Droplet charging regimes for ultrasonic atomization of a liquid electrolyte in an external electric field

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Distinct regimes of droplet charging, determined by the dominant charge transport process, are identified for an ultrasonic droplet ejector using electrohydrodynamic computational simulations, a fundamental scale analysis, and experimental measurements. The regimes of droplet charging are determined by the relative magnitudes of the dimensionless Strouhal and electric Reynolds numbers, which are a function of the process (pressure forcing), advection, and charge relaxation time scales for charge transport. Optimal (net maximum) droplet charging has been identified to exist for conditions in which the electric Reynolds number is of the order of the inverse Strouhal number, i.e., the charge relaxation time is on the order of the pressure forcing (droplet formation) time scale. The conditions necessary for optimal droplet charging have been identified as a function of the dimensionless Debye number (i.e., liquid conductivity), external electric field (magnitude and duration), and atomization drive signal (frequency and amplitude). The specific regime of droplet charging also determines the functional relationship between droplet charge and charging electric field strength. The commonly expected linear relationship between droplet charge and external electric field strength is only found when either the inverse of the Strouhal number is less than the electric Reynolds number, i.e., the charge relaxation is slower than both the advection and external pressure forcing, or in the electrostatic limit, i.e., when charge relaxation is much faster than all other processes. The analysis provides a basic understanding of the dominant physics of droplet charging with implications to many important applications, such as electrospray mass spectrometry, ink jet printing, and drop-on-demand manufacturing. © 2011 American Institute of Physics. [doi:10.1063/1.3541818]

I. INTRODUCTION

Charged droplets have been under investigation for over a century. Studies of the dynamics of drop formation and evolution under the application of an electric field date back to the early works of Rayleigh,¹ Zeleny,² and Taylor,³ continuing all the way through the present.^{4,5} The utility of producing droplets of a specific charge under the application of an electric field has been demonstrated on numerous occasions since the initial development of ink jet printing technologies.^{6–8} These early devices utilized Rayleigh instabilities⁹ for capillary stream breakup and droplet production. Another common technique, electrohydrodynamic atomization and tip streaming, relies on the application of a high electric field for fluid dispersion.^{10–14} Still, there is a wide range of techniques for production of discretely charged droplets for applications including mass spectrometry,^{15–21} drop-on-demand manufacturing of multilayer parts and circuits,^{22,23} spray coatings,^{24,25} biosensing and other lab-on-a-chip applications,^{26–29} and wet scrubber systems for pollution control,³⁰ among others. The focus of this work is on mechanically driven atomization, which is coupled to an external electric field for droplet charging. One

such technique exploits the piezoelectrically induced instabilities of a pressure-driven jet, resulting in Rayleigh breakup.^{7,8,19,22,23,31,32} Methods of incorporating pulsed-electric-field-induced instabilities for jet breakup have also been introduced.³¹ The latter family of techniques, irrespective of the application, incorporates a charging electrode in the region of capillary jet breakup to induce preferential charge transport into the forming droplet. In the cases of ink jet printing^{7,8,13,31} and drop-on-demand manufacturing,^{22,23} the flight path of these charged droplets is appropriately controlled as they traverse through an in-flight electric field to achieve a desired deposition (printing) pattern. In a similar manner, Grimm and Beauchamp¹⁹ charged droplets emitted from a vibrating orifice aerosol generator, followed by an induced droplet fission as the droplets fly through an elevated electric field region for mass spectrometry applications.¹⁹ Pneumatically assisted atomization is another common technique that utilizes electrostatic charging for droplet generation often used for spray coatings.^{24,25} Anestos *et al.*²⁴ and more recently McCarthy and Senser²⁵ conducted interesting electric current and charge-to-mass measurements for pneumatic atomization from an electrostatic air gun, comparing the relative electric charge and mass carried by parent droplets versus expelled ions. Another common method for producing discretely charged droplets is through piezoelectri-

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FIG. 1. (Color online) Schematic representation of the ultrasonic droplet generator, including relevant components and an externally applied electric field for droplet charging.

cally actuated ultrasonic pressure wave focusing.^{33,34} Again, an electric field in the region of droplet pinch-off is used to control the transport of charge into a forming droplet.^{17,18}

In these applications, precise control over droplet charging is imperative. For example, in mass spectrometry the charge-per-droplet level, as produced by the ion source, determines the level of available charge carriers for ionization of the analyte molecule.^{16,18,20} This, in turn, determines the ion source's ionization efficiency. Forbes *et al.*¹⁷ recently demonstrated the ability to control droplet charging as a function of static (dc) and dynamic (ac) charging electric fields for an ultrasonic droplet-based ion source. Drop-on-demand manufacturing applications utilize charged droplets in a similar manner to ink jet printing.^{22,23} In high-resolution printing and/or manufacturing, the droplet charging and electric fields must be accurately controlled to achieve a desired printing quality. For example, Orme *et al.*²² demonstrated the use of a pulsed charging signal for generating precisely charged droplets of a eutectic solder. As mentioned, a separate in-flight deflection electric field was used to control the flight path of each droplet.

