is charged, this also implies a net current, I . It will be seen that these flows and currents are (in the regime of interest) extremely small: $Q \approx 10^{-13} \text{ m}^3/\text{s}$ per needle. The tip jet is likewise extremely thin (of the order of $20 - 50 \text{ nm}$). This operational regime is known as the *Cone-Jet* mode, which is obtained with practically all conductive liquids, in particular electrolytic solutions.



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Not very near the cone's tip, the current is mostly carried by ionic conduction in the electrolytic solution. In a good, highly polar solvent (i.e., one with $\epsilon \gg 1$), the salt in solution is highly dissociated, at least at low concentration. For example, LiCl in Formamide dissociates into Li^+ and Cl^- and each of these ions, probably "solvated" (i.e., with several molecules of formamide attached), will drift at some terminal velocity (in opposite directions) in response to an electric field. At high concentrations (several molar) the degree of dissociation decreases. Following are the measured electrical conductivities K , of solutions of LiCl in Formamide (CH_3NO).

Concentration (mol/l)	K (Siemens/m)
1.47×10^{-3}	3.16×10^{-3}
1.47×10^{-2}	5.49×10^{-2}
0.147	0.27
1.0	1.12
3	2.2

This finite conductivity implies that, under current, there will be some electric field directed radially ($E_r \neq 0$). This contradicts the assumption made that the Taylor Cone's surface is an equipotential, especially near the tip, where the current density must be strongest. Hopefully, E_r is at least much less than E_θ over most of the cone.

Let us assume that we have such a conical structure, in which because of the liquid flow, charges move very slowly everywhere, except very near the cone apex. Near this cone-jet

transition region (of size r^*), the liquid surface will stop to be an equipotential as the liquid passage time r^{*3}/Q , becomes of the order of the charge relaxation time, $\varepsilon\varepsilon_0/K$,

$$\frac{r^{*3}}{Q} \approx \frac{\varepsilon\varepsilon_0}{K} \quad (1)$$

from here, we obtain the “characteristic dimension” of the cone-jet transition region,

$$r^* = \left(\frac{\varepsilon\varepsilon_0 Q}{K} \right)^{1/3} \quad (2)$$

It turns out that the dimension r^* plays a fundamental role on the scaling and understanding of electrospay thrusters. In this region, we assume that most of the surface transport will be convected, such that $I \approx I_s$, but still most of the surface is relaxed $\sigma \approx \varepsilon_0 E_\theta$. The surface current I_s , associated with a fluid velocity u , will be,

$$I_s = 2\pi(r^* \sin \theta_T) \sigma u \quad \text{with} \quad \sigma = \varepsilon_0 E_\theta = \varepsilon_0 \sqrt{\frac{2\gamma \cot \theta_T}{\varepsilon r}} \quad (3)$$

where,

$$u = \frac{Q}{2\pi(1 - \cos \theta_T)r^{*2}} \quad (4)$$

Under these assumptions, the current carried by the cone-jet will be,

$$I \approx \frac{\sqrt{2 \cos \theta_T \sin \theta_T}}{1 - \cos \theta_T} \sqrt{\frac{\gamma K Q}{\varepsilon}} \quad \text{with} \quad \frac{\sqrt{2 \cos \theta_T \sin \theta_T}}{1 - \cos \theta_T} = 2.86 \quad (5)$$

