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The effect of charge emission from electrified liquid cones

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The formation of stable cones in electrified liquid interfaces was explained by Taylor as a balance between electrical and capillary tensions, where the electrostatic potential varies as $\phi \sim r^{\frac{1}{2}}$ with the distance r from the cone tip. Although Taylor's predictions for the dependence of the onset voltage for cone formation on the liquid surface tension γ and the cone dimensions agree with observed trends, his conclusion that the cone semiangle α can only take the value $\alpha = \alpha_T = 49.3°$ does not. A more general theory free from this paradox is constructed for highly conducting fluids by accounting for the space charge of the droplets emanating from the cone apex, whose potential has the remarkable property of also obeying Taylor's $r^{\frac{1}{2}}$ law. In this formulation, where the apex of a conical meniscus of semiangle α emits an angularly uniform opposed coaxial conical spray of semiangle $\pi-\beta$, both β and the spray current I turn out to be fixed as functions of α; namely, $\beta = \beta(\alpha)$, and $I = 2\pi\gamma KqG(\alpha)$, where Kq and q are the droplet's electrical mobility and total charge, respectively. In experiments with 5% H_2SO_4 in 1-octanol, the observed sprays are approximately conical with an apex nearly touching the meniscus tip. The measured and predicted $\beta(\alpha)$ relations are in reasonable agreement in the range $46° > \alpha > 32°$, where the liquid cone is stable and the spray is visible, though the data fall clearly below the theoretical curve. The predicted spray current I is also in rough agreement with preliminary experiments. The analysis applies neither to sprays of large droplets with significant inertia, nor to liquid cones *in vacuo*.

1. Introduction

The formation of conical protrusions at the interface between a charged liquid conductor and an insulating fluid has intrigued scientists for over a century. These liquid cones often appear shortly after the surface charge density reaches the critical value at which the interface becomes unstable, a phenomenon which is relatively well understood for simple geometries. Rayleigh's famous criterion for the maximum charge q_R that a droplet of radius R and coefficient of surface tension γ can hold is (see Landau & Lifshitz 1960, Ch. 1, problem 6):

$$q_R = 8\pi(\epsilon_0 \gamma R^3)^{\frac{1}{2}}, \tag{1}$$

where ϵ_0 is the electrical permittivity of vacuum. For a horizontal fluid interface in a vertical electric field, the condition for the so-called Frenkel instability can also be derived analytically (Landau & Lifshitz 1960, ch. 1, problem 5). Although both criteria have been verified experimentally, the behaviour of the interface beyond the critical threshold for instability is not well understood, even though a new steady-state configuration with sharply conical liquid protrusions appears shortly after. Such cones have a remarkable universality in many of their properties and structure.

They always carry current, and their tip invariably emits a thin liquid filament or microjet which breaks into droplets forming a charged cloud, commonly referred to as an 'electrospray'. These menisci also remain conical through extremely wide changes in the dimensions of their associated microjet and spray. (The diameter of the emitted microjet may vary from some 100 μm in hydrocarbons seeded with antistatic additives (Jones & Thong 1971; Gomez & Tang 1991*a*, *b*) down to nanometers or atomic dimensions in the case of liquid metals (Benasayag & Sudraud 1985).) The cones arise not only when held at the exit of a capillary tube or in the planar geometry analysed by Frenkel (see Taylor 1965, plate 1). In a striking in-flight photograph, Gomez & Tang (1992) have recently shown that the Coulombic explosion of a spherical droplet past the Rayleigh limit also involves the formation of a relatively long-lived cone that emits a stream of daughters less than 10 times smaller than the parent drop.

Because multiple wandering cones form in the planar configuration, these structures have been studied primarily when stabilized at the exit of a capillary tube (figure 1), as in Zeleny's (1914, 1915, 1917) pioneering and still very well worth reading studies. Accordingly, the experimental aspects of the present work will be based on Zeleny's particular geometry, which has the additional advantage that the liquid flowrate Q can be controlled externally. In spite of this restriction, the basic features of the cones to be discussed are very likely to hold generally, independently of the supporting geometry.

Aside from their theoretical and aesthetical interest, the electrosprays produced by charged conical menisci have inspired numerous practical applications (Bailey 1988). In particular, the recent discovery of highly charged gas-phase ions of macromolecules field-evaporated from electrosprayed droplets of volatile liquids, has led to a revolution in the analysis of proteins and other large biomolecules by mass spectrometry (see Fenn *et al.* 1989, or the more than hundred related extended abstracts appearing in the proceedings of the 1991 meeting of the American Society of Mass Spectrometry, Nashville, Tennessee, May 1991). Because many of these applications have so far been based more on inspired intuition than on firm scientific knowledge, an improved understanding of electrosprays would very likely bring significant technological progress.

