Universal scaling laws for the disintegration of electrified drops

Robert T. Collins¹, Krishnaraj Sambath, Michael T. Harris, and Osman A. Basaran²

School of Chemical Engineering, Purdue University, West Lafayette, IN 47907

Edited by William R. Schowalter, Princeton University, Princeton, NJ, and approved February 1, 2013 (received for review August 8, 2012)

Drops subjected to strong electric fields emit charged jets from their pointed tips. The disintegration of such jets into a spray consisting of charged droplets is common to electrospray ionization mass spectrometry, printing and coating processes, and raindrops in thunderclouds. Currently, there exist conflicting theories and measurements on the size and charge of these small electrospray droplets. We use theory and simulation to show that conductivity can be tuned to yield three scaling regimes for droplet radius and charge, a finding missed by previous studies. The amount of charge $\tilde{Q}$ that electrospray droplets carry determines whether they are coulombically stable and charged below the Rayleigh limit of stability ($\tilde{Q}_R$) or are unstable and hence prone to further explosions once they are formed. Previous experiments reported droplet charge values ranging from 10% to in excess of $\tilde{Q}_R$. Simulations unequivocally show that electrospray droplets are coulombically stable at the instant they are created and that there exists a universal scaling law for droplet charge, $\tilde{Q} = 0.44 \tilde{Q}_R$.

electrohydrodynamics | tip-streaming | microfluidics | charged drops | nonlinearity

Electrified drops have intrigued scientists, and studying them has proved useful for more than a century because of applications to fields as diverse as raindrops in meteorology (1, 2), the liquid drop model in nuclear fission (3), and aerosol science (4). Almost 100 years ago, Zeleny (5) and Wilson and Taylor (6) showed experimentally that a pendant drop hanging from a capillary and a sessile soap bubble sitting on a plate may be deformed into spheroidal shapes by subjecting them to an electric field. Moreover, if the field strength were sufficiently high, the tip of the pendant drop, and that of the sessile bubble, would take on a conical profile and emit a fine jet that would break up into a spray of small droplets. Subsequently, Nolan (7) and Macky (8) demonstrated experimentally that similar phenomena occurred when a spherical free drop bearing zero net charge was subjected to an electric field. In contrast to the pendant drop and the sessile soap bubble, an uncharged or neutral drop in a strong electric field forms two opposing conical ends and emits opposing jets of positively and negatively charged droplets. The conical menisci now are called Taylor cones (9), and the emission of fine jets from the tips of the cones is referred to as electrohydrodynamic (EHD) tip-streaming (10) or EHD cone-jetting (11). In the past few decades, it has become widely appreciated that the emission of charged jets from conical surfaces and the disintegration of such jets into aerosols of tiny charged droplets (electrospraying) are common to diverse but seemingly unrelated situations in technology and nature, including electrospray ionization mass spectrometry (ESI-MS) (12), raindrops in thunderclouds (13), and printing and coating processes (14).

Interest in how charged jets and droplets form grew rapidly after Fenn and coworkers (12, 15) adapted Zeleny's approach by flowing a volatile solvent containing large biomolecules through an electrified capillary and developed the novel method of ESI-MS, now widely used for assaying macromolecules (16) and which resulted in the awarding of the 2002 Nobel Prize in Chemistry to John Fenn. The quest for a mechanistic understanding of electrospraying has led to the development of several competing and

contradictory scaling laws to describe how the size of electrospray droplets and the emitted current should vary with fluid properties and other system parameters (17–20). These scaling laws, all of which have been developed to describe the important but limiting case of steady cone-jetting of fluids of high conductivity, are based on an analysis of the cone-to-jet transition region, asymptotically matched to the dynamics of the Taylor cone and a tip-streaming jet of indefinite length. Aside from the fact that such analyses require making ad hoc assumptions about the tip-streaming jet far from the transition region, they cannot predict how electrospray droplets actually are formed. An interesting result from the electrospray literature is that the radii of the small droplets thus formed are independent of viscosity if the conductivity of the fluid is high. More recently, Grimm and Beauchamp (21) adapted Nolan's and Macky's approach to generate desolvated ions in the gas phase and demonstrated that free drops also may be used in mass spectrometric analysis.