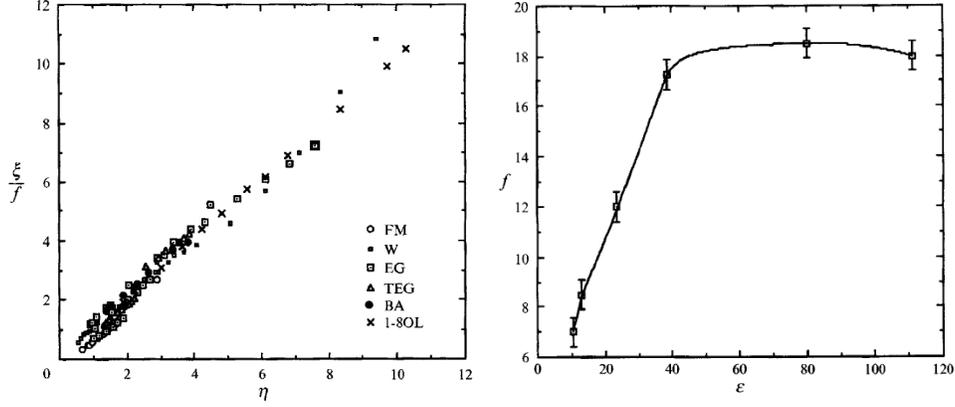
Fernandez de la Mora (1994) used a similar argument and verified experimentally that the current transported by cone-jet electrospays is given by,

$$I = f(\varepsilon) \sqrt{\frac{\gamma K Q}{\varepsilon}} \quad (6)$$

The quantity $f(\varepsilon)$ has a value of about 18 for $\varepsilon > 40$, which is somewhat different from the value obtained in (5). Our oversimplified analysis neglected conduction contributions and the effects of internal fields (the dependence on ε). Nevertheless, Eqs. (5) or (6) are remarkable in several respects:

- (a) Current is independent of applied voltage.
- (b) Current is independent of electrode shape.
- (c) Current is independent of fluid viscosity - even though some of the fluids tested are very viscous.

The degree of experimental validity of (6) is shown in the figure (F. de la Mora 1994). Here, non-dimensional parameters are defined as follows:



$$\xi = \frac{I}{\gamma\sqrt{\epsilon_0/\rho}} \quad (7)$$

and,

$$\eta = \sqrt{\frac{\rho K Q}{\gamma \epsilon \epsilon_0}} \quad (8)$$

where ρ is the liquid mass density. With these definitions, Eq. (6) becomes,

$$\xi = f(\epsilon) \eta \quad (9)$$

For six different fluids, and over a wide range of flows, the correlation in the data is remarkable.

Droplet Size and Charge

From the nature of the Taylor Cone, the liquid, as it progresses towards the tip jet, maintains an equilibrium on its surface between electrostatic and surface tension forces. This equilibrium is disturbed near the tip, but it is reasonable to conjecture that something close to it will be sustained into the jet, and even after jet break-up, into the droplets which result. If we postulated this for a droplet of radius R and charge q , the equilibrium condition becomes,

$$\frac{1}{2}\epsilon_0 E_n^2 = \frac{2\gamma}{R} \quad \text{with} \quad E_n = \frac{q}{4\pi\epsilon_0 R^2} \quad (10)$$

from which we can solve for the maximum charge that a droplet could hold,

$$q_R = 8\pi\sqrt{\epsilon_0\gamma}R^{3/2} \quad (11)$$

which is known as the **Rayleigh** Limit above which the droplet will experience a ‘‘Coulombic’’ explosion. In practice, however, a small departure from the full spherical shape will trigger the instability when close to this limit. Experiments have shown that electrosprays produce streams of droplets charged to about $\frac{1}{2}$ of their Rayleigh limit. The outcome of a Coulombic explosion is fragmentation into small spherical droplets. It is easy to prove that daughter

droplets, if fragmenting symmetrically from a droplet at the Rayleigh limit (or half of it), will be charged to about 71% of their corresponding limit, and therefore will be stable (neglecting solvent evaporation).

