Surface tension effects on submerged electrosprays

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Electrosprays are a powerful technique to generate charged micro/nanodroplets. In the last century, the technique has been extensively studied, developed, and recognized with a shared Nobel price in Chemistry in 2002 for its wide spread application in mass spectrometry. However, nowadays techniques based on microfluidic devices are competing to be the next generation in atomization techniques. Therefore, an interesting development would be to integrate the electrospray technique into a microfluidic liquid-liquid device. Several works in the literature have attempted to build a microfluidic electrospray with disputable results. The main problem for its integration is the lack of knowledge of the working parameters of the liquid-liquid electrospray. The “submerged electrosprays” share similar properties as their counterparts in air. However, in the microfluidic generation of micro/nanodroplets, the liquid-liquid interfaces are normally stabilized with surface active agents, which might have critical effects on the electrospray behavior. In this work, we review the main properties of the submerged electrosprays in liquid baths with no surfactant, and we methodically study the behavior of the system for increasing surfactant concentrations. The different regimes found are then analyzed and compared with both classical and more recent experimental, theoretical and numerical studies. A very rich phenomenology is found when the surface tension is allowed to vary in the system. More concretely, the lower states of electrification achieved with the reduced surface tension regimes might be of interest in biological or biomedical applications in which excessive electrification can be hazardous for the encapsulated entities.

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I. INTRODUCTION

The generation of emulsions with phases of controllable size and structure motivates hundreds of publications in the literature and finds applications in numerous industries: optics,¹ cosmetics,² and biomedicine.³ MEMS (micro-electromechanical systems) and microfluidic technology⁴ permit high control on droplet size and easy post-processing on the produced particles. Nonetheless, most of the existing techniques based on these microfluidic technologies for particle production have two serious constraints: First, the low production rate yielded by a single microfluidic device. Second, the limitation in particle diameter, since in most of these techniques, the minimum drop diameter achievable is on the same scale of the smallest element in the system. For example, the droplet size scales with the channel diameter in the T-junction systems, with the orifice size in the microfluidic flow focusing, or with the channel height in one of the latest methods developed.⁶² The construction of such fine devices is a great engineering achievement, but makes the methods very tedious and expensive. An alternative is to employ techniques on which the final droplet size does not depend on the channel geometry. Using this approach, Anna and Mayer⁵ employed surfactants at critical concentrations on a microfluidic flow-focusing device to find regimes similar to the so-called *tip-streaming*. On a

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different approach, Suryo and Basaran⁶ predicted numerically a regime with the same qualities as *tip-streaming* in surfactant-free co-flowing devices under special conditions; Marín *et al.*⁷ recently confirmed it experimentally and demonstrated that the regime is able to generate particles down to the micron size.

Among those techniques able to atomize liquid solutions into submicrometric scales, the electrospray is probably one of the most popular due to its widespread use in mass spectrometry, an application which was honored in 2002 with a shared Noble Prize of Chemistry to Professor John Fenn. The progress in the development of electrospray ionization mass spectrometry in the last two decades has increased the levels of sensitivity and throughput exponentially. Nonetheless, there are several other interesting potential applications for the electrospray in very different fields as controlled drug delivery,^{8–10} colloidal micro-thrusters,¹¹ thin-film deposition,¹² cooling of electronic systems,¹³ enhancement of vacuum diffusion pumps,¹⁴ etc.

In a typical electrospray configuration, a conductive liquid is pumped at certain flow rate through a tube, forming a meniscus at its end. The liquid is then connected to a high voltage power supply, and a counter electrode is placed at some distance from the exit of the tube. Due to the electrical field produced, the free charge in the conductive liquid meniscus will tend to relax at the liquid surface, generating a net normal electric stress that opposes surface tension. As Taylor explained in his pioneering article on electrified menisci,¹⁵ as the voltage is increased an interesting equilibrium is then reached between the surface tension and the normal electrical stress, which obliges the meniscus to adopt a conical shape. This equilibrium would be stationary only if the charges were frozen at the interface, which would ideally happen for liquids with infinite conductivity. In contrast, liquids with finite conductivity manifest electrical shear stresses that lead to the formation of a liquid jet close to the cone apex, which breaks eventually downstream into drops due to capillary instabilities, giving rise to an aerosol of charged droplets. The jet or droplet diameter can vary substantially depending mainly on the liquid conductivity, ranging from hundreds of micrometers for the least conducting liquids to a few nanometers for the most conducting ones. Finer control on the jet diameters can be achieved by manipulating the injected flow rate¹⁶ or the voltage^{17,18} depending on the regime in which the electrospray is manipulated.

Additionally, the technique permits great flexibility in the applications, e.g., it also permits encapsulation of substances by the combination of two liquids into the so-called “coaxial-jet electrospray.”¹⁹ The technique has proved to be extremely efficient for encapsulating substances not only as spherical micro-capsules but also in the shape of micro/nano-fibers.^{20–22} Most of the applications would benefit enormously if the recollection of the outcome (mostly the spray droplets) were improved. An interesting approach would be to implement the electrospray into a microfluidic device, which would improve the control and manipulation of the generated droplets. Barrero *et al.*²³ made the first step towards such objective demonstrating that electrosprays operated in liquid dielectric baths (from now on “submerged electrosprays”) have analogue properties as their counterparts in air. Since then, some have attempted to implement the technique in microfluidic devices,^{24,25} with positive but only exploratory results so far. Unfortunately, the main issue for the implementation of electrospray systems in microfluidics is related with the control of the generated charged hydrosol. The charged micro/nanodroplets tend to expand and repeal each other within the whole volume of the microdevice, and due to the confinement of the system, they end up colliding and accumulating at the micro device walls. This produces disturbances in the electrical field surrounding the Taylor cone, which has crucial consequences to its stability. Gundabala *et al.*^{17,26} solved such situation by implementing the electrospray in a cylindrical co-flow system consisting of concentric capillaries.

Recently, it has been shown that electrosprays are actually able to perform living cell encapsulation with good viability.²⁷ Other competing mechanical methods for encapsulation require high shear stresses and high pressure that results detrimental for the cell. The electrical shear stress generated at the electrospray surface can be indeed as harmful as the mechanical stress. Nevertheless, Jayasinghe and co-workers found out that they could greatly increase the cell viability by either coating the electrified meniscus as in the coaxial-jet electrosprays or by submerging them into an immiscible insulating liquid.²⁸ This last approach has recently yield cell viability of more than 90% when combined with UV photopolymerization for cell

encapsulation.²⁹ Regardless of the good perspective, most the authors report a lack of stability in the submerged electrospray when compared with the high stability and reproducibility of their counterparts in air. Quite often the solutions employed require stabilizing agents as surfactants. Although surfactants are widespread in daily life and in laboratories, their use can have serious impact on biochemical assays³⁰ as well as in systems as those reported here. The electrified meniscus in an electrospray maintains a delicate equilibrium of normal and shear stresses at its interface, and, therefore, the presence of surfactants can be extremely harmful for its stability. Interfacial effects on electrosprays have been only marginally treated in the literature, and there is, therefore, a lack of understanding on their effects.