Fig. 1 shows the evolution in time of an initially spherical, uncharged, free drop of a fluid of finite conductivity (Fig. 1A) subjected to a strong electric field, as in the experiments of Nolan (7), Macky (8), and Grimm and Beauchamp (21), determined by simulation (*Materials and Methods*). The simulation results show deformation of the drop into a nearly prolate spheroid (Fig. 1B), formation of Taylor cones (Fig. 1C), emission of tip-streaming jets (Fig. 1D), and incipience of formation of two small electrospray droplets (each with a volume equivalent to a sphere of radius $\tilde{r}$, Fig. 1E and F). The new simulations and all previous experiments show that the radii of the tip-streaming jets and the electrospray droplets are orders of magnitude smaller than that of the parent drop. Given this disparity in length scales, we expect the phenomena to be universal (22) and therefore independent of whether pendant drops or free drops are used. We show in this paper that there are three scaling regimes for droplet size, a fact missed by previous studies. An issue of importance equal to that of droplet size is the coulombic stability of the small droplets. An isolated charged droplet of radius $\tilde{r}$ was shown by Lord Rayleigh (1) to be stable to all infinitesimal amplitude perturbations when its charge $\tilde{Q}$ is less than $\tilde{Q}_R$, where $\tilde{Q}_R = (64\pi^2\epsilon_G\gamma\tilde{r}^3)^{1/2}$ is known as the Rayleigh limit (*Materials and Methods*). A droplet with charge exceeding this limit is coulombically unstable and will explode in a manner analogous to the disintegration of an uncharged drop in a strong electric field (i.e., by cone-jetting) (23). Previous estimates of the charge of droplets produced from EHD tip-streaming range from close to $\tilde{Q}_R$ to a tiny fraction thereof (24). If droplets formed from EHD tip-streaming are unstable, or nearly so, the resulting aerosol will not be optimally monodisperse or of uniform charge distribution, which has important ramifications in applications. We show further that electrospray

Author contributions: O.A.B. designed research; R.T.C., K.S., M.T.H., and O.A.B. performed research; R.T.C., K.S., M.T.H., and O.A.B. contributed new reagents/analytic tools; R.T.C., K.S., M.T.H., and O.A.B. analyzed data; and R.T.C., K.S., and O.A.B. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

¹Oak Ridge National Laboratory, Oak Ridge, TN 37831.

²To whom correspondence should be addressed. E-mail: obasaran@purdue.edu.

Fig. 1. EHD tip-streaming from an uncharged, slightly conducting liquid drop subject to a uniform external electric field for the situation in which $Oh = 0.15$, $\kappa = 7.5$, $\alpha = 0.034$, and $\Gamma = 0.2$. (A) Definition sketch showing the initially spherical drop. (B) Shortly after the impulsive imposition of the electric field, the drop takes on a nearly spheroidal shape. (C) Later, the drop develops two Taylor cones at its opposing ends. (D) Onset of tip-streaming from the opposing ends. (E) Emission of fully developed tip-streaming jets and the incipience of the pinch-off of two small electrospray droplets. (F) Blow-up of one of the tip-streaming jets in (E) detailing the about-to-form electrospray droplet and the microthread connecting the droplet to the jet.

droplets are coulombically stable at the instant they are created and present a universal scaling law for droplet charge.

Results and Discussion

The electrically induced disintegration of the drop (*Materials and Methods*) is governed by the axisymmetric Navier–Stokes system,

$$\nabla \cdot \mathbf{v} = 0 \quad \text{in } \Omega_L \quad [1]$$

$$\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p + Oh \nabla^2 \mathbf{v} \quad \text{in } \Omega_L, \quad [2]$$

which is solved for the velocity $\mathbf{v}$ and pressure p inside the drop, and Laplace's equation,

$$\nabla^2 \Phi = 0 \quad \text{in } \Omega_L \cup \Omega_G, \quad [3]$$

for the electric potential Φ , and hence the electric field $\mathbf{E} = -\nabla \Phi$, in both phases. In the leaky-dielectric model (25, 26), bulk density of free charge is zero but density of surface charge q along the L–G interface is governed by a surface charge transport equation:

$$\frac{\partial q}{\partial t} + \nabla_s \cdot (q\mathbf{v}) - \frac{1}{Pe} \nabla_s^2 q = \frac{\kappa}{\alpha} \mathbf{n} \cdot \mathbf{E}_L \quad \text{on } S_f. \quad [4]$$

Here, $\mathbf{E}_L$ is the electric field evaluated along S_f on the liquid side of the interface, $\mathbf{n}$ is the unit normal to S_f , and ∇_s is the surface gradient. The source-like term on the right side of Eq. 4 represents charge transport from the drop to the free surface by ohmic conduction. Surface charge diffusion typically is insignificant relative to other modes of charge transport but is included here for completeness. All results discussed herein use $Pe = 10^4$. Any increase in Pe above $O(10^4)$ has been shown to have no effect on the dynamics.

The electric field inside and outside the drop and the flow within the drop are coupled through the traction condition,

$$\begin{aligned} & -\mathbf{n} \cdot \left(-p\mathbf{I} + Oh \left(\nabla \mathbf{v} + (\nabla \mathbf{v})^T \right) \right) \\ & + 2\Gamma \mathbf{n} \cdot \left[c_i \nabla \Phi_i \nabla \Phi_i - \frac{c_i}{2} (\nabla \Phi_i)^2 \mathbf{I} \right]_L^G = -2\mathcal{H} \mathbf{n} \quad \text{on } S_f, \end{aligned} \quad [5]$$

where $-2\mathcal{H}$ is twice the local mean curvature and the notation $[x]_L^G$ denotes the jump in a quantity x , here the Maxwell stress, across the L–G interface; L and G denote quantities evaluated on the liquid and gas sides of S_f , with $c_i = 1$ on the gas side and $c_i = \kappa$ on the liquid side. Also along the L–G interface, the tangential electric field E_t is continuous but the normal component of the electric displacement suffers a jump, $q = -\mathbf{n} \cdot [c_i \nabla \Phi_i]_L^G$ on S_f . The prohibition of mass transfer across S_f is guaranteed by the

