

## Universal Cone Angle of ac Electrospays Due to Net Charge Entrainment

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The half-angle of an ac cone is shown to exhibit a universal (length-scale independent) asymptotic value of  $12.6^\circ$  at high-permittivity ratio, which is quite distinct from the  $49.3^\circ$  of dc Taylor cones. Our theory and experiments suggest that ac entrainment of low-mobility anions, generated by field-assisted ion dissociation, sustains a net charge at the ac cone. Mutual Coulombic repulsion between these free charges compensates the singular azimuthal capillary force and elongates the cone with an axial force that does not exist in dc cones.

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Since Zeleny's earlier observation [1] that an applied dc potential across a drop can deform it into a conical meniscus and eject charged droplets, dc electro spray has become the key soft ionization method in mass spectrometry for genomic, proteomic, and drug discovery research [2]. In his seminal work, Taylor [3] first deciphered the mystery behind such a conical meniscus with a singular capillary pressure that blows up as  $\rho^{-1}$  with respect to the lateral length of cone  $\rho$ . Assuming the cone to be at constant potential for a conducting liquid, he showed that the induced polarization at the interface can produce a Maxwell pressure that also scales as  $\rho^{-1}$  and hence can cancel the singular capillary pressure to sustain a cone. Taylor's angle of  $49.3^\circ$  was later extended to liquids with finite permittivity [4–6] and the half-angle is shown to decrease to  $30^\circ$  at  $\epsilon_l/\epsilon_g = 17.59$ , below which no dc cones exist.

In the present Letter, we explore an anomalous ac cone first reported by Maheshwari and Chang [7,8]. This conical meniscus sustains a steady half cone angle of  $\sim 11^\circ$  while it grows continuously over a period much larger than the half period of applied ac field without showing any oscillations [9]. Maheshwari and Chang [7] suggest preferential entrainment of low-mobility anions that occurs at frequencies higher than the inverse charge relaxation time,  $\tau_{MW} = \epsilon_l/\sigma$ , where  $\sigma$  is the liquid conductivity, of the conducting liquid such that the anion distribution never equilibrates within the interfacial double layer during the anodic half cycle. Hence, unlike the dielectric interfacial polarization mechanism for dc Taylor cones, which is induced by an external field, the ac cone is sustained by an entrained net free (space) charge and hence is independent of the external field. We confirm the above mechanism in this report with a theoretical confirmation of the observed universal cone angle, a charge deflection experiment and a novel ac electro-spray mass spectrometric analysis.

Our experimental setup resembled that of a conventional dc spray experiments. For generation of an ac electro spray, the parametric window of 80–180 kHz in frequency space and a voltage range of 4–6 kV (peak to peak) were used. The entire phenomenon was imaged by an inverted micro-

scope (Olympus IX-71) and recorded using a high-speed camera (Olympus I speed). When the drops generated from a butanol ac cone were passed between parallel electrodes across which a dc field at 4 kV is applied, we observed a continuous deflection of the drops towards the anode despite the periodic reversal in polarity of the applied ac field, as shown in Fig. 1(b). The same phenomenon was observed if the polarity of the dc electric field on the parallel plates was reversed, thus suggesting that the drops carry a negative charge. This was not true when drops generated by mechanical atomization were passed between the dc field, proving that that deflection of the ac spray drops is not due to charges being induced by the dc field. We also verified that the drop deflection is due solely to Coulombic attraction and not dielectrophoretic motion by using disparate electrode sizes in order to create a nonuniform dc electric field.

To identify the anionic species generated by the ac electro spray, we injected the emitted drops from the spray into a mass spectrometer. When the mass spectrometer was operated in the negative mode to allow for identification of