In all atomization cases, droplet charging is not only a function of the charging (external) electric field, but also depends on the liquid conductivity, driving frequency of droplet generation, and internal flow velocity within an atomized droplet/jet. In this work, we develop a theoretical framework, based on a time scale analysis of relevant charge transport processes, for prediction of droplet charging regimes in ultrasonic atomization of liquid electrolytes. The predictions of the time scale analysis are expressed in terms of relevant dimensionless numbers and validated using detailed electrohydrodynamic simulations and complementary experimental charge-per-droplet measurements.

II. EXPERIMENTAL CHARGE MEASUREMENTS

Ultrasonic atomization of varying ionic strength electrolytes is used to experimentally investigate droplet charging as a function of liquid conductivity and charging electric field. An Array of Micromachined UltraSonic ElectroSprays (AMUSE) device enables ultrasonic atomization in the presence of a local external electric field. It utilizes piezoelectric actuation, cavity resonances, and acoustic pressure wave focusing to periodically eject discrete droplets down to a few micrometers in diameter. As displayed in Fig. 1, this device consists of a single piezoelectric transducer that drives ejec-

tion through an array of pyramidal-shaped liquid horn structures. Details of the device operation and microfabrication processes are described elsewhere.³³ Characterization of the droplet formation and ejection physics, using stroboscopic visualization and scaling analysis has previously been conducted.³⁴ Finally, the AMUSE has recently been demonstrated as a “soft” ion source for bioanalytical mass spectrometry,^{15,20,21} including investigations into charge separation¹⁸ and droplet charging under static and dynamic electric fields.¹⁷ We now consider droplet charging under static electric fields of varying magnitude for electrolytes of varying ionic strength.

A. Experimental setup

To investigate charging regimes enabled by the ultrasonic atomizer, experimental charge measurements have been carried out. Charge-per-droplet values are evaluated from electrical current measurements correlated with ejected mass, using an AMUSE type ultrasonic atomizer (Fig. 1). Details of the experimental setup and equipment for the charge collection measurements are described in depth elsewhere.¹⁷ As described in Forbes *et al.*,¹⁸ this specific configuration of the ultrasonic atomizer (AMUSE) is equipped for application of external electric fields. The local electric field for droplet charging is applied between the inner electrode of the piezoelectric transducer, V_{PZT} , and an external counter electrode, V_{ext} (Fig. 1). Experiments were conducted using aqueous (de-ionized water, Ricca Chemical Co., Arlington, Texas, USA) solutions containing 0.001%–5.7% (v/v) glacial acetic acid (BDH Aristar, Westchester, PA, USA) (pH 4.26–2.38).

B. Experimental results

Ejected droplets produced by AMUSE are monodisperse, with diameter approximately equal to the orifice diameter (dependent on frequency of operation).³⁵ Experimental data on collected current and ejected mass yield charge-per-droplet estimates in the range of 1×10^{-16} – 1×10^{-14} C across the range of dc electric field magnitudes (1×10^5 – 1×10^6 V/m) and liquid conductivities (0.01–0.16 1/Ω m) considered here. Additionally, for the range of electric fields and liquid conductivities considered experimentally, the charge-per-droplet measurements are an order of magnitude less than the Rayleigh limit for a water drop of similar size

FIG. 2. Experimental measurements of normalized charge-per-droplet as a function of the Debye number for a dimensionless dc electric field strength $E^* = 33.8$ and device operation at 0.905 MHz. Ejected droplets are $\sim 6 \mu\text{m}$ in diameter. Data points and error bars represent the average values and standard deviations, respectively, of the results obtained from five replicate experimental measurements at each value of the Debye number. The solid curve represents a trendline of the experimental data.

($\sim 1 \times 10^{-13}$ C). The maximum local charge density at the droplet pole(s) is $\sim 800 \text{ C/m}^3$ and approaches the local Rayleigh limit ($\sim 980 \text{ C/m}^3$). Figure 2 shows the charge-per-droplet measurements, normalized by the Rayleigh limit ($Q_{\text{drop}}/Q_{\text{RL}}$), as a function of the dimensionless Debye number [$\text{Db} = (l/\lambda_D)^2$]. The Debye number is a function of the characteristic length scale, l , taken as the nozzle radius and the Debye length, $\lambda_D = (\epsilon_0 \epsilon_r RT / 2F^2 \sum z_i^2 c_i)^{1/2}$, where ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the material, R is the universal gas constant, T is the temperature, F is the Faraday constant, z_i is charge of species i , and c_i is the concentration of species i . The Debye length is the length scale over which free charge carriers shield out electric fields and is inversely proportional to the square root of the liquid conductivity. As a consequence, the dimensionless Debye number is directly proportional to the liquid conductivity. The range of liquid conductivities investigated here

(0.01–0.16 $1/\Omega \text{ m}$) result in Debye numbers in the range 0.34–7.54 ($\times 10^5$). Data presented in Fig. 2 are for a dimensionless dc external electric field of 33.8 ($3.5 \times 10^5 \text{ V/m}$) with the ultrasonic atomization operated at a 0.905 MHz frequency ($\sim 6 \mu\text{m}$ diameter droplets). The dimensionless electric field is given by $E^* = E_o e / k_B T$, where E_o is the characteristic electric field (taken as the applied external electric field), e is the elementary charge, and k_B is the Boltzmann constant. Each discrete data point (Debye number) in Fig. 2 is the average charge-per-droplet from five individual experimental measurements, as described in detail in Forbes *et al.*¹⁷ Somewhat surprisingly, the experimental results demonstrate first a gradual increase and then a decrease with the existence of a local maximum in droplet charging. This separates the parameter space into two regions separated by the local maximum.