The droplet mass is $m = \frac{4}{3}\pi R^3\rho$, so that the maximum specific charge carried by droplets would be,

$$\frac{q}{m} \Big|_{max} = \frac{6\sqrt{\varepsilon_0\gamma}}{\rho R^{3/2}} \quad (12)$$

A plausible explanation of the $\frac{1}{2}$ factor of the Rayleigh limit could be articulated if we ask what is the least-energy subdivision of a given total mass m_t and charge q_t . If this subdivision is made into N equal drops of radius R , we have,

$$N = \frac{m_t}{\rho \frac{4}{3}\pi R^3}$$

and each drop will carry a charge,

$$q = \frac{q_t}{N} = \rho \frac{4}{3}\pi R^3 \frac{q_t}{m_t}$$

The energy per drop comprises an electrostatic part $\frac{1}{2}q\phi$, and a surface part $4\pi R^2\gamma$,

$$E = N \left(\frac{1}{2} \frac{q^2}{4\pi\varepsilon_0 R} + 4\pi R^2\gamma \right) \quad (13)$$

Differentiating and equating to zero, we obtain,

$$R = \left(9 \left(\frac{m_t}{q_t} \right)^2 \varepsilon_0 \gamma \right)^{1/3}$$

or,

$$\left(\frac{q}{m} \right)_{minE} = \frac{3(\varepsilon_0\gamma)^{1/2}}{\rho R^{3/2}} \quad (14)$$

So, the minimum-energy assembly of drops has a specific charge exactly $\frac{1}{2}$ the maximum possible, which agrees with experimental observations, although some difficulty of interpretation arises with polydisperse clouds (many sizes present).

If the droplet size R is assumed known, we can deduce the radius R_{jet} of the jet from whose breakdown they originate. Several experiments confirm that this jet breakup conforms closely to the classical Rayleigh-Taylor stability theory for uncharged jets, which predicts a ratio,

$$\frac{R}{R_{jet}} = 1.89 \quad (15)$$

We can express R_{jet} as a function of flow and fluid quantities by assuming Rayleigh-limited drops Eq. (12), and using,

$$\frac{q}{m} = \frac{I}{\rho Q} \quad \text{then} \quad \frac{I}{Q} = \frac{6\sqrt{\varepsilon_0\gamma}}{(1.89R_{jet})^{3/2}}$$

or,

$$R_{jet} = \frac{1}{1.89} \left(\frac{6}{f}\right)^{2/3} r^* \approx \frac{1}{4} r^* \quad (\text{with } f \approx 20) \quad (16)$$

This value is in the range of the data published in the literature, which strongly supports the validity of the arguments used. It can be also observed that $f(\varepsilon)$ is known to fall for less than about 40, and Eq. (16) constitutes a prediction for a corresponding increase in the jet diameter. No direct data appear to be available on this point.

To conclude this discussion, we observe that,

$$\frac{q}{m} = \frac{f(\varepsilon)}{\rho} \left(\frac{\gamma K}{\varepsilon Q}\right)^{1/2} \quad (17)$$

which means that the highest charge per unit mass is obtained with the smallest flow rate. A high q/m can be important in order to reduce the needed accelerating voltage V for a prescribed specific impulse $I_{sp} = c/g$,

$$V = \frac{c^2}{2(q/m)} \quad (18)$$

For concreteness, suppose we desire $c = 8000$ m/s ($I_{sp} = 800$ s) without exceeding $V = 5$ kV. From (18), we need $q/m > 6400$ C/kg. Suppose we use a Formamide solution with $K = 1$ Si/m and $\varepsilon = 100$, $f = 18$, $\rho = 1130$ kg/m³ and $\gamma = 0.059$ N/m. Using Eq. (17), we calculate a flow rate $Q < 7.1 \times 10^{-15}$ m³/s, corresponding to a mass flow of less than 8 ng/s, or a current of less than 50 nA.

These are really small flow rates and currents. The input power per emitter is then less than $P = VI = 0.26$ mW and the thrust is less than $F = \dot{m}c = 0.064$ μ N.

For this example, we also calculate $r^* = 18.5$ nm, which gives a jet diameter of about 7.5 nm, and a droplet radius of 7 nm. The drop charge is $q \approx 1 \times 10^{-17}$ C (65 elementary charges for about 21,000 Formamide molecules).

Notice also the scalings,

$$Q \propto K \frac{V^2}{c^4} \quad \text{and} \quad F \propto K \frac{V^2}{c^3}$$

The required flow rate is quite sensitive to the prescribed specific impulse. For small Δv missions, where high specific impulse is not imperative, the design can be facilitated by both, reducing V and increasing Q .

