Electrospray in Crossflow

By

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Abstract

Characteristics of an electrospray ion source in an air crossflow is investigated. The effect of crossflow on the Taylor cone, the emitting jet, and the plume spray trajectory, are studied experimentally. The trajectory of a plume in the cone jet mode is related to the crossflow velocity, applied voltage to the nozzle, and the location of the ion source inside a dissovation chamber. An analytical model is developed for the prediction of the trajectory of an electrified jet in an electric field and a crossflow. A numerical solution is developed in order to simulate the traveling paths of single droplets inside the chamber, which is used to estimate the plume trajectory. The results of both models are discussed and compared with the experimental cases.
I wish to express my sincere gratitude to

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<th>Description</th>
<th>Unit</th>
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<tr>
<td>a</td>
<td>Acceleration</td>
<td>m s(^{-2})</td>
</tr>
<tr>
<td>(a_j)</td>
<td>Perturbation amplitude of jet surface</td>
<td>m</td>
</tr>
<tr>
<td>(A_{Fr})</td>
<td>Frontal Area</td>
<td>m(^2)</td>
</tr>
<tr>
<td>(A_{surf})</td>
<td>Surface area of jet</td>
<td>m(^2)</td>
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<td>B</td>
<td>Magnetic field</td>
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<td>(B_T)</td>
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<td>Vapor concentration at droplet surface</td>
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<td>(c_\infty)</td>
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<td>kg m(^{-3})</td>
</tr>
<tr>
<td>(C_D)</td>
<td>Drag Coefficient</td>
<td>J kg(^{-1})K(^{-1})</td>
</tr>
<tr>
<td>(C_{p_g})</td>
<td>Specific heat of gas/air</td>
<td>J kg(^{-1})K(^{-1})</td>
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<td>Vessel diameter</td>
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<tr>
<td>$d^*$</td>
<td>Kelvin Diameter</td>
<td>[m]</td>
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<tr>
<td>$D$</td>
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<td>$E_{on}$</td>
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<td>[N]</td>
</tr>
<tr>
<td>$F_{Shear}$</td>
<td>Shear force</td>
<td>[N]</td>
</tr>
<tr>
<td>$\mathcal{F}$</td>
<td>Ratio of initial drag force to electric force</td>
<td></td>
</tr>
<tr>
<td>$g$</td>
<td>Gravity acceleration</td>
<td>[$m s^{-2}$]</td>
</tr>
<tr>
<td>$h_{Step}$</td>
<td>Step size in sudden expansion</td>
<td>[m]</td>
</tr>
<tr>
<td>$h$</td>
<td>Height of cylindrical element</td>
<td>[m]</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------------------------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>( h )</td>
<td>Convective heat transfer coefficient</td>
<td>([\text{W m}^{-2}\text{K}^{-1}])</td>
</tr>
<tr>
<td>I</td>
<td>Electrospray current</td>
<td>([\text{A}])</td>
</tr>
<tr>
<td>( K_g )</td>
<td>Thermal conductivity of gas/air solution</td>
<td>([\text{W m}^{-1}\text{K}^{-1}])</td>
</tr>
<tr>
<td>( K_v )</td>
<td>Thermal conductivity of vapor solution</td>
<td>([\text{W m}^{-1}\text{K}^{-1}])</td>
</tr>
<tr>
<td>( K_{\text{Mix}} )</td>
<td>Thermal conductivity of vapor and gas mixture</td>
<td>([\text{W m}^{-1}\text{K}^{-1}])</td>
</tr>
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<td>( L_{\text{tip–CL}} )</td>
<td>Capillary to vessel centerline distance</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( L_{\text{tip–in}} )</td>
<td>Vessel inlet to the capillary distance</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( L_v )</td>
<td>Length of vessel</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( L_{\text{RE}} )</td>
<td>Flow recirculation length in sudden expansion</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( L_{\text{Gr}} )</td>
<td>Capillary tip to ground electrode distance</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( L_{\text{Apex}} )</td>
<td>Distance between the capillary tip and the location of jet emission (height of the cone)</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( L_{\text{off}} )</td>
<td>Offset of the cone with respect to capillary’s centerline</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( L_j )</td>
<td>Length of jet</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( L_{\text{d–Gr}} )</td>
<td>Droplet to ground distance</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( L_{\text{fl}} )</td>
<td>Flight path length</td>
<td>([\text{m}])</td>
</tr>
<tr>
<td>( L_{\text{sol}} )</td>
<td>Latent heat of solution</td>
<td>([\text{J kg}^{-1}])</td>
</tr>
<tr>
<td>( m_d )</td>
<td>Droplet mass</td>
<td>([\text{kg}])</td>
</tr>
<tr>
<td>( m_{\text{gs}} )</td>
<td>Mass of gas at droplet surface</td>
<td>([\text{kg}])</td>
</tr>
</tbody>
</table>
\( m_{vs} \) Mass of vapor solution at droplet surface [kg]

