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Electrospray cone-jet breakup and droplet production for electrolyte solutions

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Abstract – The production of charge droplets via the electrospray of an electrolyte is experimentally and theoretically found to be a Coulombic fission phenomenon that occurs when induced space charge at the microjet interface reaches a critical density as the charge separation approaches the Bjerrum length. The field surrounding the cone is dominated by the Taylor harmonic, which is responsible for inducing space charge within an interfacial Debye layer, such that the jet breakup length and plume angle are strong functions of both the ionic strength and interfacial surface tension.

When a sufficiently high direct current (DC) electric field is applied to liquid exiting a capillary, it deforms into a conic structure called a Taylor cone [1]. In typical practice, the tip of this cone extends to form a liquid microjet (cone-jet mode), and charged droplets are ejected from the end of the microjet [2]. Among other applications, electrospray ionization has become a workhorse in mass spectrometry because it enables soft ionization of large biomolecules, such as proteins, from an aqueous solution [3]. However, the droplets are ejected in a large, expanding plume that negatively impacts transport into a mass spectrometer, with injection efficiencies less than 1% [4]. Moreover, the size and charge of each aerosol directly influences the all-important degree of ionization of the analyte molecules within the droplets. Therefore, understanding the phenomena that lead to microjet breakup and droplet production is essential to controlling and manipulating the droplets and enhancing electrospray performance. This work reports a theory, verified by imaging experiments, that elucidates the mechanisms of microjet breakup and plume formation for an electrolyte and provides quantitative estimates of the various important parameters that govern the phenomena.

Taylor [1] offered the first theoretical description of the conic meniscus for an electrospray, which has been studied since the pioneering work of Zeleny [5]. The cone's universal half-angle of $\theta = 49°$ for any high permittivity (or high conductivity) liquid corresponds to a unique and discrete spherical harmonic of the Laplace operator for the potential φ in the gas phase. The Legendre function P_n is of order $n = 1/2$ in the polar angle θ direction and $r^{1/2}$ in the radial direction, such that this specific harmonic gives rise to a Maxwell pressure that scales as $1/r$ and hence offsets the singular capillary pressure of the cone that has the same $1/r$ scaling. It is a very elegant real-life example of a discrete spectrum in (semi-)unbounded domains that can only occur near geometric singularities, such that the local electric field has a generic functional dependence that is insensitive to far-field conditions. Because of the universal functional dependence of the harmonic potential near the cone, in the limit of high liquid/gas permittivity ratio, parametric effects on the field are contained in the coefficient of the potential. Balancing the Maxwell pressure $\varepsilon_0 |\nabla\varphi|^2$ with the singular azimuthal capillary pressure of a cone γ_f/r gives rise to the coefficient of the potential, which must scale as $(\gamma_f/\varepsilon_0)^{1/2}$. Therefore, the potential along the cone axis ($\theta = 0°$) away from the tip is

$$\varphi_{Taylor} = B(\gamma_f/\varepsilon_0)^{1/2}r^{1/2}, \qquad (1)$$

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where B is a dimensionless constant that is specified by the far-field conditions. Here, ε_0 is the gas permittivity and γ_f is the surface tension of the liquid. While Taylor's local theory is confined to the cone such that this coefficient would be of unit order if the potential drop is measured across the cone, connection to the measurable potential drop across real electrodes requires B to be roughly the ratio of cone/drop size to the electrode separation [6]. Notably, this Taylor potential increases away from the tip of the cone but the corresponding electric field decreases.