The aim of the present work is to study in detail the effect of surfactants and give some rule of thumb when choosing the experimental parameters for a submerged electrospray to work according to the needs of the user. To achieve these objectives, we performed electrical current and droplet size measurements for a viscous conducting liquid (which is normally the case for the dispersed liquid in many biological applications), at different electrical conductivities, surfactant concentrations, and flow rates in a non-confined device. Such measurements will yield information about the regimes in which the electrospray is being run, and, therefore, about its mass and charge transport mechanisms. With such information, we will be able to make a proper comparison with the standard electroatomization in air and to draw conclusions on which regimes would be appropriate for confined experiments in microfluidics or for the so-called “bio-electrosprays.”³¹

The article is organized as follows: Sec. II reviews the classical scaling laws of electrospraying in air. In Sec. III, we give details of the experimental setup, liquids employed, and measurement techniques. Section IV reviews results submerged electrosprays in clean baths (without surfactants). We continue with baths containing surfactants in Sec. V, which we separate in two extreme cases: high (Subsection VA) and low conductivity dispersed liquids (Subsection VB). A brief discussion is made on intermediate cases in Sec. VC. The article finishes with summary and final conclusions in Sec. VI.

II. SCALING LAWS IN ELECTROSPRAYS

The mass and charge transport mechanisms in the electrospray follow experimentally scaling laws for the electrical current and the droplet size versus the flow rate. In the last 20 years, many have explored different electrospray regimes, with different scalings and properties.³² However, it is generally accepted that the regime with the most steady and robust performance, and which yields the most monodisperse aerosols, is the so-called *cone-jet* regime.^{10,33} Recent numerical simulations have confirmed some of these scaling laws using different approaches.^{34–37} In the current study we will not discuss details of the scaling laws found, but will only use the most widely accepted.

The cone-jet regime³³ is characterized by its stability, and specially by the independence of the emitted current from the applied electrical voltage.³⁸ Additionally, we can find scaling laws to relate the input parameters of the system, basically the flow rate Q and the applied voltage drop V , with the output parameters, i.e., the electrical current transported by the liquid I and the droplets size d . Along the paper, we will use the scaling laws developed by Loscertales and de la Mora¹⁶ and by Gañan *et al.*³⁹ They are mostly applicable when high conductivity liquids with intermediate viscosities are operated at small flow rates in a gaseous medium. In the following, we show the scaling laws for the electrical current and for the droplet size, expressed in dimensionless form

$$\frac{I}{I_o} = a \left(\frac{Q}{Q_o} \right)^{1/2}, \quad (1)$$

$$\frac{d}{d_o} = b \left(\frac{Q}{Q_o} \right)^{1/3}, \quad (2)$$

where we have defined the characteristic values of flow rate Q_o , electrical current I_o , and drop-let diameter d_o using the density ρ , conductivity K , and surface tension γ of the conducting liquid as follows:

$$Q_o = \frac{\epsilon_o \gamma}{\rho K}, \quad (3)$$

$$I_o = \gamma \sqrt{\frac{\epsilon_o}{\rho}}, \quad (4)$$

$$d_o = \left(\frac{\gamma \epsilon_o^2}{\rho K^2} \right)^{1/3}. \quad (5)$$

These scaling laws will change for different parametric scenarios. For example, when viscosity becomes important, the drop diameter might be proportional to the conducting liquid viscosity, as in the scaling laws suggested by Collins *et al.* and supported by simulations.⁴⁰ Analogously, when the flow rates are high enough, or the external liquid viscosity increases, or surface tension decreases, the assumptions made in the scaling laws (1) and (2) fail and different ones should be applied.³⁶

III. EXPERIMENTAL SETUP AND METHODS

The experiments were carried out in a small cell (see Fig. 1) made of Plexiglas with glass windows to permit clear visualization. The cell was open in the upper part to insert the injection needle, whose diameter ranged from 0.8/0.6 mm (O.D./I.D.), for the less conductive liquids, down to 340/20 μm with silica capillaries (Polymicro) for the most conductive ones. The electrical field is generated by applying a high voltage drop from the injection needle (working as upper electrode) to an electrode placed in the bottom of the cell. Different types of bottom electrodes were chosen depending on the characteristics of the generated hydrosol. The liquid was forced through the capillaries using either a syringe pump (Harvard Instruments) or compressed air, depending on the viscosity and conductivity of the sample. Higher conductivity samples require higher control on their flow rates, which can be as small as some nanoliters per hour.

A laser diffraction system (Helos-Sympatec GmbH) was employed to perform droplet diameter measurements. In this method, a laser beam passes through the hydrosol, the diffraction pattern obtained in this process is collected on a highly sensible multi-element detector. With this pattern as an input, the system deconvolutes the particle size distribution using the Fraunhofer or the Mie solutions for light scattering in spherical particles.⁴¹ The measurements

FIG. 1. Sketch of the experimental setup employed.

TABLE I. Liquid properties.

	ρ (g/ml)	μ (mPa·s)	β	γ (mN/m)	I.T.(mN/m)
Glycerol	1.261	1100	42.5	64	
Hexane	0.655	0.294	1.9	30	28.3

have been contrasted with direct optical measurements of the resulting emulsion with a powerful microscope (Axiovert 40 Inverted Fluorescence Microscope, Zeiss).

In Table I, we show the main physical properties of the liquids employed. We chose glycerine as conductive liquid to be dispersed and hexane, as host dielectric liquid of the bath. All the experiments were also repeated with heptane, with no appreciable differences on the results. Different samples of glycerine with different conductivities were employed ranging from 10^{-6} S/m to almost 10^{-2} S/m. These conductivities were achieved by adding different types of salt to the glycerine samples (basically NaCl or HCl). The inner (glycerine) and outer (hexane and heptane) liquids were mainly chosen for their viscosities, since we will base our studies to cases in which the viscosity ratio $\lambda = \mu_i/\mu_o \gg 1$ (where μ_i and μ_o are, respectively, the viscosities of the inner and outer liquid), which is also the case of atomization in air. The inversion of the viscosity ratio (those cases in which $\lambda \leq 1$) has crucial effects on the stability of the electrospray.⁴²

For the electrical current measurements, the injecting needle was connected indirectly to the positive pole of a high voltage power supply (Bertran PS-205A-10R), and a floating ammeter was employed to measure the current supplied through the Taylor cone: for the highest currents (close to 1 μ A for the G2 sample), a simple voltmeter with resolution of 1 nA was employed. While for the lowest currents (of the order of 1 nA for sample G6), a Keithley pico/ammeter was used instead.

Controlling the flow rate accurately is a mayor issue on these experiments. It is well known that the electrostatic pressure can modify the real flow rate circulating through the meniscus,⁴³ and for this reason, we employed high hydrodynamic resistance lines of small diameters. In order to force the liquid through the lines, compressed air was used in most of the cases except for the lowest conducting one, for which a syringe pump (Harvard Instruments) was then employed, since it requires the highest flow rates in these series of experiments (of order of several milliliters per hour).

Special care was taken in the measurements of the liquid-liquid interfacial tension with surfactants. In our case, the surfactant has been added only to the external dielectric liquid (continuous phase), in order to preserve the properties of the inner conductive liquid (dispersed phase). For this purpose, Span 80 (Sorbitan monooleate) was employed for all experiments. In order to find the appropriate surfactant concentration range, surface tension was measured for different concentrations using two different techniques: Wilhemy plate (Kruss) and pendant drop measurements (KSV Instruments), the results are shown in Figure 2. As can be seen in the plot, surface tension decreases slowly until it approaches a critical concentration when the graph becomes more stepped and reaches its minimum value. This value is reached approximately at $C_{crit} = 1.1$ mol/m³, which we will call critical concentration, i.e., the concentration value at which the surface tension reaches its minimum. Since we are not interested in studying colloidal properties of the surfactant in these processes, we will avoid using the term *critical micellar concentration*, but just critical concentration instead defined as defined above. From now on, all surfactant concentrations $\tilde{C}$ (mol/m³) will be made dimensionless with the critical concentration, so that $C = \tilde{C}/C_{crit}$.