Next we consider droplet charging as a function of the dc electric field strength for two Debye numbers from Fig. 2; specifically, one is in the region of increasing droplet charging with increasing Debye number, and the other is in the region of decreasing droplet charge with increasing Debye number. Figure 3 displays the normalized charge-per-droplet behavior for Debye numbers, $\text{Db} = 0.68 \times 10^5$ (0.020 $1/\Omega \text{ m}$) and $\text{Db} = 2.74 \times 10^5$ (0.082 $1/\Omega \text{ m}$), as a function of the external dc electric field. Droplet charging as a function of electric field for a relatively “low” Debye number ($\text{Db} = 0.68 \times 10^5$) demonstrates a linear relationship between the charge and electric field [Fig. 3(a)], similar to that frequently found in the literature.^{7,8,22,31,32} At an elevated Debye number ($\text{Db} = 2.74 \times 10^5$), the charge-per-droplet trend initially increases with increasing electric field. However, upon reaching a strong enough electric field ($E^* \sim 29.0$) the droplet charging begins to decrease. For this Debye number, collection of data past $E^* \sim 72.5$ (i.e., $7.5 \times 10^5 \text{ V/m}$) was not possible in experiments due to the increased frequency of the atomizer “flooding” with electrolyte, leading to dielectric breakdown between the liquid and counter electrode (wires), tripping the power supply.

FIG. 3. Experimental measurements of normalized charge-per-droplet as a function of dimensionless electric field strength at (a) lower ($\text{Db} = 0.68 \times 10^5$) and (b) higher ($\text{Db} = 2.74 \times 10^5$) Debye numbers, for device operation at 0.905 MHz. Ejected droplets are $\sim 6 \mu\text{m}$ in diameter. Data points and error bars represent the average values and standard deviations, respectively, of the results obtained from five replicate experimental measurements at each value of the Debye number. Solid curves represent trendlines of the experimental data.

To explain this atypical charging behavior, we develop a computational model and time scale analysis of relevant charge transport processes to investigate the droplet charging regimes observed in experimental atomization of liquid electrolytes of different ionic strength. The first-principle electrohydrodynamic simulations are compared to the experimental charge-per-droplet measurements and droplet charging regimes are theoretically predicted through a time scale analysis, which is generalized by the use of relevant dimensionless parameters.

III. ANALYSIS OF CHARGE TRANSPORT

An electrohydrodynamics (EHD) model with minimal simplifications¹⁷ is used to study charge transport and droplet ejection from an ultrasonic droplet generator under an external electric field. The computational model enables investigation of the microscopic details of charge transport phenomena on the microsecond time scale. The regimes of droplet charging are identified theoretically and used to analyze the simulated and experimental trends.

A. Simulation background

The computational model employs the full set of EHD and charge transport equations with the liquid electrolyte modeled as an ionic conductor.¹⁷ The model consists of the following nondimensional set of incompressible electrohydrodynamic equations, where the electric field is solved in all domains comprising a unit cell from the ejector (Fig. 1), i.e., the solid device structure (silicon and silicon nitride), liquid electrolyte being atomized, and surrounding gas, the flow field is solved in both liquid and gas phases, and the charge transport equation(s) are only solved in the liquid phase.

$$\text{Electric field equation} \quad \nabla \cdot (\epsilon_r \vec{E}) = \frac{E_{HD}}{Md} q, \quad (1)$$

charge transport equation

$$\frac{\partial q_{\pm}}{\partial t} + \nabla \cdot \left[\frac{F_E}{Re Sc} (q_{\pm} \vec{E}) + q_{\pm} \vec{u} \right] = 0, \quad (2)$$

$$\text{continuity equation} \quad \nabla \cdot \vec{u} = 0, \quad (3)$$

Navier–Stokes equations of motion

$$\begin{aligned} St \left[\frac{\partial \vec{u}}{\partial t} \right] + [\vec{u} \cdot \nabla \vec{u}] \\ = -Eu[\nabla p] + \frac{1}{Re} [\nabla^2 \vec{u}] + \frac{E_{HD}}{Re^2} [q \vec{E}] \\ - \frac{Md}{Re^2} \left[\frac{1}{2} E^2 \nabla \epsilon \right]. \end{aligned} \quad (4)$$