Microjet breakup is typically attributed to hydrodynamic (Rayleigh) instabilities [7] leading to drop sizes ~ 1.9 times the jet diameter, and this is especially true if the charging of the drop is low. Such sprays typically have two families of drops, primary and satellite, with the smaller satellite drops pushed to the extremes of the droplet plume by Coulombic repulsion. Though a number of scaling laws, often in direct contrast to each other [8,9], have been proposed to describe cone-jet breakup and the ensuing droplet production, this is still a rich and not fully understood phenomenon with important implications for various applications. Here, we present evidence that the microjet breakup is due to a Coulombic fission mechanism when using an electrolyte, without any evidence of the Rayleigh instability and its primary and satellite drops (see fig. 1). We also show that the Coulombic fission mechanism directly influences the geometry of the droplet plume. We then use a scaling theory to quantitatively delineate the role Taylor potential, that goes as $\varphi_{Taylor} \sim r^{1/2}$, plays in polarizing the microjet leading to breakup and plume formation.

For the experiments, a syringe pump (Model 601553, KD Scientific) was used to supply aqueous solutions at $50\,\mu\mathrm{L/h}$ through a stainless steel capillary needle with inner and outer diameters of $100\,\mu\mathrm{m}$ and $200\,\mu\mathrm{m}$, respectively (Agilent Technologies, Inc.). The capillary needle was mounted in a commercial electrospray apparatus (Bruker Daltonics, Inc.), and electrosprays were generated by applying high DC voltage (UltraVolt, Inc.) to the needle housing (~ 1–$5\,\mathrm{kV}$). A copper plate connected to earth ground was used as a counter electrode. The ensuing electrosprays were visualized with a high-speed video camera (Fastcam SA4, Photron, Inc.) connected with a $12\times$ long distance lens, a $2\times$ lens, and a $2\times$ adapter (Navitar, Inc.) to provide a total magnification of $48\times$, and a high intensity light source (ILP-1, Olympus). Ethanol (99.5% purity, Sigma-Aldrich) solutions, whose conductivity was varied by adding sodium chloride for ionic strengths from 0.06 to $2.2\,\mathrm{mM}$, were employed. Surface tension was varied by mixing ethanol and deionized water at different ratios ranging from 20–90% ethanol content at an ionic strength of $0.1\,\mu\mathrm{M}$.

Figure 1(a) shows the cone-jet structure and droplet plumes for solutions of various ionic strengths C_∞. The length of the microjet L_j emanating from the cone clearly decreases as the conductivity increases. Further, the angle of the droplet plume θ_{plume} clearly increases
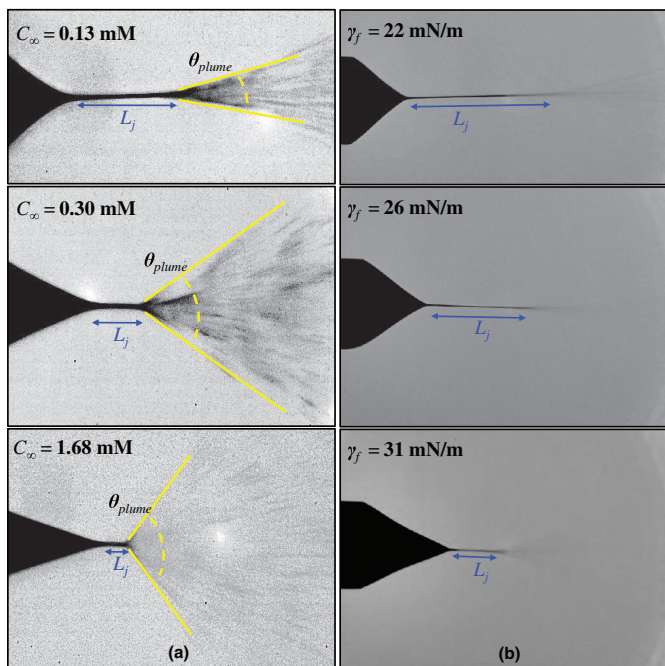