Perhaps the most interesting fluid dynamic challenge posed by electrified liquid cones is to explain the origin and dynamic structure of the microjet emitted at their apex. There lies the key to controlling an atomizer capable of producing monodisperse droplets varying in diameter from hundreds of μm down to submicrometer and perhaps nanometer dimensions. Although a theory for the jet is essential to determine the diameter and the charge on the electrosprayed droplets, very little is known even on the rough scaling laws for these quantities. In a highly idealized approach which assumes that the charge is carried by the jet mostly by convection and that Bernouilli's law holds inside the liquid, Fernández de la Mora *et al.* (1990) have recently shown that the radius R of the jet varies with the flow rate Q and the density ρ of the liquid as $2R \sim (\rho Q^2/\gamma)^{\frac{1}{3}}$, which agrees with all available experimental data in the size range from 0.1 μm up to some 100 μm to within a factor of 2. This result follows also from purely dimensional considerations for a problem where conduction and viscosity are irrelevant and where the large disparity of geometrical scales makes all external characteristic lengths irrelevant. Unfortunately, although the semi-predictive power of this scaling law is quite useful, the physical model on which it is based is probably unjustifiable and its partial success cannot be viewed as explaining anything.

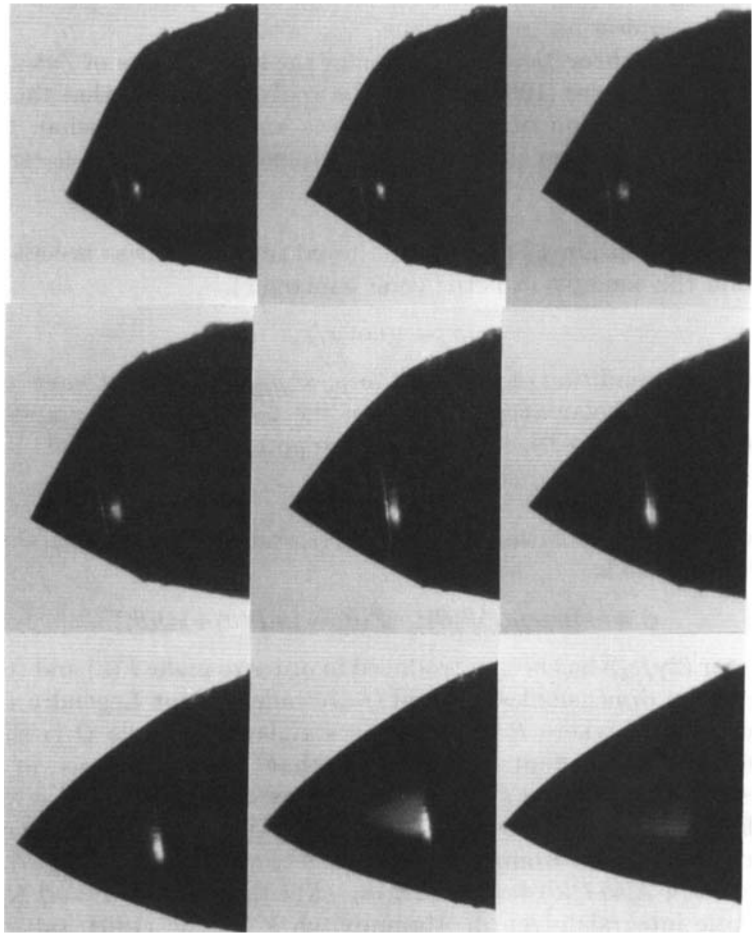

FIGURE 1. Conical menisci of 5% (vol) H_2SO_4 in 1-octanol (conductivity of 0.05 mho/m) supported on a metal capillary kept at 6 KV and immersed in air. The needle has outer and inner diameters of 1.07 and 0.806 mm, respectively, and is tapered in an approximately conical fashion down to nearly zero thickness at its tip. The electrode configuration is fixed and the flow rate Q is increased from left to right and top to bottom. The meniscus has just lost stability at the smallest flow rate shown, at an angle $\alpha = 49°$, only slightly smaller than Taylor's $\alpha_T = 49.29°$.

In spite of our present state of ignorance regarding the jet, much can still be learned on this problem thanks to the large separation of scales present, where the cone base has a diameter several orders of magnitude larger than the microjet. For instance, in typical experiments where the spray consists of submicron droplets, the jet diameter is 0.3 μm, and the cone rests on a needle 1 mm in diameter. The ratio of jet speed to mean speed at the cone is thus 10^7. In a conical meniscus of SO_4H_2 we have measured droplet diameters of 0.03 μm, with an associated jet diameter which can be estimated to be roughly half that value. The problem is therefore nearly hydrostatic except in a negligibly small zone around the apex, and it may accordingly be subdivided into two regions: the outer 'cone' and an inner 'apex'. At the largest scale of the cone, the jet-apex zone appears as a point, speeds are negligible almost everywhere, and the problem is effectively hydrostatic. Because a clear description of the statics of electrified liquid cones is an essential prerequisite for understanding the dynamics of these microjets, the present paper will consider exclusively this simplest outer behaviour.

The best available theoretical description of the hydrostatics of Zelenyan menisci was put forward by Taylor (1964, p. 393). His analysis assumes that the cone is held together by a combination of electrical forces and surface tension. Because the electrical pressure p_E pulling the liquid out is quadratic with the electric field $\boldsymbol{E}$,

$$p_E = \tfrac{1}{2}\epsilon_0 E^2, \tag{2}$$

while the capillary tension p_γ pulling the liquid inwards varies inversely with the distance r from the cone tip (α is the cone semiangle),

$$p_\gamma = \gamma \cot\alpha / r, \tag{3}$$

it follows from the condition of equilibrium $p_\gamma = p_E$ that $\boldsymbol{E}$ must vary as $1/r^{\frac{1}{2}}$ times some function of the polar angle θ between the position vector $\boldsymbol{r}$ and the axis of symmetry of the cone ($\theta = 0$). Introducing the potential ϕ such that