Here, all variables, i.e., the local net free charge density (q), pressure (p), time (t), velocity ($\vec{u}$), and electric field ($\vec{E}$), are rendered dimensionless by introducing the following dimensionless groups: Strouhal number ($St = fl/u_o$), Euler number ($Eu = p_o / \rho u_o^2$), Reynolds number ($Re = \rho u_o l / \mu$), EHD number ($E_{HD} = q_o E_o l^3 \rho / \mu^2$), Masuda number ($Md = \epsilon_o E_o^2 l^2 \rho / \mu^2$), ion

drift number ($F_E = \mu_{em} E_o l / D$), and the Ion Schmidt number ($Sc = \nu / D$).^{36,37} In these dimensionless parameters, f is the atomization frequency, u_o is the ejection velocity (i.e., initial droplet velocity), p_o is the characteristic pressure taken as the dynamic pressure, ρu_o^2 , ρ is the fluid density, μ is the dynamic viscosity of the fluid, q_o is the characteristic charge density taken as the bulk liquid charge density before the application of an external electric field, μ_{em} is the charge electrical mobility, D is the charged species diffusion coefficient, and ν is the kinematic viscosity of the fluid. For the application considered here, the electric fields are relatively strong and therefore the diffusion time scale for charge transport is much longer than the other transport processes and is neglected, leaving only advection and migration in Eq. (2). Details of the nondimensionalization of the charge transport equation and neglecting of diffusion are discussed in the next section of the paper.

The liquid-gas interface boundary conditions for this set of governing equations take the following form:

$$\text{electric field:} \quad \vec{n} \cdot \|\epsilon_r \vec{E}\| = q_s, \quad \vec{n} \times \|\vec{E}\| = 0, \quad (5)$$

surface charge transport:

$$\frac{\partial q_s}{\partial t} + \nabla_s \cdot (q_s \vec{u}) = - \frac{F_E}{Re Sc} \vec{n} \cdot \|\sigma \vec{E}\|, \quad (6)$$

stress balance:

$$\begin{aligned} \frac{1}{Re} [\nabla \vec{u} + (\nabla \vec{u})^T] + \Pi_E \left(\vec{E} \vec{E} - \frac{1}{2} |E|^2 \vec{I} \right) \\ = St^2(p) + \frac{1}{We} (\vec{n} \nabla \cdot \vec{n}), \end{aligned} \quad (7)$$

$$\text{velocity continuity:} \quad \vec{n} \cdot \|\vec{u}\| = 0, \quad \vec{n} \times \|\vec{u}\| = 0. \quad (8)$$

Here, the following dimensionless groups and variables are introduced: the Weber number ($We = \gamma / \rho u_o^2 l$), the dimensionless electric stress ($\Pi_E = \epsilon_r \epsilon_o E_o^2 / \rho u_o^2$), and q_s is the surface charge density (with surface charge density scale $\epsilon_o E_o$), $\vec{n}$ is the outward-pointing normal (relative to the liquid domain), the notation $\|x\|$ denotes a jump across the liquid-gas interface of x , ∇_s is the surface gradient [$\nabla_s = \nabla - \vec{n}(\vec{n} \cdot \nabla)$], σ is a dimensionless liquid conductivity scaled by $\mu_{em} q_o$, and γ is the surface tension.^{10,38,39} Equation (5) defines the jump in electric displacement across the liquid-gas interface, which is equal to the local surface charge density as predicted by surface charge transport [Eq. (6)]. Equation (7) provides the stress balance at the interface, which includes the viscous shear and Maxwell stress tensors and the normal stress due to the pressure jump across the interface balanced by the interfacial tension. Equation (8) is simply a continuity of the velocity field across the interface. Additionally, no-slip and no-penetration conditions are imposed on the velocity field at all solid surfaces, and symmetry conditions are set on the velocity field, electric field, and fluid interface profile at the center axis and far-field boundaries. Pressure and electric field (potential bias relative to reference ground) boundary conditions

are discussed below upon introduction of the simulation domain.

The computational fluid dynamics software FLUENTTM is used for numerical implementation of the model, using the standard routine for hydrodynamics of the free surface flow and fluid interface evolution, but incorporating additional hand-coded transient advective-diffusive equations and boundary conditions to solve the electric field and charge transport equations.⁴⁰ The modeling of periodic droplet evolution and pinch-off in the ultrasonic atomizer involves free surface flows, interface breakup, and coalescence. Therefore, the volume of fluid (VOF) technique^{41–46} is utilized for tracking interface evolution. The volume of fluid technique produces a diffuse interface that consists of several computational cells, instead of a sharp inter-phase boundary. Therefore, a control volume approach is applied to governing equations on each computational cell throughout the entire simulation domain, including the cells that form the liquid-gas “interface.” Volume-fraction-weighted governing equations are solved for computational cells in which the interface exists. The algorithms employed here utilize volumetric body forces in the momentum equation to account for surface stresses along the interface. An advection equation is incorporated to track the interface evolution by advancing fluid volumes forward in time. In these simulations, FLUENT employs the geometric reconstruction scheme, based on Youngs’ method,⁴⁷ to represent the interface between liquid and gas phases. The geometric reconstruction scheme uses a piecewise-linear approach to determine the face fluxes for the partially filled cells at the interface. The pressure-linked momentum and mass conservation equations are solved by a built-in solver based on a semi-implicit method for pressure-linked equations algorithm. To incorporate the electric field and charge transport equations, the user-defined transient advection-diffusion equations are added to the solution algorithm, which are solved simultaneously with the Navier–Stokes equations and boundary conditions. In order to properly incorporate charge migration into the user-defined transient advection-diffusion equation, the overall charge velocity component, $\vec{u}$, is replaced with $\vec{V} = \vec{u} + \mu_{em}\vec{E}$, representing both the charge transport by bulk advection as well as migration under the local electric field. A detailed description of the computational techniques and solution methodology are covered in Forbes *et al.*,¹⁷ as well as in the associated supplementary material, which is available online.