\( M_v \) Vapor’s molecular weight [kg mol\(^{-1}\)]

\( \dot{m} \) Vapor diffusion rate across the droplet [kg s\(^{-1}\)]

\( \dot{m}_0 \) Constant diffusion rate across the droplet [kg s\(^{-1}\)]

\( \dot{m}_{st} \) Corrected evaporation rate of droplet by Stefan flow [kg s\(^{-1}\)]

\( \dot{m}_c \) Convective evaporation rate of droplet [kg s\(^{-1}\)]

\( m/z \) Ion mass to number of charges [kg]

\( \text{Nu} \) Nusselt number

\( \text{Oh} \) Ohnesorge number

\( P_g \) Pressure of gas [N m\(^{-2}\)]

\( P_{gs} \) Partial pressure of gas at droplet surface [N m\(^{-2}\)]

\( P_v \) Vapor’s partial pressure [N m\(^{-2}\)]

\( P_{vs} \) Partial pressure of vapor solution at droplet surface [N m\(^{-2}\)]

\( P_{Sat} \) Saturation pressure at flat surface of a liquid [N m\(^{-2}\)]

\( P_{stp} \) Pressure of gas at standard conditions [N m\(^{-2}\)]

\( P_{eq} \) Kelvin equilibrium pressure of a liquid [N m\(^{-2}\)]

\( q \) Jet inertia over gas inertia

\( q_d \) Droplet charge [C]

\( q_{RL} \) Droplet charge at Rayleigh limit [C]
\( Q_{\text{ind}} \) Reading of Volumetric flow rate at rotameter \([\text{m}^3 \text{s}^{-1}]\)

\( Q_{\text{sol}} \) Solution volumetric flow rate \([\text{m}^3 \text{s}^{-1}]\)

\( Q_{\text{stp}} \) Standard volumetric flow rate \([\text{m}^3 \text{s}^{-1}]\)

\( R_0 \) Initial droplet radius \([\text{m}]\)

\( r_c \) Outer radius of the capillary \([\text{m}]\)

\( R_d \) Droplet radius \([\text{m}]\)

\( r \) Distance from the center of an evaporating droplet \([\text{m}]\)

\( r_{\text{Ex}} \) Flow expanding radius \([\text{m}]\)

\( r_{\text{ion}} \) Radius of circular ion path \([\text{m}]\)

\( r_{\text{qdl}} \) Half of distance between the opposing rods in a quadrupole mass spectrometer \([\text{m}]\)

\( \mathcal{R} \) Ideal gas constant \([\text{kg m}^{-3}]\)

\( r, z \) Location parameters in an axisymmetric Cylindrical coordinates \([\text{m}]\)

\( \text{Re}_{\text{cyl}} \) Flow Reynolds past a cylinder

\( \text{Re}_{\text{in}} \) Inlet flow Reynolds to the vessel

\( \text{Re}_j \) Jet Reynolds number

\( S \) Droplet surface area \([\text{m}^2]\)

\( S_0 \) Initial droplet surface area \([\text{m}^2]\)

\( \text{Sc} \) Schmidt number
Sh  Sherwood number

Scfh  Standard cubic feet per hour (volumetric unit of a unit)

Slpm  Standard liter per minute (volumetric unit of a unit)

t  Time  [s]

t*  Non-dimensional time

ts_c  Jet collapsing time  [s]

t_r  Charge relaxation time  [s]

T  Temperature  [K]

T_\infty  Gas temperature (far from the surface)  [K]

T_{ref}  Averaged reference temperature (film temperature)  [K]

T_s  Droplet temperature (surface temperature)  [K]