$$\boldsymbol{E} = -\nabla\phi, \tag{4}$$

the only axisymmetric solution to the electrostatic problem $\nabla^2\phi = 0$ with the required r dependence is

$$\phi = -(2\gamma r/\epsilon_0)^{\frac{1}{2}} F(\theta); \quad F(\theta) = [mP(\theta) + sQ(\theta)], \tag{5a, b}$$

where the factor $(2\gamma/\epsilon_0)^{\frac{1}{2}}$ has been introduced in order to make $F(\theta)$ and the arbitrary constants m and n dimensionless. P and Q are independent Legendre functions of degree $\frac{1}{2}$ and order 0, where P denotes the standard $P_{\frac{1}{2}}$, while Q is the standard $Q_{\frac{1}{2}}$ multiplied by a constant factor such that the conditions of symmetry $Q(\theta) = P(\pi - \theta)$, and $P(0) = Q(\pi) = 1$ hold. Q has zero slope at $\theta = \pi$, decreases monotonically to become $-\infty$ logarithmically as $\theta \rightarrow 0$, and changes sign at $\theta = \alpha_\mathrm{T} = 49.29°$. It can be obtained from the hypergeometric function F as $Q(\theta) = F(-0.5; 1.5; 1; \frac{1}{2}(1+\cos\theta))$. Also $Q(\theta) = (2/\pi)[2E(m) - K(m)]$, where $E(m)$ and $K(m)$ are the complete elliptic integrals given in Abramovitch & Stegun (1964, table 17.1), and $m = \frac{1}{2}(1+\cos\theta)$.† Taylor used $P_{\frac{1}{2}}$ rather than $Q_{\frac{1}{2}}$ to represent his potential, so that his angle was really 130.71°, and the axis $\theta = 0$ was outside the meniscus. The more common convention followed here is, however, that $\alpha_\mathrm{T} = 49.29°$, and the origin of θ is in the interior of the liquid cone.

Taylor chose as his boundary conditions that the liquid surface $\theta = \alpha$ be equipotential and that the field be regular outside the cone. In this particular case, because P is singular at $\theta = \pi$ and analytic at $\theta = 0$, the regularity condition at the axis on the air side ($\theta = \pi$) requires that $m = 0$, while the equipotentiality condition $F(\alpha) = 0$ forces that $Q(\alpha) = 0$. Solutions are only possible for the special Taylor cone angle $\alpha_\mathrm{T} = 49.29°$ at which Q vanishes. Finally, the constant s in (5*b*) is fixed by the condition of mechanical equilibrium $p_E = p_\gamma$ at $\theta = \alpha$, such that

$$F_\mathrm{T}(\theta) = [Q(\theta)/Q'(\alpha)]/(\tan\alpha)^{\frac{1}{2}}. \tag{6}$$

An immediate consequence of these results (advanced and confirmed experimentally long before by Zeleny) is that the square of the potential V_0 at which the cone first forms is linear with both the liquid surface tension and the diameter of the basis of the cone (Zeleny 1915, Equation 10 and table 1; Shorey & Michelson 1970; Smith 1986). This scaling law follows from Taylor's analysis even when the meniscus is not

† Notice, an error in the argument $m = [\frac{1}{2}(1+\cos\theta)]^{\frac{1}{2}}$ given by Abramovitch & Stegun (1964) in their equation (8.13) relating P to the elliptic integrals E and K.

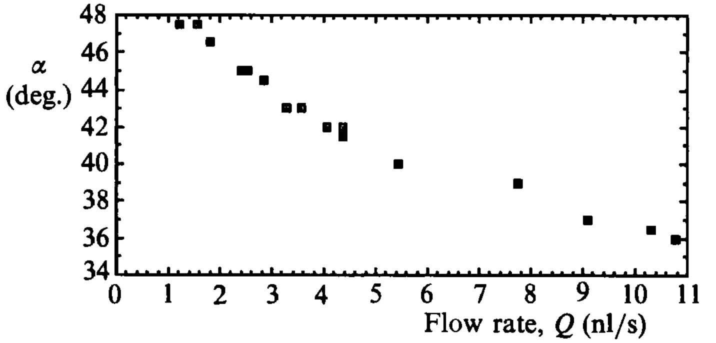

FIGURE 2. Liquid cone angle versus flow rate as measured from photographs similar to those in figure 1, for the same liquid and needle. The capillary tube is held at 3715 V, perpendicularly to a plane grounded electrode 7 mm away from its tip.

conical down to its basis, provided it is equipotential and gravitational effects are small. Indeed, in this case, and for geometrically similar electrode configurations, the meniscus shape at the onset voltage V_0 must be independent of γ and the diameter D of the supporting tube. The electrostatic problem may thus be solved as $\phi = V_0 H(\theta), r/D)$, in terms of a function $H(\theta, r/D)$ independent of the liquid properties. Near the apex the meniscus is conical, and H must tend to $F(\theta)(r/D)^{\frac{1}{2}}$, which, compared with (5*a*) shows immediately that $V_0^2 \sim \gamma D/\epsilon_0$.