Fig. 2. (A–D) Profiles of tip-streaming jets at the incipience of pinch-off when $\beta = 10$ for α values of (A) $10^{-1.5}$, (B) $10^{-2.0}$, (C) $10^{-2.5}$, and (D) $10^{-3.0}$, and where $Oh = (\alpha\beta)^{1/3}$. The radii of the droplets and the lengths of the tip-streaming jets shown here, which have both been scaled by the original drop radius $\tilde{R}$, vary from the smallest to the largest by an order of magnitude. (E and F) If, however, $\tilde{l}_\mu$ is used as the length scale in both the axial and radial directions, all the profiles in A–D collapse onto a single universal profile for the entire length of the tip-streaming jet, including the transition region that connects the tip-streaming jet to the Taylor cone. This demonstrates conclusively that the dynamics of EHD tip-streaming are independent of the size of the original drop. In this figure, $\kappa = 7.5$ and $\Gamma = 0.2$.

kinematic condition, $\mathbf{n} \cdot (\mathbf{v} - \mathbf{v}_s) = 0$ on S_f , where $\mathbf{v}_s$ is the velocity of points on S_f . The remaining boundary conditions and solution procedure are given in *Materials and Methods*.

Previous studies (10, 17, 18, 27, 28) suggest that cone-jetting is nearly independent of the boundary conditions of the problem, such as the size of the original drop and the strength of the external electric field (so long as it exceeds the critical value required to destabilize the interface). For the system considered here, if the radius and charge on the small droplets formed (Fig. 1F) are independent of the global boundary conditions, dimensional analysis requires that

$$\tilde{r} = \tilde{l}_\mu f(\kappa, \beta); \quad \tilde{Q} = \left(\varepsilon_G \gamma \tilde{l}_\mu^3 \right)^{1/2} g(\kappa, \beta). \quad [6]$$

Here, $\tilde{l}_\mu = \mu^2 / \rho \gamma$ is the viscous length, $\beta \equiv \tilde{t}_e / \tilde{t}_\mu$, $\tilde{t}_\mu = \mu^3 / \rho \gamma^2$ is the viscous time, and f and g are dimensionless functions of κ and β . In terms of the dimensionless groups used in this work, $\beta = \alpha / Oh^3$.

Are $\tilde{r}$ and $\tilde{Q}$ truly independent of the global length scale $\tilde{R}$ and applied electric field strength $|\tilde{\mathbf{E}}_0|$? Consider the alternate dimensionless droplet radius $r^* \equiv \tilde{r} / \tilde{l}_\mu$ and charge $Q^* \equiv \tilde{Q} / (\varepsilon_G \gamma \tilde{l}_\mu^3)^{1/2}$. If this expectation is correct, we should find that r^* and Q^* are invariant with α and Oh , so long as κ and β are fixed. Results of simulations carried out to test this hypothesis are shown in Fig. 2. The tip-streaming jet profiles shown in Fig. 2A–D depict simulation results when $\beta = 10$ and $\kappa = 7.5$ over a wide range of α values. When scaled by the original drop radius $\tilde{R}$ such that $x = \tilde{x} / \tilde{R}$, $z = \tilde{z} / \tilde{R}$, and $r = \tilde{r} / \tilde{R}$, the thickest jet/largest droplet shown is an order of magnitude larger than the thinnest jet/smallest droplet shown. However, when scaled by the viscous length, such that $x^* = \tilde{x} / \tilde{l}_\mu$, $z^* = \tilde{z} / \tilde{l}_\mu$, and $r^* = \tilde{r} / \tilde{l}_\mu$, all these jet profiles collapse onto a single universal profile (Fig. 2E and F). This universal profile captures every detail of the individual scaled profiles, including the sizes and shapes of the small droplet, the microthread connecting the droplet to the tip-streaming jet, and the shape of the transition region that connects the tip-streaming jet to the Taylor cone. Similar universal profiles have

Fig. 3. Scaling laws for (A) the radius r^* and (B) charge Q^* of the droplets formed from EHD tip-streaming. The colored symbols represent results from simulations in which only α has been varied while holding Oh fixed (red, $Oh = 0.1$) or only Oh has been varied while holding α fixed (brown, $\alpha = 0.1$; blue, $\alpha = 0.01$; green, $\alpha = 0.001$). In all simulations, $\Gamma = 0.2$ and $\kappa = 7.5$. (A) Simulations show, for $\beta > 0.1$, that r^* follows a $2/3$ power law in β (dashed/double-dotted line), which transitions to a $1/2$ power law in β (dashed/dotted line) at about $\beta \sim 5$. At $\beta \sim 50$, r^* transitions to a $1/3$ power law (dashed line) in β . (B) Similarly, over the same three ranges of β , Q^* follows power laws in β of β , $\beta^{3/4}$, and $\beta^{1/2}$, respectively. In both this figure and Fig. 4, the subscript fit denotes lines of best fit for results from simulations.