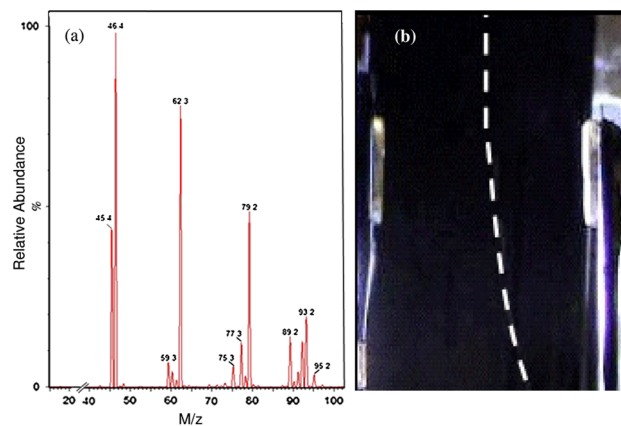


FIG. 1 (color online). (a) Negative-mode ac electro spray mass spectrum of ethanol solution. (b) Migration of microdrop issued from ac electro spray towards the positively charged anode of a parallel-plate capacitor across which a dc voltage was applied.

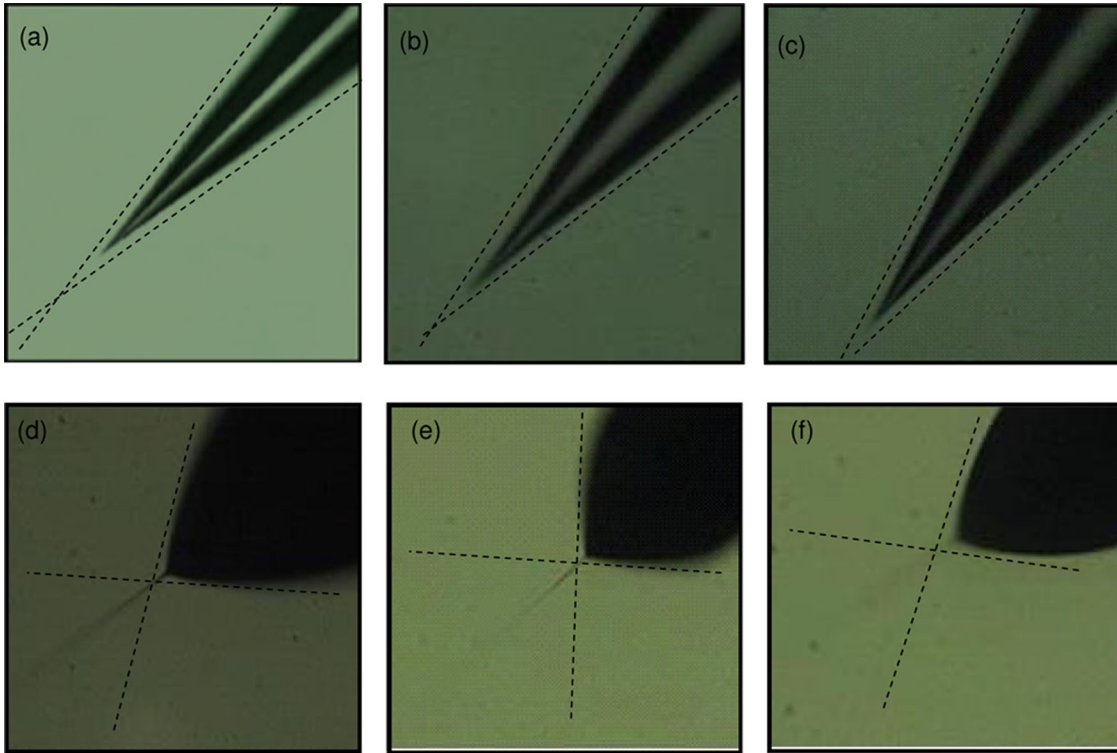


FIG. 2 (color online). Frames (a) to (c) are ac conical menisci for ethanol ( $\beta = 24.5$ ), acetonitrile ( $\beta = 37.5$ ), and isopropanol ( $\beta = 18.3$ ). The half cone angle remains independent of the dielectric constant of the liquid. Frames (d) to (f) represent their dc counterparts, respectively.

anions, a clear ethoxide ( $M/z = 45.4$ ) peak was evident next to the ethanol anion peak in the mass spectrum [Fig. 1(a)]. The other peaks that appear in the negative-mode mass spectrum are shown to be strongly correlated to the ethanol molecule (or ethoxide ion), via tandem mass spectrometry (MS/MS) and hence eliminate the possibility of any sample contamination [9]. The positive-mode spectrum of ac electro spray showed only background noise without any discernable cation, in contrast to distinct peaks in positive-mode mass spectra of ethanol using dc electro spray ionization [9]. The dissociation time scale of ethanol at the kV range is known to be about 100 ns [10], which is less than the half cycle of the applied field at about 50 ms. The mobilities of the proton and the ethoxide ion differ by an order of magnitude [11], which allows the entrainment of ethoxide ions at the tip.