A second experimental confirmation of Taylor's results is that angles quite close to his α_T have actually been observed (see, for instance, Taylor 1964). However, highly and moderately conducting liquids in air also exhibit cone angles smaller than α_T, as illustrated in figures 1 and 2. The photographs in figure 1 record how, upon decreasing the liquid flow rate Q pushed through the jet, one sees an increasing value of α until the cone eventually loses stability. In the particular case shown in figure 1, the smallest flow rate leading to a stable cone was slightly smaller than the value corresponding to the middle top photograph, with an angle α of 48.5°, fairly close to α_T. α is 49° for the top left photograph, taken just after the cone became unstable. These close quantitative coincidences provide compelling evidence that Taylor's description must contain some fundamental essence of the real cones.

Our present objective is to show that some of the paradoxes arising from Taylor's ideas may be overcome with slight modifications which preserve his $\phi \sim r^{\frac{1}{2}}$ law. In particular, for the case of highly conducting liquids, the charged spray streaming from the apex will be seen to provide a simple explanation of the observed varying cone angles, and will additionally relate the magnitude of the emitted electrical current to the cone geometry and the mobility of the droplets.

2. Effect of the charge emitted from the cone tip

An explanation of the paradoxical observation of cone angles α substantially smaller than α_T may be based on the fact that the emitted spray is charged. It could thus modify the electrical potential due exclusively to the charges on the cone surface, the only ones accounted for in Taylor's formula (6). The magnitude of the contribution of the charged droplets to the overall field can be assessed by direct visual observation of the spray boundary, at least when the droplets are small enough for their trajectories to follow closely the electrical lines of force. In the absence of free charges all field lines would originate at the conical meniscus, and the

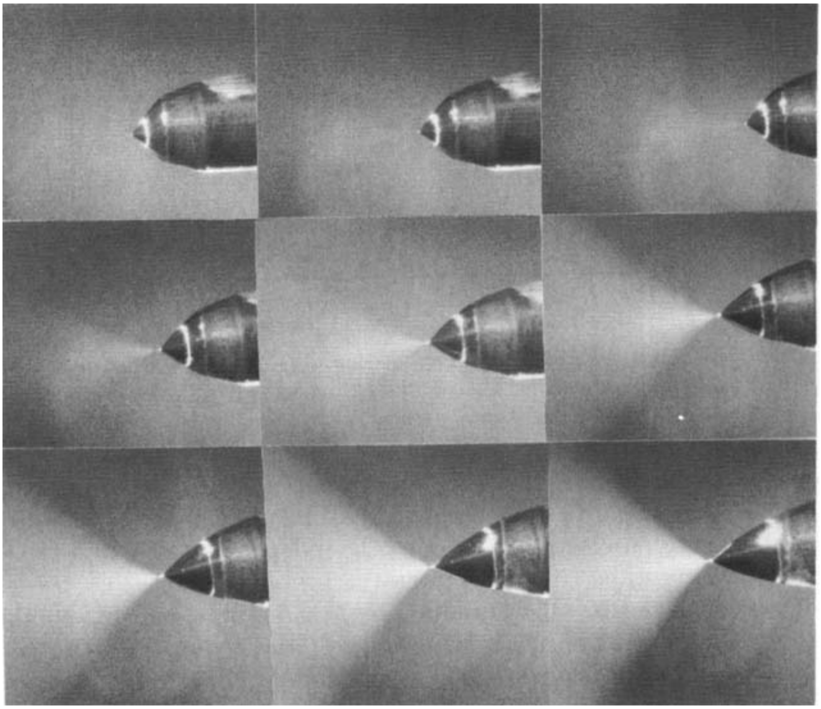

FIGURE 3. Conical menisci and sprays for the same conditions as figure 2. From left to right and top to bottom, the liquid flow rates Q in nl/s are 1.5; 2.0; 2.75; 4.0; 5.1; 6.8; 8.1; 9.7 and 10.9. Notice the initially conical shape of the spray whose apex nearly coincides with the liquid point.

E_θ component of the field in the vicinity of the negative half-axis ($\theta = \pi$) would be positive, pointing towards the axis. Yet, as shown in figure 3, the spray droplets can have trajectories diverging from the negative semiaxis with half-angles as large as 40°, even sufficiently close to the liquid cone apex for the field to be negligibly affected by the disposition of the ground electrodes. This behaviour implies that the local value of E_θ is null or negative, which can only result from the space charge from neighbouring droplets closer to the axis. Because the observed angles of divergence are of order one, the amount of charge around the negative semiaxis leading to them must be comparable to the charge on the cone surface. Accordingly, the space charge effect of the spray on the overall field is not negligible and must be accounted for. The question is how to do so in a form compatible with Taylor's $\phi \sim r^{\frac{1}{2}}$ law.