Specifics of the mesh sensitivity, numerical discretization, resolution, and numerical errors are discussed in detail in Forbes *et al.*¹⁷ and Meacham.³⁵ The hydrodynamics model has previously been validated through extensive comparison between simulated and experimental droplet interface evolution (captured by stroboscopic visualization of droplet ejection).^{34,35} The simulated profiles are in excellent agreement with the stroboscopic visualization of droplet ejection.³⁵ The model has also been successfully used to simulate the cone-jet structure for electrospraying a fluid with finite electrical conductivity, as well as the Taylor cone formation for a perfectly conducting fluid. Additionally, charge separation under both static (dc) and dynamic (ac)

FIG. 4. Simulated fluid interface evolution during ejection of a droplet from a 5 μm diameter nozzle orifice by the ultrasonic atomizer through a single 1 MHz pressure wave cycle. There is a 125 ns delay between successive profiles.

electric fields has been demonstrated for the AMUSE ion source and validated using charge-per-droplet measurements as function of the applied electric field.¹⁷ However, it should be noted that the presented model and its volume-of-fluid-based numerical implementation have only been able to qualitatively simulate the tip streaming phenomena of electrospray.¹⁷ To accurately predict the emission of charged drops by tip streaming more sophisticated numerical techniques and explicit incorporation of surface charge transfer are required to properly resolve the high charge densities at the liquid-gas interface.^{10,39}

Figure 4 shows the formation and ejection of a single droplet during an ultrasonic pressure wave cycle from an axisymmetric domain that includes the truncated apex of a single nozzle. The representative results presented here are for a 1 MHz drive signal and a 5 μm diameter nozzle orifice. Figure 4 displays the droplet evolution and pinch-off at periodic steady state, i.e., the interface profile at a specific point in the ejection cycle matches from cycle to cycle. The hemispherical “inlet” of the simulated domain is represented as an oscillating pressure boundary predicted by a harmonic response acoustic simulation of the atomizer’s transient pressure field using the finite element analysis software ANSYS.⁴⁸ The external electric field is specified by a bias electric potential difference across the simulation domain between the hemispherical inlet (charging electric potential) and far-field pressure outlet (reference potential). Additional details on the simulation domain and mesh characteristics can be found in Forbes *et al.*¹⁷ and the associated supplementary material (available online).

B. Electrohydrodynamics of ultrasonic atomization: Simulation of a single droplet

Utilizing the EHD computational model, a numerical investigation of droplet charging is performed. The simulated results are reported for an individually ejected droplet, neglecting electric field “shielding” effects produced by previously ejected droplets. All simulations are conducted for ejection from a 5 μm diameter nozzle, atomization frequency of 1 MHz, and an aqueous electrolyte containing a specified amount of acetic acid to introduce free charge carriers and produce a specified liquid conductivity. Figure 5 depicts the simulated charge-per-droplet, normalized by the Rayleigh limit, as a function of the Debye number (i.e., dimensionless liquid conductivity) for several representative

FIG. 5. (Color online) Simulated charge-per-droplet normalized by the Rayleigh limit, as a function of the Debye number for several dimensionless dc electric field magnitudes. Results are for ejection from a $5 \mu\text{m}$ nozzle at 1 MHz atomization frequency.

electric field strengths. Quite unexpectedly, the charge-per-droplet trends do not monotonically increase with increasing liquid conductivity. In fact, negatively charged droplets are obtained upon application of a positive dc electric field for Debye numbers in the range of around $1.82 \times 10^5 - 4.45 \times 10^5$.

To take a closer look, Fig. 6 displays the droplet charging trends as a function of dimensionless electric field strength for a range of Debye numbers. In Fig. 6(a), at lower Debye numbers, a linear trend between droplet charge and electric field magnitude is observed. This is in agreement with the experimental results found in Forbes *et al.*¹⁷ and displayed in the previous sections [Fig. 3(a)]. However, with increasing Debye number, the charge-per-droplet trends as a function of electric field start to deviate from monotonically increasing, to having a local maximum, and then even decreasing [Fig. 6(b)]. As the Debye number is increased further, a monotonically decreasing droplet charging trend is recovered [Fig. 6(c)]. In this range, negatively charged drop-

lets are produced under the application of a positive electric field! Increasing the Debye number even further reverses this trend and results again in monotonically increasing positive charge-per-droplet, although in a nonlinear fashion [Fig. 6(d)]. In general, at these high Debye numbers, the ejected droplets are consistently negative at low electric field strengths and transition to positive charging at high electric fields (Fig. 5).

The transient nature of droplet ejection in the ultrasonic droplet generator is a root-cause of the complex interplay between charge transport affected by fluid motion, the liquid conductivity, and the external electric field. Thus, the physics of interacting charge and fluid transport under periodic ejection must be investigated to expand the present understanding of droplet charging. To this end, we use a scale analysis to develop insight and predictive relationships that determine droplet charging mechanism(s) for a range of electric fields (E^*) and liquid conductivities (Db).