Fig. 4. Fundamental scaling law of electrospraying: variation of droplet charge with droplet radius. In addition to the color scheme described in Fig. 3, the following scheme is used here to show simulation results where κ is varied (purple, $\alpha = 0.001$, $Oh = 0.1$; pink, $\alpha = 0.01$, $Oh = 0.1$; gray, $\alpha = 0.1$, $Oh = 0.1$). Simulations show that $Q^* \propto r^{*3/2}$ (solid line) for all β and κ , indicating that $Q \propto \bar{Q}_R$.

been obtained for other combinations of κ and β , indicating that EHD tip-streaming indeed is independent of the global scales in the problem (*Materials and Methods*).

Having shown that when properly scaled, EHD tip-streaming is solely a function of β and κ , we now seek to determine how these parameters influence r^* and Q^* . Before doing so, it is instructive first to consider two limiting cases: $\beta \rightarrow \infty$ and $\beta \rightarrow 0$.

The limit $\beta \rightarrow \infty$ may be realized if the drop is perfectly insulating ($\sigma \rightarrow 0$ and hence $\tilde{t}_e \rightarrow \infty$) and/or inviscid ($\mu \rightarrow 0$ and hence $\tilde{t}_\mu \rightarrow 0$). As was shown recently for the closely related problem of tip-streaming from a semi-insulating film (10), tip-streaming should not occur for any of the interpretations of this limit. The mechanism responsible for the formation of a tip-streaming jet (10) requires that a strong tangential electric stress, $\tau_e = qE_t$ (25), exist near the tip of the developing Taylor cone—impossible for a perfect insulator because the density of surface charge $q = 0$. Moreover, this electric shear stress must be balanced by a viscous shear stress—impossible for an inviscid liquid because its viscosity $\mu = 0$ —which is required for transporting momentum into the interior of the drop for accelerating the protojet out of the cone. Indeed, the case of an inviscid, perfectly insulating fluid was shown theoretically by Zubarev (29), for sufficiently large κ , to result in a conic cusping singularity (i.e., the curvature at the tip of the developing Taylor cone goes to infinity in finite time) rather than tip-streaming.

The limit as $\beta \rightarrow 0$, on the other hand, may be realized if the drop is perfectly conducting ($\sigma \rightarrow \infty$ and hence $\tilde{t}_e \rightarrow 0$). Because $E_t = 0$ at the surface of a perfect conductor, a tangential electric stress, τ_e , cannot develop along S_f for such a fluid. Therefore, the mechanism responsible for EHD tip-streaming suggests that perfectly conducting fluids should not tip-stream. Simulations in the closely related problem of thin films subjected to electric fields show that perfectly conducting films $\tilde{t}_e \rightarrow 0$ of nonzero viscosity $\tilde{t}_\mu \neq 0$ exhibit a conic cusping singularity (10). Moreover, Zubarev (30) showed theoretically that a conic cusping singularity results in the case of an inviscid, perfectly conducting fluid as well. Therefore, as the limit of $\beta \rightarrow 0$ is approached, we anticipate that r^* will become progressively smaller, with tip-streaming eventually giving way to the conic cusping singularity predicted from analyses of perfectly conducting fluids.

Fig. 3 shows how r^* and Q^* obtained from our simulations vary with β at fixed κ . Three distinct scaling regimes are observed: (i) For $\beta < 5$, i.e., for fluids of relatively large conductivity, $r^* \propto \beta^{2/3}$, whereas $Q^* \propto \beta$. When expressed in dimensional form, these relations become $\tilde{r} \propto (\gamma \varepsilon_L^2 / \rho \sigma^2)^{1/3} \equiv [(\gamma / \rho) \tilde{t}_e^2]^{1/3}$ and $\tilde{Q} \propto (\gamma^2 \varepsilon_L^3 / \rho \sigma^2)^{1/2} \equiv [\varepsilon_L \gamma (\gamma / \rho) \tilde{t}_e^2]^{1/2}$. This scaling regime, in which the radius of and the charge carried by the small droplets are independent of viscosity and which has been obtained here from simulations, is analogous to the experimentally oft-studied scaling regime in steady cone-jetting of highly conducting fluids (see below). (ii) For $5 < \beta < 50$, i.e., for moderately conducting fluids, $r^* \propto \beta^{1/2}$ and $Q^* \propto \beta^{3/4}$. This scaling regime that is reported here was heretofore unknown in the literature. (iii) At $\beta \sim 50$, a transition occurs in the scaling of both r^* and Q^* , above which, i.e., for fluids of relatively small conductivity, $r^* \propto \beta^{1/3}$ and $Q^* \propto \beta^{1/2}$. The latter scaling law for r^* was reported in our recent study of tip-streaming from a fluid film in the same portion of the (β, κ) space (10), giving further credence to the idea that tip-streaming is independent of the boundary conditions of the problem considered. For $\beta > 200$, the latter scalings for r^* and Q^* give way to a region of decreasing dependence on β , where the β dependence of both quantities eventually is lost.