The only way in which the space charge surrounding the negative semiaxis can be incorporated within Taylor's analysis is by relaxing his boundary condition $\phi(\pi) \neq \infty$ to retain the Legendre function P in (5*b*). This new freedom amounts physically to allowing a line of charge singularity at the semiaxis $\theta = \pi$, with a charge density $\mathrm{d}q/\mathrm{d}r$ per unit axial length proportional to $r^{\frac{1}{2}}$. How such an arrangement of charge might actually come about will be discussed subsequently. However, one can readily see that retaining the function P in (5*b*) leads to the right effect on the cone angle, allowing values of α different from and strictly smaller than Taylor's. Indeed, for every conceivable value of α one may choose the ratio m/s in (5*b*) as

$$m/s = -Q(\alpha)/P(\alpha), \tag{7}$$

such that the half-cone $\theta = \alpha$ is actually an equipotential surface. In addition, the ratio m/s must be positive because the liquid tip emits charge of its own polarity. But

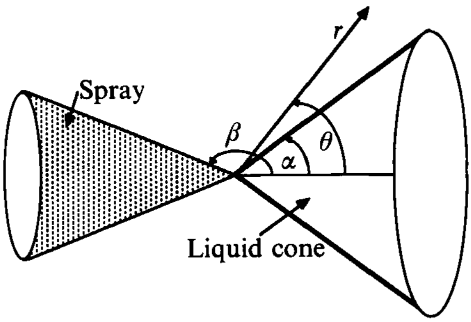

FIGURE 4. Schematic view of the conical spray model, showing the meniscus angle α, the spray angle β and the coordinates r, θ.

then, in order for the ratio $Q(\alpha)/P(\alpha)$ to be negative, α must be either smaller than α_T or larger than $\pi - \alpha_T$, implying that only angles smaller than Taylor's are acceptable, in agreement with observations (figures 1 and 2).

Having introduced the function $P(\theta)$ in (5*b*), one must now justify physically the presence of its associated charge singularity along the negative semiaxis. A first line of reasoning could be the following: experiments often show that the liquid extends past the conical region into a thin charged filament occupying the semiaxis $\theta = \pi$. Because this microjet is a fair approximation for a line of charge singularities at the negative semiaxis, the latter becomes physically acceptable, and may in fact seem to constitute an essential feature of the actual problem. Unfortunately, however, $P(\theta)$ is associated with a charge density $\mathrm{d}q/\mathrm{d}r$ varying as $r^{\frac{1}{2}}$, while the reasons why the charge would so distribute itself along the jet length are not at all obvious. Even if a future fluid dynamic description of the jet were to succeed at justifying this special charge arrangement, it would most likely produce a complex coupling between the structure of the cone and that of the tip region, while the observed universality of the former seems to indicate that this coupling is in fact rather simple. For this reason, and for lack of a more satisfactory approach, we will proceed differently. In this paper, the presence of the peculiar type of charge distribution associated with the function $P(\theta)$ will be justified physically by the remarkable coincidence that the spherical expansion of a cloud of identical charged particles propelled through a carrier gas by their own space charge field leads to an electrical potential varying like Taylor's as $\phi \sim r^{\frac{1}{2}}$. Thus, ignoring the jet structure and assuming that the cone emits a stream of identical droplets with angular uniformity within the conical region $\beta < \theta < \pi$, as sketched in figure 4, the problem admits a rather simple completely self-consistent analytical solution which is compatible with Taylor's extended potential (5) in the region $\alpha < \theta < \beta$.

The structure of the paper is the following. Because the charge emitted at the cone tip affects the whole problem, the conical model for the spray will be presented first in §3. Section 4 closes the problem for the particular limit of liquids with very high conductivity. The paper ends in §5 with a general discussion comparing the predictions of this model with experiments.

3. A conical model for the spray structure

Consider the idealized model of the spray sketched in figure 4.

(i) The apex of a conical meniscus of semiangle α emits an angularly uniform opposed coaxial conical spray of identical droplets, with angular uniformity within the spherical sector $\pi \geqslant \theta \geqslant \beta$, while there is no spray in the region $\alpha < \theta < \beta$. Accordingly, the electrical potential ϕ is harmonic in the region $\alpha < \theta < \beta$, where it is given by (5). Within the spray region $\pi \geqslant \theta \geqslant \beta$, ϕ satisfies Poisson's equation:

$$\nabla^2\phi = -nq/\epsilon_0, \tag{8}$$

where q is the charge on each of the droplets, whose number density n (cm^{-3}) obeys the continuity equation

$$\nabla\cdot(n\nabla\phi) = 0, \tag{9}$$

in which the droplets have been assumed to have negligible inertia and diffusivity, so that their velocity $\boldsymbol{u}$ is linear with the field through a proportionality coefficient Kq, the electrical mobility,

$$\boldsymbol{u} = -Kq\,\nabla\phi. \tag{10}$$

(ii) The boundary conditions for ϕ follow from the requirement that the electric field in the spray matches with Taylor's extended solution (5) at $\theta = \beta$, where ϕ must be continuous and the spray boundary is a droplet streamline ($E_\theta = 0$):

$$\phi = -(2\gamma r/\epsilon_0)^{\frac{1}{2}}F(\beta) \quad \text{and} \quad \partial\phi/\partial\theta = 0 \quad \text{for all} \quad r \quad \text{at} \quad \theta = \beta, \tag{11}$$

where $F(\beta)$ is the combination (5*b*) of Legendre functions particularized at $\theta = \beta$, which can be treated as a constant in the present setting. The initial conditions for n as $r \rightarrow 0$ have already been fixed in the assumption that n is independent of θ within the spray, and null elsewhere.

The assumption that all the droplets have the same charge q, diameter d_p, and electrical mobility Kq is approximately justified as a consequence of the natural tendency of a jet to break up periodically into similar fragments. All these quantities will furthermore be taken to remain constant within the spray region (no significant evaporation).