T_g  Temperature of gas  [K]

T_c  Critical temperature  [K]

T_{stp}  Temperature of gas at standard conditions  [K]

u  Droplet velocity component in the x direction  [m s^{-1}]

u_j  Jet velocity  [m s^{-1}]

u_g  Crossflow gas/air velocity  [m s^{-1}]

U_{rel}  Relative Velocity  [m s^{-1}]

U_{in}  Average inlet velocity  [m s^{-1}]

xxv
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_{\text{Avg}}$</td>
<td>Average gas velocity in each cross section</td>
<td>$[\text{m s}^{-1}]$</td>
</tr>
<tr>
<td>$u_{\text{ion}}$</td>
<td>Ion velocity</td>
<td></td>
</tr>
<tr>
<td>$V$</td>
<td>Electric potential</td>
<td>$[\text{V}]$</td>
</tr>
<tr>
<td>$V_{\text{on}}$</td>
<td>Onset voltage</td>
<td>$[\text{V}]$</td>
</tr>
<tr>
<td>$V_c$</td>
<td>Applied voltage to the capillary tip</td>
<td>$[\text{V}]$</td>
</tr>
<tr>
<td>$V_{\text{Dir}}$</td>
<td>Direct potential in a quadrupole mass spectrometer</td>
<td>$[\text{V}]$</td>
</tr>
<tr>
<td>$V_{\text{RF}}$</td>
<td>Zero to peak amplitude of RF voltage in a quadrupole mass spectrometer</td>
<td>$[\text{V}]$</td>
</tr>
<tr>
<td>$w$</td>
<td>Droplet velocity component in the $y$ direction</td>
<td>$[\text{m s}^{-1}]$</td>
</tr>
<tr>
<td>$W_{\text{e_d}}$</td>
<td>Droplet Weber number</td>
<td></td>
</tr>
<tr>
<td>$W_{\text{e_j}}$</td>
<td>Jet Weber number</td>
<td></td>
</tr>
<tr>
<td>$x, y$</td>
<td>Location parameters in Cartesian coordinates</td>
<td>$[\text{m}]$</td>
</tr>
<tr>
<td>$x', y'$</td>
<td>Location parameters in a rotated Cartesian coordinates</td>
<td>$[\text{m}]$</td>
</tr>
<tr>
<td>$x^<em>, y^</em>$</td>
<td>Non-dimensional location parameters in Cartesian coordinates</td>
<td></td>
</tr>
<tr>
<td>$X, r$</td>
<td>Location parameters in an axisymmetric Cylindrical coordinates</td>
<td>$[\text{m}]$</td>
</tr>
<tr>
<td>$x_1, x_2$</td>
<td>Mole fraction of water and methanol in the solution</td>
<td></td>
</tr>
<tr>
<td>$y_{\text{gf}}$</td>
<td>Mass fraction of gas/air in the film mixture</td>
<td></td>
</tr>
<tr>
<td>$y_{\text{vo}}$</td>
<td>Mass fraction of vapor solution far from droplet surface</td>
<td></td>
</tr>
<tr>
<td>$y_{\text{vf}}$</td>
<td>Mass fraction of vapor solution in the film mixture</td>
<td></td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>$y_{vs}$</td>
<td>Mass fraction of vapor solution at droplet surface</td>
<td></td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>Jet angle</td>
<td>[Deg]</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>Initial plume angle</td>
<td>[Deg]</td>
</tr>
<tr>
<td>$\alpha_3$</td>
<td>Plume bending angle</td>
<td>[Deg]</td>
</tr>
<tr>
<td>$\alpha_4$</td>
<td>Dispersed plume angle</td>
<td>[Deg]</td>
</tr>
<tr>
<td>$\beta_0$</td>
<td>Jet initial emission angle with respect to the y axis</td>
<td>[Deg]</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>Time step of the numerical solution</td>
<td>[s]</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Solution electric permittivity</td>
<td>[F m$^{-1}$]</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Free space, or vacuum, electric permittivity</td>
<td>[F m$^{-1}$]</td>
</tr>
<tr>
<td>$\varphi_0$</td>
<td>Relative velocity angle with respect to the x axis</td>
<td>[Deg]</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Electrical conductivity</td>
<td>[S m$^{-1}$]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Mean free path of gas</td>
<td>[m]</td>
</tr>
<tr>
<td>$\lambda_j$</td>
<td>Perturbation wavelength of jet</td>
<td>[m]</td>
</tr>
<tr>
<td>$\mu_g$</td>
<td>Dynamic viscosity of gas/air</td>
<td>[kg s$^{-1}$ m$^{-1}$]</td>
</tr>
<tr>
<td>$\mu_j$</td>
<td>Jet dynamic viscosity</td>
<td>[kg s$^{-1}$ m$^{-1}$]</td>
</tr>
<tr>
<td>$\rho_d$</td>
<td>Droplet density</td>
<td>[kg m$^{-3}$]</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>Crossflow gas/air density</td>
<td>[kg m$^{-3}$]</td>
</tr>
<tr>
<td>$\rho_j$</td>
<td>Jet density</td>
<td>[kg m$^{-3}$]</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
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<td>------</td>
</tr>
<tr>
<td>( \rho_{\text{sol}} )</td>
<td>Density of liquid solution</td>
<td>[kg m(^{-3})]</td>
</tr>
<tr>
<td>( \rho_{\text{stp}} )</td>
<td>Gas density at standard conditions</td>
<td>[kg m(^{-3})]</td>
</tr>
<tr>
<td>( \sigma_e )</td>
<td>Effective surface tension</td>
<td>[N m(^{-1})]</td>
</tr>
<tr>
<td>( \sigma_j )</td>
<td>Surface charge density of jet</td>
<td>[C m(^{-2})]</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Surface tension</td>
<td>[N m(^{-1})]</td>
</tr>
<tr>
<td>( \theta )</td>
<td>Half angle of Taylor cone</td>
<td>[Deg]</td>
</tr>
<tr>
<td>( \tau_{\text{surf}} )</td>
<td>Shear stress at surface</td>
<td>[N m(^{-2})]</td>
</tr>
<tr>
<td>( \nu )</td>
<td>Kinematic viscosity</td>
<td>[m(^2) s(^{-1})]</td>
</tr>
<tr>
<td>( \omega )</td>
<td>Angular frequency of RF in a quadrupole mass spectrometer</td>
<td>[Rad s(^{-1})]</td>
</tr>
<tr>
<td>( \omega_{\text{Max}} )</td>
<td>Maximum jet perturbation growth rate</td>
<td>[s(^{-1})]</td>
</tr>
</tbody>
</table>
Chapter 1