A highly noteworthy outcome of the above analysis is that for the entire portion of (β, κ) space, $Q^* \propto r^{*3/2}$ and the constant of proportionality is independent of both β and κ (Fig. 4). Because this relationship is obeyed in all three scaling regimes for r^* and Q^* described above, this expression is the most fundamental scaling law for EHD tip-streaming from semi-insulating liquids. It also has the most important implications. When recast in terms of the dimensional droplet charge Q , it is equivalent to $Q = 0.44 \bar{Q}_R$. This means that droplets formed from cone-jetting are, at least at the point of formation, coulombically stable, i.e., they do not carry sufficient charge at that point to break up into still smaller droplets. We may infer from this that an aerosol resulting from EHD tip-streaming should be roughly as monodisperse as the droplets formed from capillary pinching of tip-streaming jets—which are quite monodisperse indeed. It also is noteworthy that in a recent experimental study, Mabbett et al. (24) measured the charge on electrospray droplets and showed that the distribution of charge on the droplets peaks at $\approx 0.40 \bar{Q}_R$. The close agreement between the measurements of ref. 24 and our simulations lends further credence to the accuracy of the scaling laws developed in this paper.

In the far more widely studied problem of steady cone-jetting, an electrified drop pendant from a capillary is used to create a steady spray of charged droplets. Liquid is supplied through the capillary at a flow rate F just sufficient to replace the liquid lost in the spraying process, and the structure of the Taylor cone and the portion of the emitted jet sufficiently upstream of the breakup region are time invariant. Several scaling laws have been proposed to describe how the emitted current I and droplet size $\tilde{r}$ vary with F , the most popular of which perhaps is due to Fernández de la Mora and Loscertales (17), hereafter referred to as FDML. We now seek to determine how well their scaling laws for steady cone-jetting can describe, with some slight modifications, the decidedly unsteady cone-jetting process examined in this work. We can determine how Q should vary with $\tilde{r}$ according to any of the scaling laws developed for steady cone-jetting by noting that $\tilde{I} \propto \tilde{Q} / \tilde{t}^\dagger$ and $\tilde{F} \propto \tilde{r}^3 / \tilde{t}^\dagger$, where $\tilde{t}^\dagger$ is the characteristic time for the formation of a single drop. Therefore, without having to make any assumptions about $\tilde{t}^\dagger$, $\tilde{Q} \propto \tilde{r}^3 \tilde{I} / F$. Hence, using FDML's scaling laws that $\tilde{r} \propto (\tilde{F} \tilde{t}_e)^{1/3}$ and $\tilde{I} \propto (\gamma \sigma \tilde{F})^{1/2}$, we find that droplet size and charge should be given by

$$\tilde{r} \propto (\tilde{F} \varepsilon_L / \sigma)^{1/3}; \quad \tilde{Q} \propto \varepsilon_L (\gamma \tilde{F} / \sigma)^{1/2}. \quad [7]$$

First, it is worth noting that Eq. 7 may be combined to show that $\bar{Q} \propto r^{3/2}$, in accordance with the simulations. We next examine the consequences of choosing F by suitably combining fluid properties with matching dimensions, as there is no external flow rate for the problem considered in this work. Previous researchers, including FDML, in exploring steady cone-jetting have argued that viscosity plays no role in determining the size of the fine jet when the fluid conductivity is large. A flow rate scale independent of viscosity μ is given by $F = F_e \equiv (\gamma \epsilon_L / \rho \sigma)$. Substitution of this expression into Eq. 7 results in the following two scaling laws— $r^* \propto \beta^{2/3}$, $Q^* \propto \beta$ —which are precisely those obtained using the simulation results reported in Fig. 3. It is noteworthy that the quantity $(\gamma \epsilon_L / \rho \sigma)$ was identified by several previous researchers as the minimum flow rate for steady cone-jetting of highly conducting fluids (17, 31). Dimensional analysis suggests $\bar{F} = F_\mu \equiv l_\mu^3 / \bar{t}_\mu$ as the characteristic flow rate scale when viscous effects are dominant. Using this expression in Eq. 7 yields the scaling laws $r^* \propto \beta^{1/3}$ and $Q^* \propto \beta^{1/2}$, which also are consistent with our simulation results. Finally, using a geometric mean of the two previously introduced flow rate scales $(F_e F_\mu)^{1/2}$ as a characteristic scale, we recover the scaling laws $r^* \propto \beta^{1/2}$, $Q^* \propto \beta^{3/4}$ appropriate for the intermediate range of values of β .