In the spherically symmetric case, (9) can be integrated once, and (8) then leads to a second-order linear ordinary differential equation for $(\mathrm{d}\phi/\mathrm{d}r)^2$, whose general solution is the sum of two terms proportional to $1/r$ and r^{-4}, respectively. The potential within the spray thus has the remarkable property of being compatible with Taylor's one-half power law, admitting the following θ-independent solution in the region $\beta < \theta < \pi$:

$$\phi = -a(2\gamma r/\epsilon_0)^{\frac{1}{2}} \tag{12a}$$

$$nq = 3a(\gamma\epsilon_0/8)^{\frac{1}{2}}r^{-\frac{3}{2}}, \tag{12b}$$

where the positive dimensionless constant a is given by

$$a^2 = 4I/(3\gamma\Omega Kq), \tag{13}$$

and I is the total spray current emitted through the solid angle $\Omega = 2\pi(1+\cos\beta)$.

In conclusion, the generalization (5*b*) of Taylor's theory allowing cone angles smaller than α_T can be justified physically on the basis of the present model, where the required charge singularity in the region near $\theta = \pi$ is spread over a conical spray. Of course, one would still have to explain how the droplets would distribute themselves with angular uniformity after the breakup of the liquid jet. However, even if this were not the case initially, it is plausible that the system would then tend to naturally smooth out the charge, as regions depleted of it would have a lower electrical potential and would thus tend to be filled.

Notice that, because the only physical quantity available with dimensions of $\phi r^{-\frac{1}{2}}$ is $(2\gamma/\epsilon_0)^{\frac{1}{2}}$, the dimensionless constant a defined in (12*a*) must be of order one.

Accordingly, (13) shows that the total current I transmitted by the spray is of the order of $\gamma K q$.

The boundary conditions (11) matching the free-space electrical potential (5) in the region $\alpha < \theta < \beta$ to its homologous function (12*a*) in the spray region $\beta < \theta < \pi$ may now be written as

$$F'(\beta) = mP'(\beta) + sQ'(\beta) = 0, \tag{14a}$$

$$F(\beta) = mP(\beta) + sQ(\beta) = a. \tag{14b}$$

4. Closure of the problem for an infinitely conducting liquid

In order to proceed further one must consider the constraints on ϕ at the interface $\theta = \alpha$. This cannot yet be done in general, because there is no reliable theory for the mechanism of conduction through the meniscus. In particular, experimental evidence discussed at the end of the paper seems to indicate that the liquid is not equipotential when its conductivity is below the range of 10^{-3} mho/m. However, for liquids with conductivities of 0.03 mho/m or higher, for which our description of the conical spray seems to hold, the evidence available from measurements of the spray current I versus the needle potential V suggests strongly that the liquid cone is in fact nearly equipotential. For mixtures of x% H_2SO_4 in 1-octanol, I is nearly independent of V when $x \geqslant 0.3$%, even though the spray and the meniscus geometries vary extensively with V. For $x < 0.02$%, however, I exhibits a relative variation of 50% or larger over the range of voltages within which the conical meniscus is stable. On the other hand, that the cone must be nearly equipotential when I is independent of V (but not otherwise) can be argued as follows: because there is an important voltage drop through the spray (equation (12*a*)), the mechanism limiting the current cannot be within the spray, since I would otherwise depend substantially on V. The current is therefore controlled within the meniscus by a certain process which cannot be purely resistive because I would otherwise depend on V. But if the liquid is a good conductor and the current limiting mechanism is not purely resistive, it is difficult to imagine what process could possibly lead to a potential drop along the liquid surface. Accordingly, the meniscus must be nearly equipotential, at least in the case of sufficiently conductive liquids. Here we shall confine our attention to this special circumstance, with the warning that there might be other regimes also leading to the formation of conical menisci. The boundary conditions at $\theta = \alpha$ are therefore exactly those of Taylor:

$$F(\alpha) = 0 \tag{15a}$$

$$F'(\alpha) = (\tan\alpha)^{-\frac{1}{2}}, \tag{15b}$$

the latter being the condition of mechanical equilibrium $\frac{1}{2}\epsilon_0 E^2 = \gamma \operatorname{cotan}\alpha / r$. $F(\theta)$ is thus fixed as

$$F(\theta) = (\sin 2\alpha)^{\frac{1}{2}}[P(\alpha)\,Q(\theta) - Q(\alpha)\,P(\theta)]/(C\sqrt{2}), \tag{16}$$

where use has been made of the fact that the function C associated to the Wronskian $C/\sin\alpha$ is a constant for Legendre's functions. For the case when P and Q are normalized such that $P(0) = Q(\pi) = 1$, C takes the value

$$C = \sin\alpha[P(\alpha)\,Q'(\alpha) - Q(\alpha)\,P'(\alpha)] = 0.63662.$$

Equations (14*a*) and (15*a*) can be combined to fix the angle β of the spray boundary in terms of α, as shown in figure 5, independently of any external parameters as

$$Q'(\beta)/P'(\beta) = Q(\alpha)/P(\alpha). \tag{17}$$

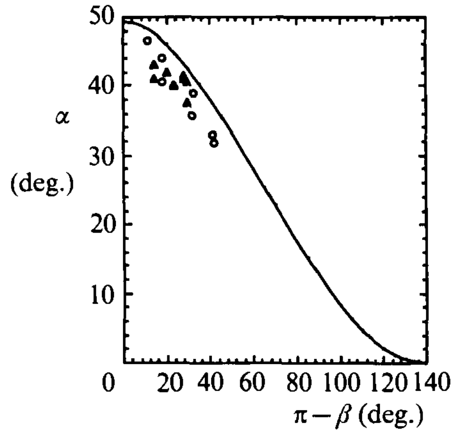

FIGURE 5. Theoretical meniscus angle α versus spray angle $\pi-\beta$ for an infinitely conducting liquid, as given by (17). Open data points are from figure 3; filled data points are for several liquids and conditions, including 5% H_2SO_4-1-octanol and methanol–glycerine mixtures seeded with HCl.