Ac cone angles measured for three different organic liquids, namely, ethanol, isopropanol, and acetonitrile with permittivities that vary by a factor of 2, show almost no change in the half cone angle of  $11^\circ$  as shown in the first row of Fig. 2. We were unable to produce a dc cone for the lower permittivity liquids of isopropanol and acetonitrile, until the addition of NaCl salt solution to increase their conductivity to  $40 \mu\text{S}/\text{cm}$  from  $7 \mu\text{S}/\text{cm}$  [4]. At the range of permittivities shown in Fig. 2, the dc cone angle of a pure dielectric liquid would have dropped precipitously from Taylor's universal value of  $49.3^\circ$  and the dc cones

may even disappear for isopropanol at  $\epsilon_l/\epsilon_g = 18.3$ , as seen in the curve summarizing the results from [4,5] in Fig. 3(a). In contrast, the ac cones do not change their angles considerably from the universal value of  $11^\circ$  for both "leaky" dielectric and conducting liquids.

The experiments suggest that ac cones entrain anions and contain a net negative charge. We adopt a new theory that neglects the external field completely and examines

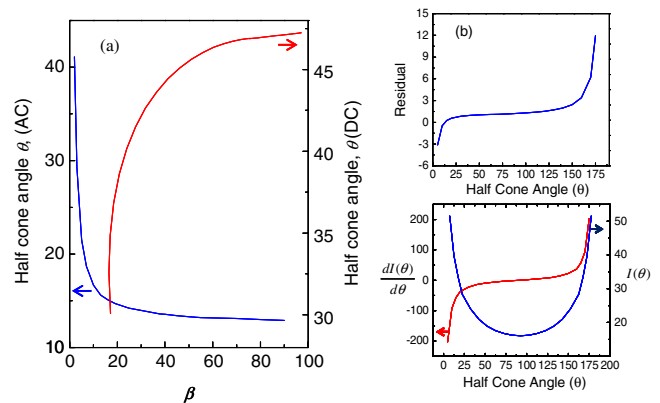


FIG. 3 (color online). (a) Comparison of theoretical values of half cone angle for dielectric ac and dc cones, respectively, as a function of permittivity ratio  $\beta$ . (b) Residual of (4) as a function of half cone angle; the universal functions  $I(\theta)$  and  $\frac{dI(\theta)}{d\theta}$ .

how Coulombic repulsive force within the unknown space charge distribution can compensate the singular azimuthal capillary pressure. We assume that the space charge has relaxed to the interface and represent it by an axisymmetric surface charge distribution  $\sigma_s$ . The normal pressure generated by electrostatic repulsion of the surface charges, which is proportional to  $\sigma_s^2$ , should have the same radial scaling  $\rho^{-1}$  as the normal capillary pressure. As such the charge density must have the following functional dependence,  $\sigma_s = \frac{F(\theta)}{\rho^{1/2}}$ , where  $F(\theta)$  is a specific function which will be determined explicitly via macroscopic tangential force balance on the cone. With this charge density distribution,

$$I(\theta) = \int_0^1 \int_0^{\rho_2} \int_0^{2\pi} \int_0^{2\pi} \frac{\sqrt{\rho_1 \rho_2}}{\sqrt{\rho_1^2 + \rho_2^2 - 2\rho_1 \rho_2 [\sin^2 \theta \cos(\phi_1 - \phi_2) + \cos^2 \theta]}} d\phi_1 d\phi_2 d\rho_1 d\rho_2 \quad (1)$$