IV. SUBMERGED ELECTROSPRAYS IN SURFACTANT-FREE LIQUID BATHS

Barrero *et al.*²³ confirmed that submerged electrosprays in clean (i.e., surfactant-free), insulating, and inviscid liquid baths behave basically as their counterparts in air. Here, we perform extended measurements that will serve us as a reference to make proper comparisons with

FIG. 2. Measured interfacial tension for glycerine/hexane against surfactant concentration (Span 80).

electrosprays in liquid baths containing surfactants. We will confirm by electrical current measurements that the electrospray is certainly being operated in the cone-jet mode. The cone-jet mode is defined as a regime in which the electrical current emitted by the electrospray is independent of the applied voltage,³³ and follows the classical scaling law $I \sim \sqrt{\gamma K Q}$ (Eq. (1)).¹⁶ The liquids employed have been chosen in order to resemble the conditions of electroatomization in air, i.e., a viscous liquid being dispersed in an inviscid fluid ($\lambda = \mu_i/\mu_o \gg 1$). In this case, we will disperse different samples of glycerol ($\mu_i \approx 1 \text{ Pa}\cdot\text{s}$) in hexane ($\mu_o \approx 10^{-6} \text{ Pa}\cdot\text{s}$). Complex liquids of biological interest usually have high viscosities, similarly as the liquids chosen here.

As can be observed in Figure 3, the aspect of a submerged electrospray is completely analogous to those in air. To outline some of the advantages of the submerged electrosprays, we compare the droplet diameters obtained with a submerged electrospray with the same liquid electrosprayed in air. As commented above, when dispersing a conducting liquid into a dielectric in the cone-jet regime, the characteristic flow rate decreases according mainly to the decrease in surface tension. Consequently, the droplet diameter decreases notably as can be clearly seen in Figure 4. Operating the electrospray in a dielectric liquid permits us to decrease the flow rate in almost one order of magnitude, with the corresponding decrease in droplet size.

FIG. 3. Typical aspect of a submerged electrospray in an inviscid dielectric liquid: Metallic capillary, Taylor cone, micro-liquid jet, and hydrosol with its characteristic plumed-shape. The outer needle diameter is 0.4 mm.

FIG. 4. Comparison of droplet size distributions: glycerol droplets in air vs glycerol droplets in hexane. The glycerol conductivity is $5 \cdot 10^{-5}$ S/m.

Additionally, the electrical current measurements plotted in Figure 5 show that most of the samples follow reasonably well a classical square root law of the type in Eq. (1). This indicates that the transition from a cone to a jet results from the so-called charge relaxation effects,¹⁶ i.e., surface charges cannot maintain the static cone anymore and they are convected by the liquid flow towards the cone apex, breaking the electrostatic equilibrium of the cone. The measurements fit an equation of the type (1) with $a = 1.3$ and less than 10% of error.

The minimum flow rate was also explored for most of the samples. According to several results in the literature,^{16,32,34} the dimensionless minimum flow rate $Q_{\min}/Q_0$ should only depend on the relative dielectric constant of the liquids. Since we always used the same pair of liquids in the series, the minimum flow rate should be constant for all the samples. However,

FIG. 5. Electrical current against flow rate for glycerol samples in hexane. Insert: Minimum Flow rates for glycerol in hexane. Full circles correspond to the minimum flow rates of submerged electrospays, the square corresponds to a measurement of the minimum flow rate of an electrospay in air for comparison.

TABLE II. Conducting liquid properties.

Sample	G6	G5	G4(1)	G4(2)	G3(1)	G3(2)	G2
$K(S/m)$	$1.84 \cdot 10^{-6}$	$5 \cdot 10^{-5}$	$3.30 \cdot 10^{-4}$	$4.29 \cdot 10^{-4}$	$2.00 \cdot 10^{-3}$	$4.90 \cdot 10^{-3}$	$9.70 \cdot 10^{-3}$

the results differs from that prediction, and as we can see in the insert of Figure 5, the minimum flow rate decreases with the conductivity of the liquid, and with values well below those predicted. This result is also found by Ku *et al.*⁴⁴ for glycerol samples in vacuum, which make us think that it is a characteristic behavior of glycerol, and the nature of the outer medium plays no role. However, their values were in general much higher than ours. We encounter here one of the main advantages of the use of electrosprays in liquid mediums: the value of the minimum flow rate is at least one order of magnitude smaller when the liquid is dispersed in liquid dielectric mediums like hexane instead of air. As an example, the samples with conductivity of order 10^{-5} S/m have a minimum flow rate in air of around $400 \mu\text{l/h}$, while for the same liquid in hexane, we can reduce the flow rate to $20 \mu\text{l/h}$. The reason can be found in both, the reduction of surface tension (which decreases Q_o) and the reduction of the dielectric constant ratio (which decreases $Q_{min}/Q_o = f(\beta)$). This means that we can obtain much smaller droplet diameters by simply dispersing the liquid into a dielectric medium instead of in air. Another advantage is the reduction of the needed voltage and current to operate the electrospray: while this particular regime shown in Figure 3 requires in air around 6 kV and around 100 nA, submerged in clean hexane, it requires circa 3 kV and a few nanoamperes.

In order to have precise measurements of the droplet diameters, and since our laser diffraction system only detects particles between 1 and $80 \mu\text{m}$, we employed only glycerol samples with conductivities above 10^{-3} S/m, with diameters ranging from 3 to $45 \mu\text{m}$. In Table II, we show the samples employed, named by their conductivity as G4 (with $K = 10^{-4}$ S/m, and so on), G5 and G6. The droplet distributions of the least conducting samples (as in G5 (1) in Figure 6(a)) are found to be bidisperse for all flow rates, even for the smallest ones. Satellite droplets are responsible for the secondary peaks observed in the plots. The presence of satellite droplets is a well known phenomenon in electrosprays, especially for viscous liquids, and is extensively discussed by Rosell-Llompart and de la Mora.⁴⁵ Although it is natural to have satellite droplets in these regimes, the unsteadiness of the jets enhances it. Certainly, in these samples, the jets manifest the so-called “whipping” instability^{46,47} for all flow rates even for the minimum ones. As Riboux *et al.* recently studied in detail,⁴⁸ the case of the sample G6 is especially impressive: when one operates pure glycerine in air, the jets are perfectly steady and they

FIG. 6. Bidisperse droplet distributions for samples G5 (left) and G4 (right).

break-up only by capillary instabilities. However, when inserted in a dielectric liquid bath as hexane, the jet becomes laterally unstable and bends developing a spiral-like path, reducing its diameter until it breaks by capillary instabilities. Therefore, its distribution of droplets sizes is affected by this disturbing instability. However, in the sample G4, we find a different situation (Fig. 6(b)) and observe a monodisperse regime without satellite droplets, which is maintained until we increase the flow rate above a critical value in which the distribution turns bidisperse. Both regimes show also very characteristic spray plumes when observed in operation with the aid of a microscope and special illuminating conditions. As shown in Figure 7, we can observe in the bimodal regime the smaller droplets located in the outer part of the aerosol while the bigger droplets stay in the inner part. This phenomenon was observed already by Zeleny⁴⁹ in the first controlled electrospray experiments ever made and explained later by Tang and Gomez⁵⁰ among others, the reason for this structure in the aerosol is the higher mobility of the satellite droplets: due to their less inertia they are electrically repelled farther in the aerosol. Rosell and de la Mora⁴⁵ made an extensive study for several different samples and noted that it was in the most viscous and less conducting ones where such dispersion was more often observed.