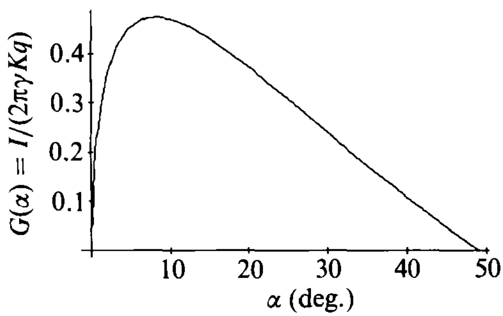

FIGURE 6. Theoretical dimensionless spray current as a function of meniscus angle for an infinitely conducting liquid, as given by (18).

α(deg.)	$\pi-\beta$(deg.)	$G(\alpha)$	$a^2(\alpha)$	α(deg.)	$\pi-\beta$(deg.)	$G(\alpha)$	$a^2(\alpha)$
49.06	5	0.00255	0.893	38.05	40	0.1338	0.762
48.41	10	0.00995	0.873	35.65	45	0.1647	0.750
47.36	15	0.02174	0.850	33.16	50	0.1975	0.737
45.99	20	0.03751	0.829	30.60	55	0.2318	0.725
44.32	25	0.05690	0.810	28.00	60	0.2671	0.712
42.42	30	0.07962	0.792	25.37	65	0.3028	0.699
40.31	35	0.1053	0.776				

TABLE 1. Predicted values of the spray angle β, the dimensionless current G and the dimensionless current per unit solid angle as functions of the liquid cone angle α, according to (17) and (18)

Finally, (13), (14*b*) and (16) fix the spray current as a function of either α or β as

$$I/(2\pi\gamma Kq) = 3\sin 2\alpha[1+\cos\beta(\alpha)]\{P(\alpha)\,Q[\beta(\alpha)]-Q(\alpha)\,P[\beta(\alpha)]\}^2/(8C^2) = G(\alpha), \quad (18)$$

where β is now interpreted not as an independent parameter but as a function of α, $\beta=\beta(\alpha)$ as given from (17). The function $G(\alpha)$ or dimensionless current is shown in figure 6, and tabulated together with $\beta(\alpha)$ in table 1. Also shown in this table is $a^2(\alpha)$, the only geometry-dependent parameter affecting the electric and density fields (12) within the spray. Notice from (13) that a^2 is a measure of the spray current per unit solid angle Ω. The fact that a varies only slightly over the whole range of permissible geometries implies that the meniscus can adjust itself to emit a current of droplets with a certain mobility by the simple mechanism of varying the spray angle β.

5. Discussion

Although the sprays shown in figure 3 conform reasonably well to the assumed conical geometry, we could find no experimental observations on which to justify such a choice when the model of §3 was first developed. Rather, what one generally sees in electrosprays is a jet, typically longer than the cone, which breaks up into a train of droplets that remain aligned for a comparable distance before opening up into a sharply defined cloud. The spray boundary thus has the appearance of a parabola emerging from the apex with zero slope. However, this description is not universally valid, being characteristic of readily visible sprays of droplets with diameters larger than several microns. By using progressively more-conducting liquids and smaller flow rates, one finds that the transitional structure between the meniscus and the spray shrinks monotonically, becoming much smaller than the cone length (as in figure 3) for droplets somewhat smaller than 1 μm. In this limit, the spray has the appearance of a cone whose apex nearly coincides with the tip of the meniscus. The probable reason why this rather simple structure has not been reported before is that the range of conditions where it is easily observable is quite restricted, as the droplets must be larger than 0.2 μm or so for the spray to be visible, but must be small enough for the apices of the two cones to nearly touch each other. As seen in the series of photographs in figure 3, the spray becomes first decreasingly discernible, and then invisible as the liquid flow rate is reduced. Yet the droplets are still there, as witnessed by the continuous variation of the spray current and the meniscus angle.

Our first observation of such conical sprays was during the visit of Professor Barrero to Yale in August 1991, while he investigated mixtures of 20% (volume fraction) glycerine in methanol doped with 0.03% HCl. After this, we have seen numerous other fairly conical sprays of submicron droplets in different liquids, including the case of 5% volume fraction of H_2SO_4 in 1-octanol (electrical conductivity near 0.05 mho/m) photographed in figure 3. The corresponding droplets have the advantage of being initially far less volatile than in the methanol–glycerine mixture and thus meet some of the assumptions of the model better. All the sprays shown in figure 3 seem to have a short initial structure associated probably with a narrow filament which persist unbroken for many jet diameters, and oscillates gently for a substantial fraction of its length (Gomez & Tang 1991 *a*, *b*; Thong & Weinberg 1971, figure 5*a*). For fixed values of the metal capillary voltage (3715 V) and the geometry (see caption to figure 1 – the needle is 7 mm away from an effectively infinite grounded plane oriented normally to its axis), upon increasing the rate Q at which the liquid is injected into the meniscus, the spray angle can be clearly seen to increase while the liquid cone angle decreases, approximately as predicted. At large flow rates the meniscus becomes elongated and eventually loses stability, so that the smallest angle α observed is somewhat larger than 30°. The phenomenon precluding smaller values is unknown.