C. Charge transport time scale analysis

The time scale analysis of the charge transport equation is used to gain insight into the dominant physics of charge transport as a function of the Debye number. The ionic current through the solution consists of transport by ionic drift, diffusion, and advection. The governing equation for charge transport is as follows:

$$\frac{\partial q}{\partial t} + \nabla \cdot (q\mu_{\text{em}}\vec{E} + q\vec{u} - D\nabla q) = 0. \quad (9)$$

For ultrasonic atomization in the presence of relatively strong external electric field (greater than $\sim 0.025 \text{ V/m}$), the diffusion time scale for charge transport is much longer than the other transport processes (e.g., charge advection and migration) and can be neglected.³⁶ Thus, only advection, $q\vec{u}$, and migration, $\mu_{\text{em}}q\vec{E}$, of charged fluid particles under the application of an electric field need to be considered (here, $\vec{E} = -\nabla\phi$ is the electric field vector).

FIG. 6. (Color online) Simulated charge-per-droplet normalized by the Rayleigh limit, as a function of applied dc electric field for (a) low [$\sim \text{Db} = 0.07 - 0.68 (\times 10^5)$], (b) low-medium [$\sim \text{Db} = 0.68 - 1.71 (\times 10^5)$], (c) medium-high [$\sim \text{Db} = 1.71 - 3.43 (\times 10^5)$], and (d) high [$\sim \text{Db} = 3.43 - 7.54 (\times 10^5)$] Debye numbers.

FIG. 7. (Color online) Charge transport time scales (left ordinate axis) for ultrasonic atomization at 1 MHz frequency, plotted together with simulated charge-per-droplet values (right ordinate axis), as a function of the Debye number for dimensionless electric field strength of ~ 24 .

By expanding the divergence of the current in the charge transport equation, Eq. (9), the relevant transport time scales can be identified as (1) the pressure forcing (process) time scale ($t_p \sim 1/f$) based on the atomization frequency, (2) the advection time scale ($t_u \sim l/u_o$) based on characteristic length and ejection velocity, and (3) the charge relaxation time scale ($t_{\text{relax}} \sim \epsilon_o \epsilon_r / \mu_{\text{em}} q_o$) based on the characteristic liquid conductivity. The ionic transit (ion migration) time scale ($t_i \sim l / \mu_{\text{em}} E_o$) is more than an order of magnitude greater than all other time scales for an electric field strength greater than ~ 0.025 V/m and therefore cannot influence the process under investigation. By casting the expanded version of Eq. (9) in dimensionless form, two important dimensionless parameters are identified as the ratio of relevant charge transport time scales. These dimensionless parameters are the Strouhal number ($St = t_u / t_p = fl / u_o$), expressing the relative dominance of free charge advection to the pressure forcing time scales, and the electric Reynolds number ($Re_E = t_{\text{relax}} / t_u = \epsilon_o \epsilon_r \mu_o / \sigma_o l$),⁴⁹ expressing the relative dominance of charge relaxation to advection. In the following discussion, the relevant charge transport time scales are nondimensionalized by the advection time scale, i.e., $t_p^* \sim 1/St$, $t_u^* \sim 1$, and $t_{\text{relax}}^* \sim Re_E$.

Figure 7 depicts the charge transport time scales for a 1 MHz drive signal as a function of the Debye number, overlaid with the normalized charge-per-droplet curve for $E^* = 24.2$ from Fig. 5. The periodic nature of the pressure field at the nozzle orifice driving ejection determines the characteristic time scale on which the dynamics of all processes must be compared. For a given set of operating conditions, the process time scale is only a function of the atomization frequency (governed by the sinusoidal oscillation of the pressure field driving ejection), and therefore constant (note that it may not be constant if a more complex waveform is employed to drive ejection). The advection time scale is a function of the characteristic length (radius of the nozzle orifice)

and characteristic velocity, both constant for a given drive signal frequency and amplitude. Consequently, for a given set of operating conditions and drive signal, the Strouhal number is constant. The charge relaxation time scale is a function of the characteristic liquid conductivity, σ_o , the liquid permittivity, and the ionic mobility of the relevant charge carrier (protons H^+ for the analysis here). In Fig. 7, the inverse relationship between the charge relaxation time scale, i.e., the electric Reynolds number, and Debye number separates the parameter space into three regimes, as the points where the charge relaxation time scale becomes comparable to the process and advection time scales, respectively. It is therefore the relative magnitude of the constant Strouhal number and varying electric Reynolds number that determines the droplet charging.

At low Debye number (regime I), the charge relaxation time is longer than both the process and advection time scales, $t_u < t_p < t_{\text{relax}}$ or $1 < 1/St < Re_E$. As long as charge relaxation, due to the application of an external disturbance (i.e., external electric field), is slower than droplet formation (atomization process time), any increase in liquid conductivity (i.e., Debye number) results in a decreased charge relaxation time, thus allowing more time for charge separation. This in turn leads to an increase in charge-per-droplet levels as more free charge carriers make it into the ejected droplets. This is clearly displayed in Fig. 6(a) by the noticeable increase in charge-per-droplet levels as the Debye number increases from 0.07×10^5 to 0.34×10^5 . It is in this regime of low Debye numbers that the relationship between droplet charging and applied electric field is linear. It must be emphasized that this behavior is only observed when the charge relaxation time scale is the longest of all relevant time scales and therefore, the electric Reynolds number is larger than the inverse of the Strouhal number.