To analyze the results, we will make use of the dimensionless diameter and flow rate defined in Eqs. (3) and (5), respectively. The results are plotted in Figure 8. As we can observe, the data approximately fit a 1/3 law as the one defined in Eq. (2). These results are in accordance with those found by Barrero *et al.*,²³ although certainly the dispersion of our data also permits a reasonably good fitting with other similar scaling laws: according to the recent work of Higuera,³⁶ a regime in which $I \sim Q^{1/2}$ and $d \sim Q^{3/8}$ would correspond to a cone-jet mode in which the electric shear stress is balanced by the inner liquid viscous drag. On the other hand, a result with $I \sim Q^{1/2}$ but a higher exponent for the drop diameter on the flow rate as $d \sim Q^{1/2}$ could be interpreted as a case in which the viscosity of the outer bath becomes dominant. As shown in Figure 8, at low flow rates, most of the data follow a scaling law with exponents 1/3 or 3/8, while higher flow rates seem to follow the more steep 1/2 law.

FIG. 7. Visualization of the hydrosol plume in sample G4. (a) Below the critical flow rate, monodisperse hydrosol. (b) Above the critical flow rate where the droplet size is bidisperse (enhanced online). [URL: <http://dx.doi.org/10.1063/1.4762854.1>] [URL: <http://dx.doi.org/10.1063/1.4762854.2>]

FIG. 8. Dimensionless representation of droplet size vs injected flow rate. The following scaling laws are plotted: $d/d_o = 4.8(Q/Q_o)^{1/3}$ as that described in Eq. (2), $d/d_o = 4.3(Q/Q_o)^{3/8}$ as proposed by Higuera,³⁶ and $d/d_o = 3.1(Q/Q_o)^{1/2}$, as proposed by Gañán-Calvo.⁵¹

V. SUBMERGED ELECTROSPRAYS IN SURFACTANT SOLUTIONS

In this section, we proceed to disperse our conducting liquid into a liquid bath containing surfactants. In order to make proper comparisons, the same liquids characterized in the previous chapter are employed. The approach taken in the experiments is the following: first, we perform a qualitative exploration varying independently conductivity and surfactant concentration. Different regimes are then identified in the parameter space constituted by the electrical conductivity K and the surfactant concentration C . Then, we proceed to make electric current and diameter measurements in selected regimes and discuss the results. The range of the parameters K and C are the following: The conductivity range is the same used in the surfactant-free case for the glycerine samples (Table I). The surfactant concentration range was chosen in terms of the value of the interfacial water/glycerine-hexane tension, from its maximum value ($C=0$) until its minimum is surpassed beyond the critical concentration ($C=1$). Due to the large amount of data and regimes found, we will illustrate the two main extreme cases with the highest surfactant concentration: highest and lowest electrical conductivity. A number of intermediate cases have been also found for different values of the parameters (K, C), which are basically combinations of the different regimes described. In Sec. VC, we briefly describe how the two limiting cases connect to each other in the K - C parametric space. More detailed information about these regimes can be found in the doctoral thesis of Marín.⁴²

A. High conductivity cases

To illustrate the extreme case of high conductivity, we choose a glycerin sample of $K = 4 \cdot 10^{-3}$ S/m. This conductivity is high enough to illustrate our purposes and is close to the maximum conductivity allowed to make precise measurements and analyze the jet and droplet diameters. In a bath clean of surfactants, this sample gives rise to narrow jets and particles below $1 \mu\text{m}$ in the low flow rate regime. Adding surfactant in small quantities does not seem in principle to modify the electrospray properties, only a timid decrease in the working voltages. However, when we increase the surfactant concentration above its critical value, what we observe is something completely different. First of all, the voltages needed to obtain the Taylor cone reduce by a factor of at least 5 (with an electrode distance of 5 cm, we have 5000 V in a clean bath, while 1000 V in this case). Lower voltage regimes might be of high

interest for applications in which the state of electrification can be detrimental, as is the case for biological solutions. We also note that the flow rate range is much wider. Finally, regarding the meniscus and spray shape, we do not observe the classical conical spray anymore, but only a blurred open spray with an almost cylindrical shape (Fig. 9).

The reason of this peculiar aerosol shape was revealed using a high speed camera (Redlake Motion Pro 10 000). A sequence of images extracted from a recording is shown in Figure 9. As we can see in the images, the jet is much thicker that it was in the clean bath, it soon becomes laterally unstable and breaks immediately in filaments. This contrasts strongly with the classical whipping instabilities, in which the jet performs several “loops” before breaking into droplets.⁴⁸

Due to experimental difficulties, it was no possible to use the diffraction system to measure the droplets diameters surfactant solution baths. The problem found was related with the enhanced stability of the generated droplets within the cell, which made difficult to maintain the bath clean of non-desirable droplets in the region of measurement. A different setup with a continuous circulating external liquid would solve the problem and would make possible to make better measurements. However, as we will discuss later, it is still not clear how the flow in the external liquid would affect the results in this case of extremely low surface tension. Nonetheless, enough information can be obtained from high resolution images, high speed videos, and electrical current measurements.

In Sec. IV, analyzing high conductive glycerine in clean baths, we concluded that the current to flow rate dependence showed a reasonable good agreement with the well known $I \sim Q^{1/2}$ scaling law. In this case, we will employ a single glycerine sample of relatively high conductivity ($K = 6 \cdot 10^{-3} \text{ S/m}$), and let the surfactant concentration ratio vary in two orders of magnitude, below and above the critical concentration. As we mentioned above, there is a critical surfactant concentration in which the regime of atomization changes completely from a regular electrified-

FIG. 9. Visualization of a high K and high C case (a) with regular long exposures (1 ms). (b) with high speed imaging at 2000 fps (enhanced online). [URL: <http://dx.doi.org/10.1063/1.4762854.3>]

capillary breakup to a regime dominated by wider jets and lateral instabilities, yielding highly polydisperse emulsions. In Figure 10, the data are plotted in dimensional form. We first note a very sensitive dependence of the electrical current on the surfactant concentration (i.e., surface tension). It is also very noticeable how the range of stable flow rates for the samples $C < 1$ is dramatically decreased due to the reduced surface tension value, as was argued in Sec. V, specially when this is compared with the dispersion in air. The different dependence on the flow rate of the different samples is also remarkable: almost all $C < 1$ samples seem to follow a similar square root law (with different offsets that can be explained by their different surface tensions), while those with $C > 1$ present a very reduced dependence with the injected flow rate. Also notice how the addition of surfactant reduces the flow rates and consequently the currents. But as the concentration increases, the output current surprisingly increases as well; this differs strongly with the classical models of charge transport developed for regular electrosprays and, therefore, indicates that there must be a different mechanism driving the current in these cases.

The dimensionless plot in Figure 11 shows these aspects in more detail; the characteristics flow rate and the current defined in expressions (3) and (4) has been used. Special care has been taken with the interfacial tension measurements (see Sec. III). First thing to note is that samples with $C < 1$ fit again reasonably well with the well-known square root laws, with some differences for those cases closer to the critical concentration. But most important and surprising is the higher concentration cases, those samples yield electrical currents much higher than those expected for charge relaxation mechanisms.¹⁶ If the current was driven by convection, electrical current would be expected to decrease with surface tension since the characteristic velocities needed to maintain a stable jet must decrease as well. This is observed for the samples with intermediate values of surfactant concentration, but not for those with high surfactant concentration ($C > 1$) in which the current increases as the surface tension decreases. Additionally, they show a much reduced dependency with the injected flow rate; in the best cases, the current increases only a 20% when the flow rate is increased in one order of magnitude. These features might indicate an electrical current transport for high surfactant concentration samples different than the classical convection-driven mechanisms. Unfortunately, the methods employed in previous chapters to obtain droplet diameter distributions were not suitable for the regimes with presence of surfactants. The presence of surfactants increased the stability of the generated droplets, which survived much longer within the liquid bath (they were not absorbed as easily in the water phase at the bottom of the cell) and hindered the laser diffraction measurements. On the other hand, regimes as the one depicted in Figure 9 gave rise to a very disordered breakup with wide droplet

FIG. 10. Electrical current vs flow rate for different surfactant concentration: for surfactants-free samples (white circles), mild surfactant concentrations ($C < 1$) (bluish circles) and high concentrations ($C > 1$) (reddish circles).