or its simplified version after integrating over the azimuthal angles,

$$I(\theta) = 8\pi \int_0^1 \int_0^{\rho_2} \frac{\sqrt{\rho_1 \rho_2} E\left(\frac{-4\rho_1 \rho_2 \sin^2 \theta}{(\rho_1 - \rho_2)^2}\right)}{|\rho_1 - \rho_2|} d\rho_1 d\rho_2 \quad (2)$$

where  $E(k) = \int_0^{\pi/2} \frac{dx}{\sqrt{1 - k^2 \sin^2 x}}$  is a complete elliptic integral of the first kind. The above singular integral was estimated numerically by computing the first integral up to a distance  $\delta$  of  $|\rho_1 - \rho_2| = 0$  and evaluating the singular integrand up to the same value of  $|\rho_1 - \rho_2|$ . This yields a distinguished limit for the double integral as  $\delta$  approaches zero and the converged  $I(\theta)$  is shown in Fig. 3(b). This self-energy can be related to that of a point charge  $Q$  with the same net charge as the cone,  $E(\rho, \theta) = \frac{9Q^2}{64\pi^3 \epsilon_1} \frac{I(\theta)}{\rho}$ .

The total energy that includes both the electrostatic energy and the surface energy is then

$$E_t(\rho, \theta) = \frac{9Q^2}{64\pi^3 \epsilon_1} \frac{I(\theta)}{\rho} + \pi T \rho^2 \sin \theta \quad (3)$$

where  $T$  is the interfacial tension.

Force equilibrium occurs at the minimum of the total energy and it corresponds to normal and tangential force balance. The equilibrium between the tangential component of electrostatic repulsive force, given by  $F_\rho = -\frac{\partial E(\rho, \theta)}{\partial \rho}$ , and the surface tension force, given by  $2\pi\rho T \sin \theta$ , where  $T$  is the surface tension, for the cone yields the magnitude of charge  $Q$  given by  $Q = \left[\frac{128\pi^4 \epsilon_1 T \rho^3 \sin \theta}{9I(\theta)}\right]^{1/2}$  which when related to the net charge determined from the surface charge distribution, specifies the latter's angular distribution  $F(\theta) = \left[\frac{8\pi^2 \epsilon_1 T}{I(\theta) \sin \theta}\right]^{1/2}$ . We note that this tangential force balance has no counterpart in dc cone theory.

The normal component of the electrostatic repulsive force is evaluated using  $F_\theta = -\frac{1}{\rho} \frac{\partial E(\rho, \theta)}{\partial \theta}$  together with

the total charge residing on a cone with half angle  $\theta$  and radial length of  $\rho$  is then  $Q = \int \sigma_s dA = \frac{4}{3} \pi \rho^{3/2} F(\theta) \sin \theta$ .

We evaluate the electrostatic self-energy of the cone by examining the Coulombic repulsion energy between a point charge at radial position  $\rho_1$  and azimuthal angular coordinate  $\phi_1$  and another charge at  $\rho_2$  and  $\phi_2$  further away from the tip. The total self-energy of the cone due to charge repulsion of the entire charge distribution is then given by a double area integral representing the Coulombic interaction between all charge pairs. It can be written as  $E(\rho, \theta) = \frac{\rho^2 [F(\theta)]^2 \sin^2 \theta}{4\pi \epsilon_1} I(\theta)$ , where  $I(\theta)$  is an elliptic integral that accounts for the conical geometry,

the net charge  $Q$ . The resulting normal pressure due to electrostatic repulsion of the entrained anions is  $P = -\frac{T}{\rho} \left(\frac{1}{I(\theta)} \frac{dI(\theta)}{d\theta}\right)$ .