Fig. 1: (Colour on-line) Images of the cone-jet and corresponding droplet plume for DC electrosprays using (a) ethanol solutions with ionic strengths of $C_\infty = 0.13\,\mathrm{mM}$, $0.30\,\mathrm{mM}$, and $1.68\,\mathrm{mM}$, and (b) in ethanol/deionized water solutions with surface tensions of $\gamma_f = 22\,\mathrm{mN/m}$, $26\,\mathrm{mN/m}$, and $31\,\mathrm{mN/m}$ at a fixed ionic strength of $C_\infty = 0.1\,\mu\mathrm{M}$. Note that the length of the microjet decreases with increasing ionic strength while the angle of the droplet plume increases with increasing ionic strength, suggesting that space charge in the microjet is playing a significant role. Similarly, the length of the microjet decreases as the surface tension increases, suggesting a symbiotic atomization effect by conductivity and capillarity.

as C_∞ increases. Such strong ionic strength dependence suggests space charge polarization is at play at the microjet interface. Additionally, both the jet length and plume angle show a strong dependence on the surface tension of the solution γ_f as shown in fig. 1(b), because this polarization must balance with capillary forces. To clarify these observations, we present a scaling theory that confirms the dependence of the jet length and plume angle on both ionic strength and surface tension.

First consider the microjet emanating from the cone axis. This small microjet is not expected to modify the gas potential appreciably, and hence the dominant Taylor harmonic (eq. (1)) will still be accurate in the presence of the microjet [10]. Because the gas potential will follow the Taylor potential as $\varphi_{Taylor} \sim r^{1/2}$, the interfacial potential between the microjet and gas must correspondingly also increase along the microjet axis. The resultant electric field normal to the jet/gas interface induces ion polarization whose intensity also increases along the jet. This induced space charge will be within a double layer on the liquid side of the interface of characteristic thickness $\lambda_D = \sqrt{\varepsilon_l RT/(2(Fz')^2 C_\infty)}$ (the Debye length) [11], where

C_∞ is the electrolyte concentration (ionic strength) in the liquid bulk of the cone and microjet before its breakup. Such polarization occurs within a charge relaxation time of $\varepsilon_l/\sigma_l = \lambda_D^2/D$ [6], for a given solution permittivity ε_l, conductivity σ_l, and ion diffusivity D. For typical Debye lengths of $\lambda_D \sim 10$–$100\,\mathrm{nm}$, this relaxation time is 0.1–1 μs depending on the ionic strength. Considering that the ion transit time from the cone through the microjet is typically more than 1 ms, there is ample time for this space charge polarization to occur. Indeed, Gañán-Calvo and colleagues have conducted a number of studies on the microjet [6,12,13] and offered a scaling theory for the current based on a surface current (perhaps due to space charge polarization within an interfacial Debye layer) and a net conduction current in the electroneutral microjet. However, how the surface charges are induced and their Coulombic repulsion were not delineated and hence atomization was not captured in their theories.

We argue that this polarization can play an important role in microjet breakup for electrolyte solutions. The potential gradient at the jet/gas interface that induces polarization will depend on the external gas potential along the microjet (r) direction, which can be estimated based on the Taylor potential φ_{Taylor} surrounding the cone (eq. (1)). Internally, the uncharged microjet bulk will be at zero potential due to its conductive nature. Because the surface potential of the microjet φ_s must match the outer (gas) potential, it follows that $\varphi_s \sim \varphi_{Taylor}$ such that the Taylor potential represents a leading order approximation of the normal potential jump across the interfacial polarized region along the jet (fig. 2(a)). Oftentimes, the potential drop through the Debye layer is assumed to be linear from the classic Debye-Hückel theory, $\varphi_s \sim \lambda_D E_s$. However, if the potential drop across the polarized region is large compared to the reference thermal potential $\varphi_0 = RT/Fz' \sim 25.7\,\mathrm{mV}$ (for one mole of unit valent charges), space charge must be accounted for. Here, the potential drop across the polarized region can be estimated to be $100\,\mathrm{mV}$ using eq. (1) by assuming an axial distance equal to the jet length ($r = L_j \sim 10\,\mu\mathrm{m}$). As such, the generic relationship between the surface potential at the polarized interface φ_s and the corresponding normal surface field E_s can be estimated using an asymptotic analysis of the nonlinear Poisson equation; the so-called Guoy-Chapman theory [6],