FIG. 11. Dimensionless electrical current vs flow rate for different surfactant concentrations: for surfactants-free samples (white circles), mild surfactant concentrations ($C < 1$) (bluish circles), and high concentrations ($C > 1$) (reddish circles).

distributions that could not give much information. For these reasons, high speed video techniques were used instead with enough resolution to make jet diameter measurements for different surfactant concentration and flow rates, fixing the liquid conductivity in $K = 3.1 \cdot 10^{-4} \text{ S/m}$ (higher conductivity would yield jets with diameters that could not be measured accurately, but the conclusions can be extrapolated to higher conductivities).

Considering classical arguments,³⁹ one should expect a decrease in jet diameter as surface tension is decreased as a consequence of the decrease of the characteristic flow rate (see expressions (3) and (5)). On the contrary, on Figure 12, we observe how the diameter increases as surface tension is being decreased (for a given conductivity and fixed flow rate). The increase is timid in the first stages and becomes critical as we reach surfactant concentration values close to saturation.

Regarding the data of $C > 1$, not only they showed a reduced dependance with the flow rate but they also showed a high dependance with the electrical voltage. This effect has not been analyzed thoroughly, but it has several analogies with the regimes found independently by Gundabala *et al.*¹⁷ and by Larriba and de la Mora.¹⁸ In the first case, Gundabala *et al.*¹⁷ integrated a submerged electrospray in a co-flow system, with relatively low surface tension (surfactant-free). They observed regimes in which the current almost does not depend on the flow rate but it depends strongly on the voltage applied. Their conclusion is that, due to the reduced size of the micro-capillary tip, the electrification of the cone-to-jet region was drastically reduced, and the electrospray was driven mainly by conduction. The case of Larriba and de la Mora is very different but the results are analogous. They constructed a coaxial electrospray consisting of an ionic liquid (EMI-BF₄) injecting charged micro/nano-droplets into an insulating liquid meniscus of heptane (also decane). It is indeed a smart and relatively simple way of atomizing insulating liquids by electrohydrodynamic forces in a controlled fashion. The authors study the atomization regimes of EMI-BF₄ by measuring the electric current against the flow rate and the applied voltage in a quiescent bath. They find a very pronounced dependance of the current with the voltage, and a much weaker one with the injected flow rate. Contrary to Gundabala *et al.*,¹⁷ the authors explain such a behavior by the appearance of space-charge effects of the charged cloud of droplets in the quiescent insulating bath, which would screen the electric field felt by the meniscus.

The regimes found by both groups strongly differ with the classical cone-jet electrosprays typically found for conducting, inviscid liquids atomized in air, in which the electrical current

FIG. 12. Jet diameter variation with interfacial tension for sample of conductivity $K = 3 \cdot 10^{-4}$ S/m at flow rate $Q = 20$ μ l/h. Inset: jet diameter is plotted against flow rate, following a scaling law $d \sim Q^{0.53}$ for a sample saturated with surfactant (minimum γ).

depends strongly and almost exclusively on the flow rate due to the convective dominance of the charge transport. It would be tempting to associate some of those regimes with ours, but their conditions do not apply to ours. Regarding the experiments of Gundabala, our smallest meniscus to jet ratio is on the order of 20, which is much higher than their case. On the other hand, we also reject the hypothesis of the space-charge effects in our experiments for two main reasons: First of all, such effects would have been noticed already in clean baths more pronouncedly, but the fact that the current-flow rate dependence showed a clear $I \sim Q^{1/2}$ discards the hypothesis. Second, if space-charge effects are important, then the electrical mobility Z of the droplets must be relatively low (Larriba and de la Mora found values of $Z \sim 10^{-7}$). We can estimate the droplet electric mobility as $Z = 2I d^2 / 9\mu Q$, which yields values of the order of $Z \sim 10^{-5}$ in the samples with $C > 1$ (Figure 9), comparable to the cases in air, probably due to the relatively large drop size and electric current. As a note, we should mention that the space-charge effects must however dominate in those cases in which the external liquid viscosity is not negligible, imposing an important drag to the charged droplet movement and, therefore, limiting their mobility.

A more likely explanation for such a regime can be found in the recent study by Higuera.³⁶ In this theoretical-numerical study of submerged electrosprays, he describes a regime in which most of the electrical shear stress is equilibrated by the external viscous stresses, which have been normally ignored in the past. Such regime would take place when the dimensional parameters $\Pi = \mu_e K^{1/3} / (\rho_i \epsilon_o \gamma^2)^{1/3} \sim O(1)$ or $\Pi R^{1/4} = \lambda (\mu_i^3 K^2 Q / \gamma^3 \epsilon_o^2)^{1/4} \sim O(1)$. In this particular case of high conductivity and $C > 1$, the dimensionless parameters take the experimental values of $\Pi \simeq 0.75 \sim O(1)$ and $R \simeq 7.75$, and, therefore, $\Pi R^{1/4} \simeq 1.22 \sim O(1)$. From which we can interpret that, besides the large viscosity ratio, the electrical shear stress on the jet is mostly invested in balancing the external viscous shear. This is experimentally supported by the large velocities induced in the external liquid bath. Moreover, a critical flow rate $Q_M = \epsilon_o \gamma^2 a / \mu_o^2 K$ is found theoretically in this regime, where a is the meniscus radius, and μ_o the outer liquid viscosity. When $Q > Q_M$, the charge transfer region becomes large compared to the meniscus size; the

surface charge is, therefore, limited, and the jets are no longer charged-stabilized. In addition, the current becomes independent on the flow rate, and the jet size scales with the flow rate as $r_j \sim Q^{1/2}$. Such scenario fits better with our data of lowest surface tension due to the strong dependance of Q_M on the surface tension. A decrease of almost one order of magnitude in surface tension in the case of $C > 1$ yields $Q_M \simeq 0.6 \text{ ml/h}$, which is not so far from the range we operate the electrospray. To give additional support such hypothesis, we measured the jet diameters for several flow rates for the case of lowest γ , revealing an exponent of 0.535, close enough to the predicted. Other symptoms observed here fit with the regime described by Higuera,³⁶ specially those regarding the lack of stability of the jets due to the reduced surface charge and the elongated shape of the meniscus (9). The reason for such critical behavior with the surfactant concentration C above its critical value can be then explained by the fast decrease of the critical flow rate $Q_M = f(\gamma)$ with the interfacial tension γ below the operating flow rates.