Another secondary component of the normal stress balance is the Maxwell stress due to dielectric polarization by the field of the free charge. As such charge will relax towards the interface for a conducting liquid, we will assume the negative space charge to be present on the liquid side at a Debye length  $\lambda$  from the interface. This negative space charge within the double layer generates an inward field across the interface and induces negative interfacial dielectric polarization because the liquid permittivity is higher than the gas. This dielectric polarization hence renders the cone even more negative and produces an extra Maxwell stress. This pressure can be evaluated by considering the force between an imaginary point charge  $Q'$ , placed on the liquid side at a distance  $d$  from a flat interface that separates two dielectric media with permittivities  $\epsilon_l$  and  $\epsilon_g$ , and the induced charge on the interface by the field of this point charge. This force, in the limit  $d \gg \lambda$ , is given by  $F = \frac{Q'^2}{16\pi \epsilon_l d^2} \left(\frac{\epsilon_l - \epsilon_g}{\epsilon_l + \epsilon_g}\right)$  [12,13]. Clearly, with  $\epsilon_l > \epsilon_g$ , the force is repulsive in nature. This force is equivalent to that of a charged sphere with a charge  $Q'$  of radius  $d$  that is tangent to the interface and has an effective charge density  $\sigma_s = \frac{Q'}{4\pi d^2}$ . Since the Maxwell pressure is just the force per unit area, the force  $F$  (due to polarization) is then converted into an isotropic normal interfacial stress independent of  $d$ ,  $P_M = \frac{\sigma_s^2}{4\epsilon_l} \left(\frac{\beta - 1}{\beta + 1}\right)$ , where  $\beta = \frac{\epsilon_l}{\epsilon_g}$  is the ratio of the permittivities of inner and external phase, respectively. Since  $Q$  and  $Q'$ , which are different, nevertheless correspond to the same surface charge density, the Maxwell pressure by the space charge  $Q$  in the double layer  $\lambda$  also produces the same Maxwell pressure as that of  $Q'$  on the imaginary sphere. Substituting for the expression

of  $\sigma_s$  and  $F(\theta)$ , the Maxwell pressure due to dielectric polarization is then given by  $P_M = \frac{T}{\rho} \left( \frac{2\pi^2}{I(\theta) \sin\theta} \right) \left( \frac{\beta-1}{\beta+1} \right)$ . It should also be noted that because of the infinitesimal distance  $\lambda$  between the free charge and the induced charges; this stress is normal to the interface and does not contribute to the electrostatic force in the radial direction.

The normal electrostatic repulsion pressure  $P$  and the Maxwell pressure  $P_M$  hence balance capillary pressure to yield

$$-\frac{T}{\rho} \left( \frac{1}{I(\theta)} \frac{dI(\theta)}{d\theta} \right) + \frac{T}{\rho} \left( \frac{2\pi^2}{I(\theta) \sin\theta} \right) \left( \frac{\beta-1}{\beta+1} \right) = \frac{T}{\rho} \cot\theta. \quad (4)$$

Both the radial length scale  $\rho$  and the surface tension  $T$  cancel from each term, and we are left with a governing equation for the cone half-angle  $\theta$  that depends only on the permittivity ratio  $\beta$ .

The computed cone angle as a function of the permittivity ratio from (4) is shown in Fig. 3(a). There is only one zero for each permittivity ratio in the interval  $[0, \pi]$ , as shown in Fig. 3(b) for  $\beta^{-1} = 0$ . The high-permittivity limit rapidly approaches the universal half-angle of  $12.6^\circ$  in good agreement with the measured value of  $11^\circ$ . This is in direct contrast to the opposite trend of the dc dielectric cone, also shown in Fig. 3, which actually ceases to exist at  $30^\circ$  when  $\beta = 17.59$ . Such opposite dependence on the permittivity ratio results because the pertinent field for the ac cone is from the entrained charges within whereas that for the dc cone is from an external applied field. Unique also to the ac cone is the presence of a tangential force due to Coulombic repulsion of the charges that serves to elongate the cylindrical stem of the cone continuously to form large aspect-ratio structures [7,8]. While a net tangential force exists and stretches the cylindrical stem, a balance between tangential capillary and electric forces exists at the tip to produce a steady universal half-angle that is sustained throughout the growth. Charged droplets containing large anions generated and entrained at the tip are ejected continuously from this stable ac cone.

Mass spectrometry for large negative molecules like DNA is known to be difficult. The unique negative-mode spectrum of Fig. 1, containing distinct peaks for ethoxide and even larger anions, is distinct from those from dc spray and other ionization techniques. ac spray may hence allow a new form of anion mass spectrometry.

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