$$\varphi_s = 2\varphi_0 \ln(\lambda_D E_s/\varphi_0). \qquad (2)$$

The surface ionic strength C_s is related to surface potential by the Boltzmann distribution $\exp(\varphi_s/\varphi_0) = C_s/C_\infty$, which gives rise to a surface electric field of $E_s = \varphi_0/\lambda_D \sqrt{C_s/C_\infty}$. Substituting this relationship for E_s and φ_{Taylor} at $r = L_j$ from eq. (1) for φ_s into eq. (2) and using the Boltzmann distribution for C_s results in a scaling relation between the local surface ionic strength within the Debye layer with its position L_j
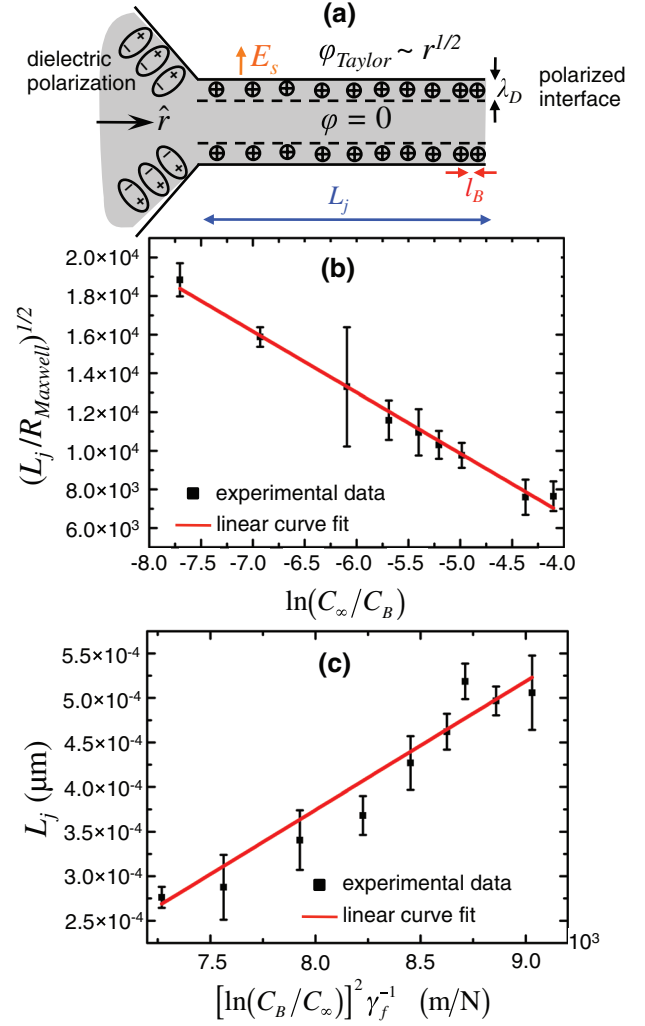

Fig. 2: (Colour on-line) (a) Schematic of the polarized interface in the microjet of thickness λ_D, where the surface potential φ_s assumes the outside Taylor potential φ_{Taylor}. (b) Normalized jet length $\sqrt{L_j/R_{Maxwell}}$ as a function of the logarithm of the ionic strength $\ln(C_B/C_\infty)$ where $\gamma_f = 22\,\mathrm{mN/m}$. (c) Jet length L_j as a function of $(\ln(C_B/C_\infty))^2 \gamma_f^{-1}$ for a fixed ionic strength of $C_\infty = 0.1\,\mu\mathrm{M}$.

along the microjet,

$$L_j^{1/2} = (\varphi_0/(B(\gamma_f \varepsilon_0)^{1/2}))\ln(C_s/C_\infty). \qquad (3)$$