We should conclude this section by adding some comments on the stability of those regimes with higher surfactant concentration. Certainly in these cases, the regimes lack the robustness of the classical cone-jet electrosprays (either in air or in clean liquid baths) manifested by oscillations in the electrical current and even in the jet diameter. We will point out two possible reasons for these fluctuations: assuming that the surfactant concentration is not homogeneous along the liquid interface, it is then very likely that its distribution will be also changing in time depending on the amount of surfactant available in the bath. The liquid in the bath recirculates due to the electrically driven movement in the conical interface, so there is no control on the amount of surfactant contained in the liquid surrounding the cone-jet. Also related, a curious phenomenon was observed close to the water phase used as bottom electrode and as a droplet collector. By doing so, the bath is kept clean of charged droplets that might otherwise disturb the electrified meniscus. However, when surfactant is present in the hexane bath, the water-hexane interface was soon covered by surfactant, and the coalescence of the charged droplets into the water phase was hindered. As a consequence, it could be observed how some droplets approached the water-hexane interface, “touched” it, and were immediately repelled back to the bath. It seems to be a similar phenomenon as that found by Ristenpart *et al.*:⁵² a charged droplet migrates towards an oppositely charged interface and, in certain circumstances, instead of being trapped and absorbed, it is repelled from the interface after a short contact. The authors demonstrated that the time required to equilibrate the charge is much shorter than the typical coalescence time; therefore, before the coalescence process is finished, the droplet is already set at the same potential as the interface and a repulsive electrical force is created among them. In our particular case, the coalescence time can be also further delayed by the presence of surfactants. Although interesting, the presence of charged droplets surrounding the electrified meniscus can be extremely disturbing and can be also responsible of electrical current and jet diameter oscillations. It is nonetheless a problem that can be easily solved using a continuous external liquid flow as is the case in Gundabala *et al.*¹⁷ and others.^{25,26}

B. Low conductivity cases

We analyze now an extreme case of low conductivity with surfactant concentration above the critical. We use here the least conducting glycerol sample: G6, pure glycerol. It should be reminded that the pure glycerine in a clean bath of hexane presents long laterally unstable jets with diameters ranging from 10 to 30 μm depending on the flow rate. Adding small quantities of surfactant gives a similar result as in the high conductivity case, lower working voltages, and wider jets diameter. But as we outreach the critical concentration, we find a surprising situation like the one showed in Figure 13.

This regime requires only 20% of the voltage needed to stabilize a submerged electrospray in a clean bath, but instead of having a thin laterally unstable jet, we find a broad widening jet that will end up growing a droplet in its end. This droplet increases its size as the jet elongates until the electrical forces are strong enough to detach it from the jet tip, then the jet retracts and a new droplet starts to grow again. The size of the droplet is still small enough to ignore gravity effects: a bond number defined as $Bo = \rho_i g R_c / \gamma$, where ρ_i is the liquid density, γ its

FIG. 13. Visualization of the “dripping-jet” in the limit of low electrical conductivity and high surfactant concentration (enhanced online). [URL: <http://dx.doi.org/10.1063/1.4762854.4>]

surface tension, and R_c its typical drop size, yields values of $Bo \sim 0.01$. Therefore, the detached droplets are directly driven to the electrode surface. Although the electrical current was extremely low, it was possible to make some spurious measurements of oscillating electrical currents varying with the same frequency as the dripping frequency. A relatively thick jet ($60 - 100 \mu\text{m}$) generates and widens in its tip until a big droplet is created ($200 - 400 \mu\text{m}$). Since new liquid is being injected, the droplet increases its diameter as the jet becomes longer and slender until a certain point in which the droplet reaches such a size that detaches from the jet. The liquid ligament then retracts, a new small droplet is formed on its tip, and the process starts again. The frequency of this cycle, lengths, and diameter of the jet and size of the droplet may vary depending on the controlled parameters: voltage and flow rate. An increase on voltage will make longer jets, and, therefore, (for the same flow rate) smaller droplets, with a slight increase in the yield frequency. A reduction in flow rate will create shorter jets, smaller droplets, and a higher frequency. The electrical current was too low and unstable to be measured accurately, but it clearly presented fluctuations synchronized to the drop generation cycles. The key of this behavior seems to be in the joint effect of reduced surface tension and low conductivity in the liquid. Certainly, the electrical field at surface of the meniscus is so reduced that it fades away not so far from its tip and consequently, the liquid jet flows downstream practically as a free jet, feeling no electrical stress at its surface. Regular Taylor cones in air behave radically differently, in their case, the electrical field close to the tip is so strong that the jet suffers a tremendous electrical stress still far from the cone. The electrical stress is responsible of the progressive decrease in size of electrified driven jets and also explains their resistance against varicose instabilities.^{53,54} In our case, the absence of this electrical stress explains the progressive widening of the jet. Additionally, the reduced electrical field on the jet also explains the absence of lateral instabilities, often related to strong accelerations due to the shear stress. The arguments exposed above however cannot explain the appearance of a droplet on the tip of the jet. On the other hand, a similar phenomenon has been observed and successfully explained in co-flow systems to generate monodisperse emulsions.⁵⁵ In that case, Utada *et al.*⁵⁶ observed how the droplet to jet diameter ratio increased its value greatly when the inner liquid jet was being slowed down by the outer slower liquid, the authors identified this phenomenon as the outcome of an absolute instability due to the decrease in inertia of the jet, which triggers the classical transition to a “dripping” regime in the jet at certain distance from the needle.⁵⁷ A classical example of absolute capillary instabilities can be found in the dripping at the end of a tube, which is characterized by the growth of perturbations in fixed points of the interface. Monodisperse droplets are, therefore, produced due to the proximity of the injection needle, which damps most of the external perturbations. On the other hand, in the case of convective instabilities, the maximum growth rate of the perturbations is found far from the injection

needles, giving rise to polydisperse droplets due to the effect of external perturbations. In our experiment, the electrical field is enough to generate an electrified conical meniscus through which the liquid is being injected at certain flow rate. Within the meniscus, the fluid is being accelerated towards the vertex until inertia overcomes the capillary tension a jet is formed. The jet is then accelerated by the electrical field of the meniscus, however, due to the low value of both electrical field and surface charge, the tangential stress over the surface decreases fast with the distance from the tip. At this point, the only force over the surface of the jet is the viscous drag from the outer liquid, which is not in any way negligible, but we have no control of it, and, therefore, its only effect is to slow the jet down, in a similar way as it does the outer liquid in Utada *et al.*⁵⁸ experiments. The jet then widens up and velocity decreases until inertia cannot maintain a stable jet anymore and finally, a droplet appears at its tip. In co-flow experiments, a series of oscillations in the interface preceded the detachment of the droplet from the tip; we are not aware of these oscillations in our experiments, but they may be visible employing higher spatial or temporal resolution techniques. Nevertheless, it must be noted that the liquid interface in this case presents certain surface charge (although low when compared to that found in classical electrosprays, but still not negligible), which seems to give the interface some resistance to varicose oscillations.⁵⁹ Although this is an extreme case of low conductivity and wide jets. The same phenomenon has been found for higher conductivities of glycerine and thinner jets, giving rise to the same type of instability but with smaller drops.

C. Intermediate regimes

The last regime examined in Sec. VB corresponded to a case of low K and high C , which we can write as $(C > 1, K_{min})$, where K_{min} is the liquid's natural (and minimum) electrical conductivity. If we slowly increase the electrical conductivity of the injected liquid, the jets will become thinner and thinner, the observed dripping frequency will increase, the droplets become smaller, but the jets also become more and more unstable, until we reach the case studied at Sec. VA of $(C > 1, K \gg K_{min})$, in which a violent lateral instability arise. If we instead reduce the surfactant concentration, we will have a similar effect: the jets will slowly narrow and eventually we will reach the case of surfactant-free submerged electrosprays, studied in Sec. IV; in this particular case of K_{min} , we will end up with steady whipping jets. However, the crossing of $C \sim 1$ brings at any K great unsteadiness in the regimes. For example at $(C \sim 1, K_{min})$, one can observe an intermittent dripping, followed within seconds by a steady whipping jet, which comes back again to drip after some time. These transient effects are observed whenever we have medium-to-low conductivities and surfactant concentrations. Such effects have been observed often in the past in systems in interfacial phenomena involving surfactant below the saturated concentration. Analogous effects have been found by the group Anna^{5,60} or by Fernandez and Homsy⁶¹ in similar configurations. The origin can be found in the complex surfactant dynamics at the moving interface with low electrical shear actuating at the interface, which is only partially covered by surfactant. At this point, the coverage of surfactant is inhomogeneous but also unsteady. Consequently, surface tension varies in time, and therefore also the spraying regimes.