Although the sizes of droplets immediately after they are created and their size distribution anywhere in an aerosol produced in electrospraying can be measured readily, experimentally determining the charge of such droplets at the instance of their formation is a formidable challenge. Indeed, the droplets may (i) deform, oscillate, and break as a result of aerodynamic and other forces (2, 13, 32); (ii) interact, collide, and possibly coalesce (33) with one another and with solid surfaces; and (iii) evaporate and shrink before their charge can be measured (24). Thus, there has been considerable variation in the experimentally reported values of droplet charge. We have used simulation to show that the charge of daughter electrospray droplets equals 44% of the Rayleigh limit ($0.44 \bar{Q}_R$) at the instant they are formed from the disintegration of an uncharged parent drop in an electric field. A question of broad significance is whether the value of $0.44 \bar{Q}_R$ is even more universal than implied here such that it holds for other systems. It now is known that isolated drops charged to the Rayleigh limit also disintegrate in the same manner as the uncharged drops of this paper (23). A study along these lines recently was carried out for the limiting case of an inviscid drop (34). Whether droplets produced by EHD tip-streaming from isolated drops of finite viscosity charged to the Rayleigh limit also bear charge equal to 44% of the Rayleigh limit is left as an open problem. Raindrops both bear net charge and are subjected to an external electric field (21, 35, 36). Hence, such drops form one conical end from which they emit a single tip-streaming jet. How much charge droplets produced from the breakup of the tip-streaming jet carry in this case also is not known.

The approach used here may be used to settle several inadequately resolved issues and to bring the power of simulation to bear on a host of concepts in EHD tip-streaming that have been studied almost exclusively by experimentation. Among these problems are differences and similarities between transient and steady tip-streaming, the latter of which has attracted much attention over the past quarter-century. However, equally important are relatively new physical situations that may be studied with the algorithm developed in this paper that involve pulsed cone-jetting from pendant drops (37), complex electrified drop formation phenomena involving leaky faucets (38), and even unique routes to EHD drop generation for advanced material science applications (39).

The approach presented here may lead to even more fruitful research endeavors. First, both the uncharged parent drop subject to an external electric field and the charged daughter droplets produced by EHD tip-streaming can be set into oscillations, as already pointed out in the paragraph before last. Grigorev and coworkers (40, 41) used high-order perturbation analyses to show that both EHD fissioning and jetting may be affected by drop shape oscillations. Therefore, it would be highly instructive to

carry out simulations in which the initial conditions are not ones for which the drops are quiescent spheres, as in this paper. The analysis presented here applies to situations in which a drop is indefinitely far from other drops. In several applications discussed in the introduction, drop breakup occurs in the presence of adjacent drops. A pioneering study (32) simulated the electrically induced interaction between pairs of drops of inviscid, perfectly conducting fluids. Although these authors demonstrated that the critical field strength for disintegration increased with separation and asymptotically approached the Taylor limit, they could not simulate the emission of tip-streaming jets from the tips of adjacent drops. More recent work (42) examined interactions of pairs of leaky dielectric drops in an electric field using boundary integral methods under Stokes flow conditions. Therefore, applying the simulation tools reported here to situations in which both finite inertia and finite charge relaxation are important when a pair of nearby drops is subjected to an electric field remains an open problem in fluid mechanics. In several applications including ESI-MS, once charged daughter droplets are produced by EHD tip-streaming, each generation of droplets formed evaporate, reach the Rayleigh limit, and undergo coulombic explosions (12, 23). In this paper, drop disintegration has been analyzed in the absence of evaporation. Variants of the algorithm used here have been developed to analyze multiphase viscous free surface flows with interphase mass transfer (43). Hence, it should be readily possible to study EHD tip-streaming in the presence of evaporation.

Materials and Methods

Oscillations of Charged Drops. When $\bar{Q} < \bar{Q}_R$, Rayleigh (1) calculated the frequencies of small-amplitude oscillations of a drop of an inviscid, perfectly conducting fluid. Effects of nonlinearity were taken up by Tsamopoulos and Brown (44), who used a multiple-timescale expansion to analyze the moderate-amplitude oscillations of a drop of an inviscid, perfectly conducting fluid. They showed that the oscillation frequency decreases with amplitude and demonstrated resonant interactions between the fundamental mode and other harmonics. Zharov et al. (45, 46) extended these results for drops of perfectly conducting fluids (44) to more complex situations, including obtaining higher-order perturbation results for inviscid oscillations (45) and accounting for viscous effects in nonlinear oscillations (46).

Problem Description. The system consists of an uncharged drop (Ω_d) surrounded by an insulating gas (Ω_g). The drop, a Taylor–Melcher leaky dielectric or semi-insulating liquid (25, 26) of finite conductivity, is an incompressible Newtonian fluid of density ρ , viscosity μ , permittivity ϵ_L , and conductivity σ . The gas has permittivity ϵ_g . The surface tension γ of the liquid–gas (L–G) interface (S_d) and the physical properties of the two phases are constant and spatially uniform. Initially, the drop is a sphere of radius R . For times $\bar{t} \geq 0$, the drop is subjected to an external electric field that at large distances from the drop approaches a constant value $\bar{E}_0$.