Since the Taylor (and thus surface) potential increases with $r^{1/2}$ along the microjet while λ_D remains constant, the charge density in the polarized interface will increase exponentially down the jet length, until repulsive interaction between the point charges is no longer screened and the resulting Coulombic fission atomizes the microjet. To estimate the microjet length L_j prior to break up, we require a relation for the critical surface ionic strength C_B, which is the maximum surface ionic strength before jet break up. We estimate that the critical ionic strength will occur when any two charges are separated by a Bjerrum length $l_B = q^2/(\varepsilon_l K_B T)$ (where q is the unit

charge) [6], which is the minimum distance between two charges when their Columbic energy is equal to the thermal energy (*i.e.*, the individual charge screening length due to thermal fluctuation). We can thus define a critical ionic strength C_B that is related to the critical charge density as $C_B = \rho_{e,crit}/Fz'$, where $\rho_{e,crit} = q/l_B^3$. Setting the surface ionic strength to the critical ionic strength $C_s = C_B$ at L_j, eq. (3) can be simplified to

$$(L_j/R_{Maxwell})^{1/2} = -B^{-1}\ln(C_\infty/C_B), \qquad (4)$$

where $R_{Maxwell}$ is defined as the diameter of a reference equilibrium cylinder with an overall potential drop equal the thermal reference potential $\varphi_0 = RT/(Fz')$ and whose Maxwell force balances the capillary force exactly, $R_{Maxwell} = \varphi_0^2(\varepsilon_0/\gamma_f)$. The critical ionic strength C_B in the polarized layer is roughly 0.13 M for unit valent ions in pure ethanol and 4.77 M in water using empirical permittivity data for ethanol and water mixtures [14].

Qualitatively, increasing the ionic strength will decrease the Debye length leading to a corresponding increase in charge density. This, in turn, will lead to more rapid microjet breakup (shorter L_j) and atomization. Figure 2(b) shows that the measured jet length obeys the predicted ionic strength logarithmic scaling. Using a reference critical ionic strength of $C_B = 0.13$ M for ethanol, we fit a curve of $(L_j/R_{Maxwell})^{1/2} = -3153.33\ln(C_\infty/C_B)$ to the data, leading to a coefficient B in eqs. (1) and (4) of $B = 3.17 \times 10^{-4}$. This value is close to the anticipated value of $B \sim 10^{-3}$ for our set-up where B is the cone dimension divided by electrode separation as discussed in eq. (1). Hence, we can conclude that Coulombic repulsion between induced charges in the polarized layer appears to be responsible for microjet breakup, and that this occurs once the average charge separation approaches the Bjerrum length.

We also anticipate that jet length should depend on the surface tension of the liquid since increasing this will increase the Taylor potential and the ensuing induced polarization. Thus, increasing surface tension should also decrease the jet length as shown in fig. 1(a). Equation (4) then provides a prediction for the effect of surface tension on microjet breakup of

$$L_j = (B^{-1}\varphi_0\varepsilon_0^{1/2})^2(\ln(C_B/C_\infty))^2\gamma_f^{-1}. \qquad (5)$$

Since both surface tension and permittivity (and hence C_B) vary simultaneously in our experiments by using ethanol/water mixtures, we can more accurately state that jet length should go as $L_j \sim (\ln(C_B/C_\infty))^2\gamma_f^{-1}$. Figure 2(c) confirms this relationship, and a curve fit produces $L_j = 1.44 \times 10^{-7}(\ln(C_B/C_\infty))^2\gamma_f^{-1}$ (in m). The slope, 1.44×10^{-7} N, is in good agreement with the theoretical value predicted by eq. (5) of $(B^{-1}\varphi_0\varepsilon_0^{1/2})^2 = 2.2 \times 10^{-7}$ N when using the previously determined value of $B = 3.17 \times 10^{-4}$. This self-consistency further verifies the polarization mechanism in the microjet
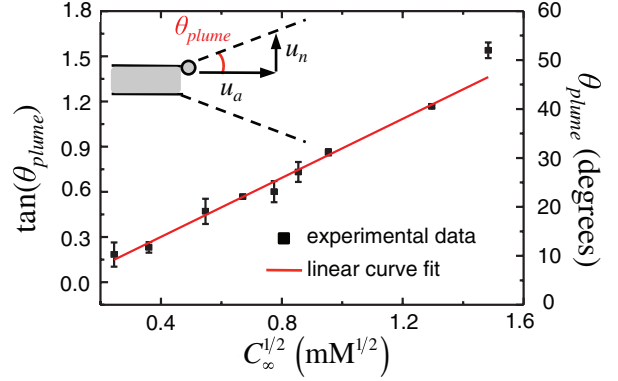