VI. SUMMARY AND CONCLUSIONS

In this work, we have reviewed the behavior of submerged electrosprays of viscous conducting liquids into insulating inviscid liquids baths, for different parametric cases, but mainly focused in the effect of surface tension variations caused by the presence of surfactants. As a summary, we have confirmed the results by Barrero *et al.*²³ regarding the reproducibility of cone-jet regimes in submerged electrosprays. We would like to put emphasis in the advantage of the submerged electrosprays for dealing with biological samples: due to the moderate reduction of surface tension, the characteristic flow rates reduce, and with them the final droplet size as well as the shear stresses. However, a more pronounced reduction of surface tension, achieved by the use of surfactants, provokes the loss of the cone-jet regime, characterized for its reproducibility and almost monodisperse emulsions. However, we have shown that the use of surfactant can reduce the working voltage even further and increases the droplet electrical

mobility (higher I/Q). The new modes of atomization found at minimum surface tension have been analyzed and compared with different new regimes recently identified by Higuera³⁶ and Larriba and de la Mora.¹⁸ The nonessential inconveniences originated from the use of surfactants, as the unsteady surfactant accumulation at the base of the meniscus, or the disturbing effect of the charged hydrosol, could be easily overcome by a controlled external flow, in a similar fashion as Gundabala *et al.*¹⁷ did in their experiments. Other effects need to be further studied, such as the effect of the inverted viscosity ratios ($\lambda \leq 1$) and the effect of the outer liquid flow. The control of the flow in the outer liquid could also solve the hypothetical space-charge effects that could appear when both liquids have similar viscosities. The effect of the external viscous shear stress on the surface of the Taylor cone has been only marginally studied and will be of special relevance in the case of reduced surface tension by surfactants, when the electrification of the meniscus is also the lowest.

To conclude, electrohydrodynamic atomization has several features that could be of great interest for lab-on-chip applications or biotechnology. The aim of this work has been to study possible solutions to the current problems that the community has been facing in the recent years.

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- ¹P. S. Drzaic, *Liquid Crystal Dispersions* (World Scientific, 1995).
- ²B. Nasto, "Biotech at the beauty counter," *Nat. Biotechnol.* **25**, 617–619 (2007).
- ³S. Y. Teh, R. Lin, L. H. Hung, and A. P. Lee, "Droplet microfluidics," *Lab Chip* **8**(2), 198 (2008).
- ⁴G. M. Whitesides, "The origins and the future of microfluidics," *Nature* **442**, 368–373 (2006).
- ⁵S. L. Anna and H. C. Mayer, "Microscale tipstreaming in a microfluidic flow focusing device," *Phys. Fluids* **18**, 121512 (2006).
- ⁶R. Surjo and O. A. Basaran, "Tip streaming from a liquid drop forming from a tube in a co-flowing outer fluid," *Phys. Fluids* **18**, 082102 (2006).
- ⁷A. G. Marín, F. del Campo, and J. M. Gordillo, "Generation of micron sized droplets in viscous coflows," *Colloids Surf., A* **344**(1–3), 2–7 (2008).
- ⁸B. Almería, T. M. Fahmy, and A. Gomez, "A multiplexed electrospray process for single-step synthesis of stabilized polymer particles for drug delivery," *J. Controlled Release* **154**(2), 203–210 (2011).
- ⁹A. Barrero and I. G. Loscertales, "Micro and nanoparticles via capillary flows," *Ann. Rev. Fluid Mech.* **25**, 89–106 (2007).
- ¹⁰A. Gomez and W. Deng, "Fundamentals of cone-jet electrospray," in *Aerosol Measurement: Principles, Techniques, and Applications*, 3rd ed., edited by P. Kulkarni, P. A. Baron, and K. Willeke (Wiley & Sons, Hoboken, NJ, 2011), pp. 435–448.
- ¹¹K. L. Smith, M. D. Paine, and J. P. W. Stark, "Voltage-modulated flow rate for precise thrust control in colloid electrospray propulsion," *J. Propul. Power* **23**(5), 1042–1048 (2007).
- ¹²J. Ju, Y. Yamagata, and T. Higuchi, "Thin-film fabrication method for organic light-emitting diodes using electrospray deposition," *Adv. Mater.* **21**, 4343–4347 (2009).
- ¹³W. Deng and A. Gomez, "Electrospray cooling for microelectronics," *Int. J. Heat Mass Transfer* **54**, 2270–2275 (2011).
- ¹⁴P. C. Lozano, P. P. L. Diaz Gómez Maqueo *et al.*, "Electrospray emitters for diffusion vacuum pumps," Ph.D. dissertation (Massachusetts Institute of Technology, 2011).
- ¹⁵G. I. Taylor, "Disintegration of water drops in an electric field," *Proc. R. Soc. London, Ser. A* **280**(1382), 383–397 (1964).
- ¹⁶I. G. Loscertales and J. F. de la Mora, "The current emitted by highly conducting Taylor cones," *J. Fluid Mech.* **260**, 155–184 (1994).
- ¹⁷V. R. Gundabala, N. Vilanova, and A. Fernández-Nieves, "Current-voltage characteristic of electrospray processes in microfluidics," *Phys. Rev. Lett.* **105**(15), 154503 (2010).
- ¹⁸C. Larriba and J. F. de la Mora, "Production of monodisperse submicron drops of dielectric liquids by charge-injection from highly conducting liquids," *Phys. Fluids* **23**, 102003 (2011).
- ¹⁹I. G. Loscertales, A. Barrero, I. Guerrero, R. Cortijo, M. Marquez, and A. M. Ganan-Calvo, "Micro/nano encapsulation via electrified coaxial liquid jets," *Science* **295**(5560), 1695–1698 (2002).
- ²⁰J. E. Díaz Gómez, Á. G. Marín, M. Marquez, A. Barrero, and I. G. Loscertales, "Encapsulation and suspension of hydrophobic liquids via electro-hydrodynamics," *Biotechnol. J.* **1**(9), 963–968 (2006).
- ²¹J. E. Díaz, A. Barrero, M. Márquez, and I. G. Loscertales, "Controlled encapsulation of hydrophobic liquids in hydrophilic polymer nanofibers by co-electrospinning," *Adv. Funct. Mater.* **16**(16), 2110–2116 (2006).
- ²²I. G. Loscertales, A. Barrero, M. Márquez, R. Spretz, R. Velarde-Ortiz, and G. Larsen, "Electrically forced coaxial nanojets for one-step hollow nanofiber design," *J. Am. Chem. Soc.* **126**(17), 5376–5377 (2004).