Dimensionless Numbers. The problem is cast into dimensionless form using $\bar{R}$ as length scale, capillary time $\bar{t}_c \equiv (\rho \bar{R}^3 / \gamma)^{1/2}$ as time scale, capillary pressure $p_c = \gamma / \bar{R}$ as pressure scale, $|\bar{E}_0|$ as electric field scale, and $\epsilon_g |\bar{E}_0|$ as surface charge density scale. Throughout this paper, variables with tildes are the dimensional counterparts of those without tildes. From this process, five dimensionless groups arise: (i) Ohnesorge number $Oh \equiv \mu / (\rho \bar{R} \gamma)^{1/2}$; (ii) electric bond number $\Gamma \equiv \epsilon_g |\bar{E}_0|^2 / (2\gamma \bar{R})$; (iii) permittivity ratio $\kappa \equiv \epsilon_L / \epsilon_g$; (iv) ratio of charge relaxation time to the capillary time $\alpha \equiv \bar{t}_e / \bar{t}_c$, where $\bar{t}_e \equiv \epsilon_L / \sigma$ is the charge relaxation time; and (v) Peclet number $Pe \equiv (\bar{R}^2 / D_s) / \bar{t}_c$, where D_s is the coefficient of surface diffusion.

Boundary Conditions. Only one quadrant of (x, z) space, where $x \equiv \bar{x} / \bar{R}$ and $z \equiv \bar{z} / \bar{R}$ denote the dimensionless radial and axial coordinates in a cylindrical coordinate system with its origin based at the center of the drop, must be considered because of axisymmetry about the center line $x = 0$ and symmetry about the midplane $z = 0$. Far from the drop, the electric potential asymptotically approaches $-L \cos \theta$, where $L \equiv \bar{L} / \bar{R}$ is the distance measured from the origin and θ is the cone angle measured from the axis of symmetry. In the simulations, the domain exterior to the drop is a sphere of large but finite radius L where this boundary condition is imposed. Testing has shown that a value of $L = 7.5$ is sufficient to produce results independent of L .

Numerics. Eqs. 1–4 are solved simultaneously as an initial-boundary-value problem by a fully implicit, method of lines, arbitrary Lagrangian–Eulerian algorithm using the Galerkin finite element method with elliptic mesh generation and an adaptive time integrator (compare ref. 10).

Bond Number Independence. In addition, both r^* and Q^* should be independent of Γ if EHD tip-streaming is independent of the global length scales

and the applied electric field strength. This criterion is found to hold as simulations show that both r^* and Q^* vary negligibly with Γ for $\Gamma > \Gamma_T = 0.105$, where Γ_T , the Taylor limit (9), is the value of Γ above which an uncharged drop subjected to an electric field becomes unstable.

ACKNOWLEDGMENTS. This work was supported by the Basic Energy Sciences program of the US Department of Energy (DE-FG02-96ER14641).