Fig. 3: (Colour on-line) Tangent of the plume angle $\tan(\theta_{plume})$ as a function of the square root of the ionic strength $(C_\infty)^{1/2}$. The inset schematic defines the normal u_n and axial u_a droplet velocities.

that ultimately leads to microjet atomization for these electrolytes, rather than dynamic or flow instabilities [6].

In addition to the changes in jet length, fig. 1(a) also shows that the angle of the droplet plume erupting from the microjet also has a strong dependence on C_∞. To resolve this, we consider a model for the velocities of the atomized droplets. Assuming each aerosol of radius R_d initially gains kinetic energy from electrostatic repulsion from the tip of the microjet, the normal droplet velocity u_n (fig. 3 inset) can be estimated as

$$u_n = \sqrt{2E_sq_dR_d/m}, \qquad (6)$$

where E_s is the surface normal electric field of the microjet at L_j. The mass of each droplet m is related to the diameter of the droplet by $m = 4/3\pi R_d^3\rho_f$, where ρ_f is the liquid mass density. The charge q_d on the droplet can be estimated by using the conservation of current: $q_d = IR_d/u_a$, where u_a is the axial (tangential) velocity of the droplet, I is the current ($I = \sqrt{KQ\gamma_f}$), and K is the conductivity of the liquid and proportional to C_∞ ($K = \alpha C_\infty$) [15]. As a limiting case, we assume that the drop size is given by the Debye length such that $R_d \approx \lambda_D$. It is well established that smaller drops will be pushed to the edges of the plume [7], and we have even demonstrated that this can be used to sort differently sized nanocolloids [16]. The smallest drops, therefore, will define the plume angle. While drops the size of the Debye length would be exceedingly small and they could not be resolved individually, they do provide a leading order estimate to determine the extreme of the plume angle. As shown in fig. 1(a), distinct drops are not captured directly in this work, but rather streaklines of the smallest drops that ultimately define the measured plume angle are imaged.

The axial aerosol velocity u_a along the jet direction can be assumed to be identical to the microjet velocity at breakup. As the normal field E_s due to space charge polarization dominates the Maxwell stress and increases rapidly as $\exp(r^{1/2})$ via eqs. (1) and (2), we do not expect

elongational or capillary stress to be significant away from the cone-jet junction. Additionally, tangential stress is already weak for an air jet. Hence, for a steady jet, we expect the jet velocity to increase along the jet length as determined by a balance between the inertial dynamic pressure and the Maxwell pressure or

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{\rho_f}{2}u_a^2 - \frac{\varepsilon_l^2}{2\varepsilon_0}E_s^2\right) = 0. \tag{7}$$

Hence, the local jet velocity can be directly linked to the Taylor potential through the E_s-φ_{Taylor} relationship across the polarized layer in eq. (2). Again induced space charge serves as the dominant physical phenomenon, and the resulting Maxwell pressure from the dominant Taylor mode drives the flow. Integrating eq. (7), setting the constant to be zero at the tip, and incorporating $E_s = (\varphi_0/\lambda_D)\sqrt{C_B/C_\infty} = \sqrt{2\rho_{e,crit}\varphi_0/\varepsilon_l}$ gives a microjet velocity and thus axial droplet velocity of

$$u_a = \sqrt{2\rho_{e,crit}\varphi_0\varepsilon_l/(\varepsilon_0\rho_f)}. \tag{8}$$