Limitations to the droplet charge and mass

As we have seen, high q/m can be obtained by increasing the conductivity K of the liquid (more concentrated solutions), and, for a given conductivity, by reducing the flow rate Q . As

Q/K is reduced, the jet becomes thinner (as $r^* \propto (Q/K)^{1/3}$), the droplets become smaller in the same proportion, and their specific charge increases as $\sqrt{\gamma K/Q}$. It would appear then that q/m can be indefinitely increased through flow reduction. Two phenomena have been identified, however, which limit this increase:

(a) Taylor Cone instability

It has been noted that the Taylor cone becomes intermittently disrupted when the non-dimensional group η introduced in Eq. (8) becomes less than some lower limit (of the order of 0.5 in conventional capillary tubes). The nature of this instability is not currently well understood, and so there is some uncertainty as to its generality. One likely explanation is the fact that q/m cannot exceed the specific charge that would result from full separation of the positive and negative ions of the salt used,

$$\left(\frac{q}{V}\right)_{max} = \left(\frac{q}{m/\rho}\right)_{max} = F \times 1000c_d \quad (\text{C/m}^3) \quad (19)$$

where $F = 96500$ C/mol is Faraday's constant, and c_d is the dissociated part of the solution's equivalent normality (mol/l). The dissociated concentration c_d is linearly related to the conductivity K through a "mobility parameter" Λ_0 ,

$$K \equiv \Lambda_0 c_d \quad (20)$$

For aqueous solutions Λ_0 is 15 (Si/m)/(mol/l) if there are no H^+ ions, in which case $\Lambda_0 \approx 40$ (Si/m)/(mol/l). We therefore can write, from (17),

$$f(\varepsilon) \left(\frac{\gamma K}{\varepsilon Q}\right)^{1/2} = \frac{1000 F}{\Lambda_0} K \quad (21)$$

or,

$$\eta_{min} \approx \sqrt{\frac{\rho}{\varepsilon_0} \frac{\Lambda_0}{1000 F} \frac{f(\varepsilon)}{\varepsilon}} \quad (22)$$

Assuming $\Lambda_0 = 20$, $\rho = 1130$ kg/m³, $f = 18$ and $\varepsilon = 100$, then Eq. (22) yields $\eta_{min} \approx 0.59$, which is of the right order. The mobility factor Λ_0 would, however, be expected to depend on viscosity, so the argument is incomplete. Using this criterion,

$$Q_{min} = \frac{\gamma \varepsilon \varepsilon_0}{\rho K} \eta_{min}^2 \quad (23)$$

and so (17) gives a maximum droplet specific charge,

$$\left(\frac{q}{m}\right)_{max} = \frac{f(\varepsilon)}{\varepsilon \eta_{min}} \frac{K}{\sqrt{\varepsilon_0 \rho}} \quad (24)$$

which reduces, as the argument above implies, to,

$$\left(\frac{q}{m}\right)_{max} = \frac{1000 F}{\rho} c_d \quad (25)$$

For Formamide, K can be raised to about 2 Si/m, and using $\eta_{min} = 0.5$, (24) yields,

$$\left(\frac{q}{m}\right)_{max} \approx 10000 \text{ C/kg}$$

This implies a relationship Voltage-Isp $V = \frac{(g I_{sp})^2}{2 \times 10^4}$ (5000 V for $I_{sp} = 1000$ s).