- ²³A. Barrero, J. M. López-Herrera, D. A. Boucard, and I. G. Loscertales, "Steady cone-jet electrosprays in insulating liquid baths," *J. Colloids Interfacial Sci.* **272**, 104–108 (2003).
- ²⁴H. Kim, D. Luo, D. Link, D. A. Weitz, M. Marquez, and Z. Cheng, "Controlled production of emulsion drops using an electric field in a flow-focusing microfluidic device," *Appl. Phys. Lett.* **91**(13), 133106 (2007).
- ²⁵N. Michihiko, T. Kazunori, K. Shinji, and M. Akira, "Electrostatic water droplet formation in oil in microchannel system," *J. Chem. Eng. Jpn.* **38**, 918–921 (2005).
- ²⁶N. Vilanova, V. R. Gundabala, and A. Fernández-Nieves, "Drop size control in electro-coflow," *Appl. Phys. Lett.* **99**(2), 021910–021910-3 (2011).
- ²⁷J. Xie and C. H. Wang, "Electrospray in the dripping mode for cell microencapsulation," *J. Colloid Interface Sci.* **312**(2), 247–255 (2007).
- ²⁸P. Patel, S. Irvine, J. R. McEwan, and S. N. Jayasinghe, "Bio-protocols for directly forming active encapsulations containing living primary cells," *Soft Matter* **4**(6), 1219–1229 (2008).
- ²⁹C. J. Young, L. A. Poole Warren, and P. J. Martens, "Combining submerged electrospray and UV photopolymerization for production of synthetic hydrogel microspheres for cell encapsulation," *Biotechnol. Bioeng.* **109**(6), 1561–1570 (2012).
- ³⁰J. C. Baret, "Surfactants in droplet-based microfluidics," *Lab Chip* **12**(3), 422–433 (2012).
- ³¹S. N. Jayasinghe and A. Townsend Nicholson, "Bioelectrosprays: The next generation of electrified jets," *Biotechnol. J.* **1**(9), 1018–1022 (2006).
- ³²J. F. de La Mora, "The fluid dynamics of Taylor cones," *Annu. Rev. Fluid Mech.* **39**, 217–243 (2007).
- ³³M. Cloupeau and B. Prunet-Foch, "Electrostatic spraying of liquids in cone-jet mode," *J. Electrostat.* **22**, 135–159 (1989).
- ³⁴F. J. Higuera, "Current/flow-rate characteristic of an electrospray with a small meniscus," *J. Fluid Mech.* **513**, 239–246 (2004).
- ³⁵F. J. Higuera and A. Barrero, "Electrosprays of very polar liquids at low flow rates," *Phys. Fluids* **17**, 018104 (2005).
- ³⁶F. J. Higuera, "Electrodispersion of a liquid of finite electrical conductivity in an immiscible dielectric liquid," *Phys. Fluids* **22**, 112107 (2010).
- ³⁷F. J. Higuera, "Numerical computation of the domain of operation of an electrospray of a very viscous liquid," *J. Fluid Mech.* **648**, 35–52 (2010).
- ³⁸I. Marginean, R. T. Kelly, J. S. Page, K. Tang, and R. D. Smith, "Electrospray characteristic curves: In pursuit of improved performance in the nanoflow regime," *Anal. Chem.* **79**(21), 8030–8036 (2007).
- ³⁹A. M. Gañan Calvo, J. Dávila, and A. Barrero, "Current and droplet size in the electrospraying of liquids. Scaling laws," *J. Aerosol Sci.* **28**, 249–275 (1997).
- ⁴⁰R. T. Collins, J. J. Jones, M. T. Harris, and O. A. Basaran, "Electrohydrodynamic tip streaming and emission of charged drops from liquid cones," *Nat. Phys.* **4**(2), 149–154 (2007).
- ⁴¹G. Mie, "Beiträge zur optik trüber medien, speziell kolloidaler metallösungen," *Ann. Phys.* **25**(3), 377–445 (1908).
- ⁴²Á. G. Marín, "Generacion de Chorros Coaxiales Electrificados: Aplicacion a la Sintesis de Emulsiones," Ph.D. dissertation, University of Sevilla, 2008.
- ⁴³K. L. Smith, M. S. Alexander, and J. P. W. Stark, "Voltage effects on the volumetric flow rate in cone-jet mode electrospraying," *J. Appl. Phys.* **99**(6), 064909 (2006).
- ⁴⁴B. K. Ku, S. S. Kim, Y. D. Kim, and S. Y. Lee, "Direct measurements of electrospray droplets in submicron diameter using a freezing method and a tem image processing technique," *J. Aerosol Sci.* **32**, 1459–1477 (2001).
- ⁴⁵J. Rosell-Llompart and J. F. de la Mora, "Generation of monodisperse droplets 0.3 to 4 microns in diameter from electrified cone-jets of highly conducting and viscous liquids," *J. Aerosol Sci.* **25**, 1093–1119 (1994).
- ⁴⁶G. I. Taylor, "Electrically driven jets," *Proc. R. Soc. London, Ser. A* **313**(1515), 453–475 (1969).
- ⁴⁷A. B. Basset, "Waves and jets in a viscous liquid," *Am. J. Math.* **16**(1), 93–110 (1894).
- ⁴⁸G. Riboux, A. G. Marín, I. G. Loscertales, and A. Barrero, "Whipping instability characterization of an electrified visco-capillary jet," *J. Fluid Mech.* **671**(1), 226–253 (2011).
- ⁴⁹J. Zeleny, "Instability of electrified liquid surfaces," *Phys. Rev.* **10**, 1–6 (1917).
- ⁵⁰K. Tang and A. Gomez, "On the structure of an electrospray of monodisperse droplets," *Phys. Fluids* **6**, 2317 (1994).
- ⁵¹A. M. Gañan-Calvo, "The surface charge in electrospraying: its nature and its universal scaling laws," *J. Aerosol Sci.* **30**(7), 863–872 (1999).
- ⁵²W. D. Ristenpart, J. C. Bird, A. Belmonte, F. Dollar, and H. A. Stone, "Non-coalescence of oppositely charged drops," *Nature* **461**(7262), 377–380 (2009).
- ⁵³J. M. López-Herrera and A. M. Gañan Calvo, "A note on charged capillary jet breakup of conducting liquids: Experimental validation of a viscous one-dimensional model," *J. Fluid Mech.* **501**, 253–259 (2004).
- ⁵⁴S. Tomotika, "On the instability of a cylindrical thread of a viscous liquid surrounded by another viscous fluid," *Proc. R. Soc. London, Ser. A* **150**(870), 322–337 (1935). Available at <http://www.jstor.org/stable/96387>.
- ⁵⁵A. Fernandez-Nieves, D. R. Link, and D. A. Weitz, "Polarization dependent bragg diffraction and electro-optic switching of three dimensional assemblies of nematic liquid crystal droplets," *Appl. Phys. Lett.* **88**, 121911 (2006).
- ⁵⁶A. S. Utada, A. Fernandez-Nieves, H. A. Stone, and D. A. Weitz, "Dripping to jetting transition in coflowing liquid streams," *Phys. Rev. Lett.* **99**, 094502 (2007).
- ⁵⁷C. Clanet and J. C. Lasheras, "Transition from dripping to jetting," *J. Fluid Mech.* **383**(1), 307–326 (1999).
- ⁵⁸A. S. Utada, A. Fernandez-Nieves, J. M. Gordillo, and D. A. Weitz, "Absolute instability of a liquid jet in a coflowing stream," *Phys. Rev. Lett.* **100**, 014502 (2008).
- ⁵⁹R. T. Collins, M. T. Harris, and O. A. Basaran, "Breakup of electrified jets," *J. Fluid Mech.* **588**, 75–129 (2007).
- ⁶⁰W. Lee, L. M. Walker, and S. L. Anna, "Competition between viscoelasticity and surfactant dynamics in flow focusing microfluidics," *Macromol. Mater. Eng.* **296**, 203–213 (2011).
- ⁶¹J. M. Fernandez and G. M. Homsy, "Chemical reaction-driven tip-streaming phenomena in a pendant drop," *Phys. Fluids* **16**(7), 2548 (2004).
- ⁶²F. Malloggi, N. Pannacci, R. Attia, F. Monti, P. Mary, H. Willaime, P. Tabeling, B. Cabane, and P. Poncet, "Monodisperse colloids synthesized with nanofluidic technology," *Langmuir* **26**(4), 2369–2373 (2010).