The plume angle can then be determined from the ratio of normal velocity u_n to the axial velocity u_a as

$$\tan(\theta_{plume}) = \frac{u_n}{u_a}\sqrt{\frac{3\varepsilon_0\rho_f C_\infty}{4\pi\varepsilon_l^2\rho_{e,crit}\varphi_0}}\sqrt{\frac{2\alpha Q\gamma_f F z'\varepsilon_0}{\varphi_0\varepsilon_l\rho_f}}. \tag{9}$$

Therefore, $\tan(\theta_{plume}) \sim C_\infty^{1/2}$. The experimental data for the measured plume angle for different solution ionic strengths confirms this scaling (fig. 3), and a curve fit produces the relationship $\tan(\theta_{plume}) = 1.06C_\infty^{1/2}$ for a reference value of $C_B = 0.13\,\mathrm{M}$ and the experimental surface tension shown in fig. 1(a). This empirical scaling coefficient of $1.06\,\mathrm{M}^{-1/2}$ is close to the theoretical value of $1.34\,\mathrm{M}^{-1/2}$ predicted by eq. (9) for the same C_B, confirming the role of ionic strength on plume formation.

In this work, we have presented experimental evidence complemented by theory that microjet breakup for electrolytes is a Coulombic fission phenomenon that occurs when induced space charge at the microjet interface reaches a density with linear charge separation approaching the Bjerrum length. The dominant Taylor harmonic extends into the jet region and is responsible for an induced space charge layer at the microjet interface that leads to a well-defined relationship between the jet length

as a function of the ionic strength and surface tension of the solution and a relationship between the plume angle and ionic strength. In both cases, the theoretical predictions match the measurements closely. This demonstrates that with electrolytes, Coulombic effects dominate hydrodynamic effects in the production of droplets from an electrospray. Such ionic polarization was also shown to be important in cone formation under an AC field but there the polarization is driven by asymmetric ion mobility [17].

$$* * *$$

REFERENCES

[1] Taylor G. I., *Proc. R. Soc. A*, **280** (1964) 383.
[2] Fenn J. B., Mann M., Meng C. K., Wong S. F. and Whitehouse C. M., *Phys. Rev. E*, **76** (2007) 026320.
[3] Marginean I., Nemes P. and Vertes A., *Science*, **246** (1989) 64.
[4] Page J. S., Kelly R. T., Tang K. and Smith R. D., *J. Am. Soc. Mass Spectrom.*, **18** (2007) 1582.
[5] Zeleny J., *Phys. Rev.*, **10** (1917) 1.
[6] Chang H.-C. and Yeo L. Y., *Electrokinetically Driven Microfluidics and Nanofluidics* (Cambridge University Press, New York) 2010, see sect. 9.2 for discussion of coefficent B, sect. 2.4 for derivation of eq. (2) and sect. 2.6 for a discussion on Bjerrum length.
[7] Tang K. and Gomez A., *Phys. Fluids*, **6** (1994) 2317.
[8] Fernandez de la Mora J., *Annu. Rev. Fluid Mech.*, **39** (2007) 217.
[9] Gañán-Calvo A. M. and Montanero J. M., *Phys. Rev. E*, **79** (2009) 066305.
[10] Cherney L. T., *J. Fluid Mech.*, **378** (1999) 167.
[11] Debye P. and Huckel E., *Phys. Z.*, **24** (1923) 305.
[12] Gañán-Calvo A. M., Dvila J. and Barrero A., *J. Aerosol Sci.*, **28** (1997) 249.
[13] Gañán-Calvo A. M., *Phys. Rev. Lett.*, **79** (1997) 217.
[14] Petong P., Pottel R. and Kaatze U., *J. Phys. Chem. A*, **104** (2000) 7420.
[15] Gañán-Calvo A. M., *J. Fluid Mech.*, **507** (2004) 203.
[16] Cheng X. and Chang H.-C., *New J. Phys.*, **11** (2009) 075023.
[17] Chetwani N., Maheshwari S. and Chang H.-C., *Phys. Rev. Lett.*, **101** (2008) 204501.