(b) Ion emission from the cone-jet transition region

The normal field E_θ increases towards the cone's tip, and will be maximum more or less at the start of the jet. We can estimate this maximum using the Taylor Cone field equation evaluated at $r = R_{jet}/\cos\theta_T = \frac{2.68}{f^{2/3}} r^*$. This gives,

$$E = \sqrt{\frac{2\gamma \cot\theta_T}{\varepsilon_0 r}} = 1.87 \times 10^7 f^{1/3}(\varepsilon)\gamma^{1/2} \left(\frac{K}{\varepsilon Q}\right)^{1/6} \quad (26)$$

This field can be very high at low flow rates and with highly conductive fluids. It is of interest to evaluate it at the lowest stable flow rate, as given by $Q_{min} = \frac{\gamma\varepsilon\varepsilon_0\eta_{min}^2}{\rho K}$. The result is then,

$$E_{max} = \frac{1.3 \times 10^9 \rho^{1/6}}{\eta_{min}^{1/3}} \left(\frac{f(\varepsilon)\gamma K}{\varepsilon}\right)^{1/3} \quad (27)$$

Using data for Formamide and assuming $\eta_{min} = 0.5$ and $K = 2$ Si/m, we get $E_{max} = 1.63$ V/nm. It is known experimentally that at normal fields in the range 1 – 2 V/nm individual ions begin to be extracted from the liquid by field evaporation.

Once the threshold field is reached, field emission increases rapidly with field: Assume the liquid used has a large enough conductivity (and surface tension) that the peak field given by (26) reaches 1-2 V/nm as the flow Q is decreased before the minimum stable flow is reached (in other words, the field given by (27) is more than 1-2 V/nm). In that case, further reductions in flow, which increase E , will result in copious emission of ions from the tip, and the emitted current will increase instead of decreasing as $Q^{1/2}$, with the ion current becoming increasingly stronger than the droplet contribution. In principle, one could expect that as the flow is reduced further, there would be a point in which the droplet component would vanish altogether. Interestingly, such behavior is observed when using pure salts (ionic liquids) as propellants, but it is not observed in electrolytic solutions. A more detailed discussion of ion evaporation and its significance to propulsion will be presented in the following lecture.

Evaporation from the liquid meniscus

As noted above, the current emitted in droplet form by an electrospray depends on the flow rate Q , but not on the emitter's diameter. The same flow rate, and hence the same current,

can be produced using a thin capillary under a high supply pressure or a wider one with correspondingly reduced supply pressure. For liquids of moderate to high volatility, it is then advantageous to reduce the emitter diameter, because the loss due to evaporation from the exposed liquid surface does scale as the square of this diameter (this is in addition to the advantage in starting voltage). The cone's surface area, for a tube diameter D , is $\frac{\pi D^2}{4 \sin \theta_T}$, so that the evaporated mass flow rate is

$$\dot{m}_v = \frac{\pi D^2}{\sin \theta_T} \frac{P_v(T) m_v}{\sqrt{2\pi m_v k T}} \quad (28)$$

where m_v is the mass of a vapor molecule, and $P_v(T)$ is the vapor pressure at the tip temperature. If a design constraint is imposed that $\dot{m}_v \leq f_v \rho Q_{min}$, with some prescribed fraction f_v of minimum emitter flow, we obtain the condition (using (23) for Q_{min}),

$$D \leq \left(2f_v \sin \theta_T \eta_{min}^2 \bar{c}_v \frac{\gamma \varepsilon \varepsilon_0}{K P_v(T)} \right)^{1/2} \quad (29)$$

where $\bar{c}_v = \sqrt{\frac{8kT}{\pi m_v}}$ is the vapor's mean thermal speed.

Consider the case of Formamide. Ignoring for this calculation the reduction in P_v due to the solute, we have,

$$P_v[\text{Pa}] = 3.31 \times 10^{12} \exp\left(-\frac{8258}{T[\text{K}]}\right) \quad (30)$$

Taking $T = 293$ K, $\eta_{min} = 0.5$, $m_v = 0.045$ Kg/mol and $K = 1$ Si/m, we calculate from (29) a maximum diameter for $f_v = 0.01$ of $D_{max} = 6.2 \mu\text{m}$. This is of the same order as the diameter required for start-up at 1 kV voltage. Both of these results point clearly to the desirability of thruster architectures with large numbers of very small emitters, which motivates research into microfabrication techniques for their production.

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