Testing the validity of the predicted $\alpha(\beta)$ curve is not straightforward because the spray boundary is curved outwards, and its apex region is not as well defined as the liquid cone apex and so does not permit a precise extrapolation of the slope as

$r \to 0$. However, with errors of several degrees for β and $\pm 1°$ for α, we have extracted values of both angles from several photographs, as shown by the symbols in figure 5. Although the measured points fall clearly below the predicted line, the general agreement is surprisingly good considering the drastic nature of some of the model assumptions.

A rough experimental test of equation (18) for the predicted spray current can also be attempted. For $\alpha = 40°$, as in a typical experimental situation, the dimensionless current G is near 0.1. Assuming $\gamma = 35$ dyn/cm, taking the medium to be air at standard conditions and the droplets to be charged at half of the Rayleigh limit (equation (1), and using for the drag coefficient of the droplets the formula given by Friedlander (1977), we compute the following currents I as a function of particle diameter d_p, which are in rough agreement with typically observed values:

d_p (μm)	0.5	0.2	0.1	0.05	0.02
I (μA)	0.27	0.24	0.26	0.32	0.47

This current has a minimum in the range of 0.2 μm, as a consequence of the fact that $q_R \sim d_p^{\frac{3}{2}}$, while K varies as $1/d_p$ for particles in the continuum regime, and as d_p^{-2} in the free-molecule regime. The predicted trend of currents increasing with decreasing diameters for very small droplets can easily be observed when using liquids with high conductivities, which produce very small droplets (Smith 1986).

For a more quantitative test one needs to know the group Kq. Although there are no such published data, Mr Rosell-Llompart has measured the electrical mobility and the diameter of the 20% involatile residue from a liquid consisting originally of 20% glycerine, 25% methanol and 55% water seeded with small amounts of NaCl. His measurement technique is similar to that reported by Fernández de la Mora *et al.* (1990), which actually determines the distribution of mobilities and confirms the assumption made that most particles have approximately the same mobility. The data for the evaporated droplets are $Kq = 0.307\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$; $d_p = 0.17$ μm (0.29 μm before drying), which implies that, before evaporation, the droplet charge was 0.57 times the Rayleigh limit. (Note that no coulombic explosions arise during evaporation because glycerine has a substantially larger surface tension than the original liquid.) The calculated current ($G = 0.1$) is 0.31 μA, not too far from the measured value of 0.23 μA. In spite of the imperfect nature of this comparison, where we do not know α well enough to assign $G(\alpha)$ with less than a 30% error, the agreement is certainly better than qualitative.

Several other qualitative checks of the theory may be made. For instance, when decreasing the liquid flow rate at a given voltage, the current decreases by a factor of three or more in the whole interval within which the cone is stable. Yet the droplet mobility varies far less within this range, so that this reduction in current must be associated mostly with variations in the cone angle, in qualitative agreement with figure 6, where $G \to 0$ as $\alpha \to \alpha_T$ (remember that the cone angle actually approaches Taylor's angle at diminishing flow rates).

In conclusion, the fragmentary experimental evidence available makes it very likely that space charge plays an important role in this problem, setting strong constraints on the relation among the meniscus angle the droplet mobility and the emitted current. Our model of an angle-independent spray density is probably just an approximation, perhaps valid asymptotically far from the apex; but it seems to provide a fair first-order description of charge emission from electrified liquid cones immersed in dielectric fluids. A theory for the jet structure is still pending, and without it one cannot know the droplet mobility and charge.

Notice finally that, even within the region of the cone far from the apex where the hydrostatic assumption holds, the hypothesis that the liquid surface is equipotential is still questionable, at least for liquids less conducting than those used here. In this case, some (conductive?) mechanism different from space charge in the spray must be responsible for the observed cone angles smaller than Taylor's. Indeed, in mixtures of 0.01 % H_2SO_4 in 1-octanol, intact jets far longer than the liquid cone can be easily seen. Because these jets move much faster than the free droplets one would then expect small space-charge effects and a meniscus angle close to α_T. Yet, although the liquid protrusion is sharply conical, one seen angles as small as 39°. The paradox addressed in this paper thus remains unsolved except for highly conducting liquids.

Craig Whitehouse (Analytica, Branford, Connecticut) first pointed out to me that space charge was important in electrosprays. Professor A. Barrero found the experimental conditions required to save this analysis from oblivion. Mr J. Rosell-Llompart made key quantitative measurement on droplet size and mobility distributions. Constant discussions with Professors J. B. Fenn and A. Gomez; Mr Rosell and Mr I. G. Loscertales (Yale); and Professors Barrero and R. Fernández-Feria (Seville) have been most stimulating. To all of them I am greatly indebted. This work has been supported by the US National Science Foundation Grant numbers CBT-88 12070, CTS-9106619 and CTS-9112601 at Yale. Our collaboration with the University of Seville was supported by the Spanish CICYT Coordinated Grant PB-89-195, and that with Analytica of Branford by the US Army Research Office Grant DAAL03-88-C-0008.

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