In regime II, for intermediate Debye numbers, the charge relaxation time decreases past the process time, but still remains greater than the advection time scale, $t_u < t_{\text{relax}} < t_p$ ($1 < Re_E < 1/St$). In this case, the charge within a forming droplet has sufficient time to fully relax before the droplet is ejected (on the process time scale), redistributing within the droplet to induce an internal electric field which locally cancels the effect of the external electric field. However, since the advection time is still faster, dominating charge transport, an excess of the already separated charge is “pushed” (advected) into the evolving droplet. From the Poisson equation [$\nabla^2 \phi = -q / \epsilon_o \epsilon_r$, derived from Eq. (1)], this excess charge, beyond equilibrium, causes an increase in the local electric potential in the ejecting droplet region above the applied external potential in the bulk reservoir (all potentials are relative to the ground at the external electrode above the ejector surface). This adverse internal electric field actually enhances migration of negative charge carriers into the droplet region, decreasing the net positive charge-per-droplet. Figure 8 demonstrates the change in the internal electric field as the interface evolves before pinch-off. As the Debye number increases, the electric Reynolds number continues to decrease, allowing more time before droplet pinch-off during which the adverse electric field can transport negative charges (acetate anions, CH_3COO^- , when acetic acid dissociation forms

FIG. 8. (Color online) Schematic representation of the internal (induced by local charge redistribution) electric field direction and net charge transport in an evolving droplet for charging in regime II. Profiles are for ejection from a $5\ \mu\text{m}$ diameter nozzle and 1 MHz atomization frequency.

the electrolyte ions) into the droplet. This preferential transport of negative charge carriers toward the evolving droplet interface results in a steady decrease in the net positive charge-per-droplet, as seen in Figs. 5, 6(b), and 6(c).

This analysis has demonstrated that the direction of the internal electric field enhances the relative transport of positive versus negative charge carriers through ionic migration. From the simulations, it is found that during the droplet formation process (before pinch-off), the net electric field direction (sum of local/internal and external electric fields) matches the sign of the slope of the charge-per-droplet curve (Figs. 7 and 8), providing solid support to the arguments on the interplay of different processes when charging occurs in regime II.

Finally in regime III, as the charge relaxation time becomes the fastest of all time scales, $t_{\text{relax}} < t_u < t_p$ ($\text{Re}_E < 1 < 1/\text{St}$), a steady increase in charge-per-droplet is again recovered, as in the case of regime I. Now, the charge relaxes sufficiently fast to dominate the effects of all other transport processes. Therefore, as the charge relaxes to cancel the external electric field, advection still pushes separated (positive) charge into the evolving droplet, inducing an adverse electric field. However, the charge moves fast enough to redistribute within a droplet and cancels the induced adverse electric field. As shown in Figs. 5 and 6(d), increasing the Debye number in this regime leads to an increase in charge-per-droplet.

Lastly, in the limit of very large Debye number (regime IV), the electric Reynolds number becomes vanishingly small and the charge relaxation time scale is so much faster than all other time scales that charge transport is effectively instantaneous, resulting in the electrostatic limit. Under these conditions, as long as the droplet evolution profiles remain approximately equivalent, droplet charging would follow the behavior of a parallel plate capacitor. In this case, while the charge-per-droplet will continue to increase linearly with an increase in the electric field magnitude, any further increase in the Debye number will no longer have an effect on the net charge residing on atomized droplets.

D. Comparison to experimental results

We next use the developed theoretical framework and simulations described in the previous section for analysis of the experimental results. Comparing the experimental (Fig. 2) and simulated (Fig. 5) droplet charging trends, for the same range of Debye numbers, a couple of noticeable

differences are apparent. Specifically, the experimental results show a much more gradual increase and decrease in droplet charging as a function of Debye number. The experimental results in Fig. 2 also fail to demonstrate the local minimum displayed in the simulated results (Fig. 5). However, due to the similarities in droplet charging trends between experiments (Fig. 2) and the individual droplet simulations (Fig. 5), it is suspected that the effect of previously ejected droplets (i.e., electric field “shielding”) is in fact relevant and causing the discrepancy. That is, the space-charge in the area above the ultrasonic ejector, due to a stream of ejected droplets, results in local electric field distortions that induce variations in droplet charging.

To investigate this further, simulations of droplet charging as a function of Debye number, which consider the average charging of several consecutively ejected droplets ($\sim 8-10$), are performed to check the hypothesis of local electric field “shielding.” Indeed, for this case, previously ejected droplets are shown to play an important role on the charging of successive droplets. Figure 9 compares the charge-per-droplet measurements with simulations of both individual droplet and multiple-droplet-average charging for dimensionless electric field strength of 96.7. In agreement with the experimentally observed trend, the computed multiple-droplet charge averages show a more gradual increase and then a decrease about a reduced-magnitude local maximum, as the Debye number increases.

FIG. 9. (Color online) Simulated charge-per-droplet normalized by the Rayleigh limit, for ultrasonic atomization at 1 MHz frequency for the first ejected droplet and the average of consecutively ejected droplets as a function of the Debye number.