1. Rayleigh L (1882) On the equilibrium of liquid conducting masses charged with electricity. *Philos Mag* 14(87):184–186.
2. Sartor JD (1969) Electricity and rain. *Phys Today* 22(8):45–51.
3. Bohr N, Wheeler JA (1939) The mechanism of nuclear fission. *Phys Rev* 56:426–450.
4. Taffin DC, Ward TL, Davis EJ (1989) Electrified droplet fission and the Rayleigh limit. *Langmuir* 5(2):376–384.
5. Zeleny J (1917) Instability of electrified liquid surfaces. *Phys Rev* 10(1):1–6.
6. Wilson CTR, Taylor GI (1925) The bursting of soap-bubbles in a uniform electric field. *Math Proc Camb Philos Soc* 22(5):728–730.
7. Nolan JJ (1926) The breaking of water-drops by electric fields. *Proc R Ir Acad Sect A* 37: 28–39.
8. Macky WA (1931) Some investigations on the deformation and breaking of water drops in strong electric fields. *Proc R Soc Lond A* 133(822):565–587.
9. Taylor GI (1964) Disintegration of water drops in an electric field. *Proc R Soc Lond A* 280(1382):383–397.
10. Collins RT, Jones JJ, Harris MT, Basaran OA (2008) Electrohydrodynamic tip streaming and emission of charged drops from liquid cones. *Nat Phys* 4(2):149–154.
11. Cloupeau M, Prunet-Foch B (1989) Electrostatic spraying of liquids in cone-jet mode. *J Electrostat* 22(2):135–159.
12. Fenn JB, Mann M, Meng CK, Wong SF, Whitehouse CM (1989) Electrospray ionization for mass spectrometry of large biomolecules. *Science* 246(4926):64–71.
13. Brazier-Smith PR, Jennings SG, Latham J (1973) Increased rates of rainfall production in electrified clouds. *Q J R Meteorol Soc* 99(422):776–786.
14. Lee D, Shin Y, Yu T, Hwang J (2007) Electrohydrodynamic printing of silver nanoparticles by using a focused nanocolloid jet. *Appl Phys Lett* 90(8):081905.
15. Yamashita M, Fenn JB (1984) Electrospray ion source. Another variation on the free-jet theme. *J Phys Chem* 88(20):4451–4459.
16. Sobott F, Robinson CV (2004) Characterising electrosprayed biomolecules using tandem-MS—the noncovalent GroEL chaperonin assembly. *Int J Mass* 236(1):25–32.
17. de la Mora JF, Loscertales I (1994) The current emitted by highly conducting Taylor cones. *J Fluid Mech* 260(1):155–184.
18. Gañán-Calvo AM, Dávila J, Barrero A (1997) Current and droplet size in the electrospraying of liquids. Scaling laws. *J Aerosol Sci* 28(2):249–275.
19. Chen CH, Saville DA, Aksay IA (2006) Scaling laws for pulsed electrohydrodynamic drop formation. *Appl Phys Lett* 89(12):124103.
20. Gañán-Calvo AM, Montanero JM (2009) Revision of capillary cone-jet physics: electrospray and flow focusing. *Phys Rev E Stat Nonlin Soft Matter Phys* 79(6):066305.
21. Grimm RL, Beauchamp JL (2003) Field-induced droplet ionization mass spectrometry. *J Phys Chem B* 107(51):14161–14163.
22. Eggers J (1993) Universal pinching of 3D axisymmetric free-surface flow. *Phys Rev Lett* 71(21):3458–3460.
23. Duft D, Achtzehn T, Müller R, Huber BA, Leisner T (2003) Coulomb fission: Rayleigh jets from levitated microdroplets. *Nature* 421(6919):128.
24. Mabbett SR, Zilch LW, Maze JT, Smith JW, Jarrold MF (2007) Pulsed acceleration charge detection mass spectrometry: application to weighing electrosprayed droplets. *Anal Chem* 79(22):8431–8439.
25. Melcher JR, Taylor GI (1969) Electrohydrodynamics: A review of the role of interfacial shear stresses. *Annu Rev Fluid Mech* 1(1):111–146.
26. Saville DA (1997) Electrohydrodynamics: The Taylor-Melcher leaky dielectric model. *Annu Rev Fluid Mech* 29(1):27–64.
27. Cherney LT (1999) Electrohydrodynamics of electrified liquid menisci and emitted jets. *J Aerosol Sci* 30(7):851–862.
28. Gamero-Castaño M, Hruby V (2002) Electric measurements of charged sprays emitted by cone-jets. *J Fluid Mech* 459(1):245–276.
29. Zubarev NM (2002) Self-similar solutions for conic cusps formation at the surface of dielectric liquids in electric field. *Phys Rev E Stat Nonlin Soft Matter Phys* 65(5 Pt 1): 055301.
30. Zubarev NM (2001) Formation of conic cusps at the surface of liquid metal in electric field. *JETP Lett* 73(10):544–548.
31. Barrero A, Loscertales I (2007) Micro- and nanoparticles via capillary flows. *Annu Rev Fluid Mech* 39:89–106.
32. Brazier-Smith PR, Jennings SG, Latham J (1971) An investigation of the behavior of drops and drop-pairs subjected to strong electrical forces. *Proc R Soc Lond A* 325(1562):363–376.
33. Ristenpart WD, Bird JC, Belmonte A, Dollar F, Stone HA (2009) Non-coalescence of oppositely charged drops. *Nature* 461(7262):377–380.
34. Burton JC, Taborek P (2011) Simulations of coulombic fission of charged inviscid drops. *Phys Rev Lett* 106(14):144501.
35. Basaran OA, Scriven LE (1989) Axisymmetric shapes and stability of isolated charged drops. *Phys Fluids* 1(5):795.
36. Adornato PM, Brown RA (1983) Shape and stability of electrostatically levitated drops. *Proc R Soc Lond A* 389(1796):101–117.
37. Stachewicz U, Dijkstra JF, Yurteri CU, Marijnissen JCM (2007) Experiments on single event electrospraying. *Appl Phys Lett* 91(25):254109.
38. Marginean I, Nemes P, Vertes A (2006) Order-chaos-order transitions in electrosprays: The electrified dripping faucet. *Phys Rev Lett* 97(6):064502.
39. Ferraro P, Coppola S, Grilli S, Paturzo M, Vespini V (2010) Dispensing nano-pico droplets and liquid patterning by pyroelectrodynamic shooting. *Nat Nanotechnol* 5(6):429–435.
40. Shiryayeva SO, Volkova MV, Grigorev AI (2005) Nonlinear oscillations of an uncharged conducting drop in an external uniform electrostatic field. *Tech Phys* 50(3): 321–329.
41. Shiryayeva SO, Grigorev AI, Kornienko DO (2010) Mechanisms behind spheroidal oscillations and electrostatic instability of a charged drop. *Tech Phys* 55(11):1558–1568.
42. Baygents JC, Rivette NJ, Stone HA (1998) Electrohydrodynamic deformation and interaction of drop pairs. *J Fluid Mech* 368(1):359–375.
43. Schunk PR, Rao RR (1994) Finite element analysis of multicomponent two-phase flows with interphase mass and momentum transport. *Int J Numer Methods Fluids* 18(9): 821–842.
44. Tsamopoulos JA, Brown RA (1984) Resonant oscillations of inviscid charged drops. *J Fluid Mech* 147:373–395.
45. Zharov AN, Grigorev AI, Shiryayeva SO (2003) Internal nonlinear four-mode interactions of capillary oscillations of a charged drop. *Tech Phys Lett* 29(5):388–391.
46. Zharov AN, Grigorev AI, Shiryayeva SO (2005) Analytical study of nonlinear vibrations of a charged viscous liquid drop. *Tech Phys* 50(12):1568–1582.