In the same way that successive droplets “shield” the external electric field in the dc simulations at low Debye numbers,¹⁷ the presence of successive droplets also attenuates the charge transport into each ejected droplet. To substantiate this point, we consider a theoretical framework of the scale analysis developed in the previous section to investigate the time scales and droplet charging for the experimental measurements and the multiple-droplet-average charging simulations. As with the individual droplet analysis, the relative magnitudes of the electric Reynolds number and Strouhal number again separate the regimes of droplet charging. The time scale analysis accurately identifies the transition from regime I to regime II in the experimental results (Fig. 2) as the point where the electric Reynolds number is of the order of the inverse of the Strouhal number ($Re_E \sim 1/St$), i.e., the charge relaxation time scale becomes comparable to the pressure forcing (process) time scale. This places a Debye number of 0.68×10^5 in regime I, which from the simulations [Fig. 6(a)] and theoretical analysis results in a linear relationship between droplet charging and electric field strength, just as seen experimentally in Fig. 3(a). Similarly, a Debye number of 2.74×10^5 falls into regime II where the electric Reynolds number becomes smaller than the inverse of the Strouhal number, which from the simulations [Figs. 6(b) and 6(c)] results in an initial increase, local maximum, and then a decrease in droplet charging as a function of increasing electric field strength. Again, this has been confirmed experimentally in Fig. 3(b). Unfortunately, experiments for Debye numbers higher than $\sim 7.54 \times 10^5$ were not possible due to the drastic increase in atomizer “flooding” and associated dielectric breakdown, which tripped the power supply and ceased ejection. However, utilizing the theoretical analysis, it may be suggested that the droplet charge curve would experience a local minimum as the charge relaxation time scale becomes faster than the advection time scale, i.e., as the electric Reynolds number becomes smaller than unity. This is hypothesized to occur around a Debye number of $Db = 1.82 \times 10^6$. This fact has not been experimentally verified due to the above stated difficulties, but is strongly supported by the time scale analysis.

E. Comparison to literature

The droplet charging regimes identified here can be applied to a number of examples found in the literature. The most common relationship identified in the literature is a linear dependence between droplet charge and charging electric field magnitude.^{7,8,22,31,32} Considering the working fluids (liquid conductivity), droplet generation frequency, and jet/droplet velocities from these investigations, the relative magnitudes of charge transport processes can be identified following the methodology we outlined. In most cases,^{8,22,31} either high conductivity ink or eutectic solder is the working fluid, resulting in very small electric Reynolds numbers and extremely fast charge relaxation. Thus, the electrostatic limit is approached (regime IV), resulting in a linear relationship between droplet charge and electric field magnitude as observed in experiments. However, in a couple of cases,^{7,32} low conductivity water was used, which would result in large

electric Reynolds numbers and slower charge relaxation times. The charge transport time scales in these investigations fall into regime I, where the linear relationship between droplet charge and electric field magnitude was still experimentally observed, as one would expect from the time scale analysis we presented. However, this linear relationship is due to the dominant effect of the charge advection and not because of the rapid charge relaxation toward the surface of the jet column that is breaking into discrete droplets, as was concluded by the authors of these experimental studies.^{7,32}

IV. CONCLUSIONS

Understanding of droplet charging mechanisms, as determined by the relative magnitudes of the charge transport time scales, has direct implications for the use of alternate waveforms, e.g., pulsed-function electric fields for charge separation, similar to the method used by Orme *et al.*²² For example, if the goal is to achieve the maximum charge-per-droplet, the atomizer needs to be operated at the boundary of regimes I and II, where the electric Reynolds number is of the order of the inverse of the Strouhal number ($Re_E \sim 1/St$), i.e., the charge relaxation time and process time scales are comparable. For Debye numbers in regime I, a linear increase in droplet charging with electric field is observed, and reduction in the duration of the applied electric field will reduce overall droplet charging. Therefore, for Debye numbers in this regime, dc (not ac)-charging yields optimal results. However, for Debye numbers in regime II, the charge has sufficient time to induce an adverse local electric field, thus reducing charge-per-droplet. In this region, it is beneficial to reduce the duration over which the electric field is applied (reduced pulse width). Specifically, using an electric field pulse right before droplet pinch-off will provide the desired charge separation without leaving time for an adverse electric field to inject negative charges into a droplet, which would lead to a net reduction of positive charge in the ejected droplet.

In summary, through a numerical investigation of droplet charging and a time scale analysis of charge transport processes, specific regimes of droplet charging are identified, as defined by the dominant charge transport mode. The regimes of droplet charging are a function of the Debye number (liquid conductivity), the external electric field (magnitude and duration), and atomization parameters (frequency and amplitude of driving pressure pulses). The transition between regimes is identified by the relative magnitudes of the dimensionless Strouhal and electric Reynolds numbers. These regimes not only predict the final net charge placed on an ejected droplet, but also how droplet charging is effected by increasing the electric field strength. Experimental charge-per-droplet measurements have validated the analytical framework, predicting the droplet charging regimes, and are in agreement with the simulation results. The theoretical ideas and droplet charging regime maps developed in this work will find utility in a number of important applications, including electrospray mass spectrometry, ink jet printing, and drop-on-demand manufacturing.

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