1 Introduction

1.1 Electrospray

1.1.1 History

The electrostatic cone formation of water droplets has been observed as early as 17th century. In 1731 Stephen Gray was the first one who noticed the emissions from the cone apex [1]. In the middle of 18th century, Abbe Nolet recorded a true electrospray (ES) experiment for the first time [1], [2]. He also observed if a person connected to a high voltage generator cuts himself, he would not bleed normally and the blood would spray from the wound [3]. Essentially, ES is a type of spray in which the fragmentation process takes place due to the applied electric pressure to the liquid at the tip of a nozzle. This electric force is induced to the liquid by applying high voltages to the nozzle, located in the vicinity of a grounded electrode. The first images of electrostatic atomization were captured in 1900s by John Zeleny, who also reported different operating modes [4], [5]

![Abbe Nolet’s ES setup](image1.png); ![One of the first images of an ES operating in the cone jet mode captured by John Zeleny](image2.png)
Efforts of recent researchers gave better understanding on the existence of various modes of electrospraying; namely: dripping, spindle, astable, cone jet, micro-dripping, multi-jet, and unstable [6]–[11]. Figure 1.2 summarizes electrospraying modes at different operating conditions. Among all of these modes, cone jet generates uniformly fine and charged droplets and operates with a good stability. These abilities have made the ES an excellent candidate for numerous industries, specially Mass Spectrometry (MS). Ink jet printing, paint spraying, combustion and fuel atomization, air pollutant control, crop spraying, surface coating, microfluidics, and MEMS are some of the other fields that ESs have found popularity [3], [12]–[16]. The cone jet mode is of more interest in our study; therefore, we mostly will concentrate on this mode.

---

**Figure 1.2 Various ES operation modes** [8]
1.1.2 ES Operation in the Cone Jet Mode

The process of ES operation in the cone jet mode is discussed in this section. Consider a capillary is located above a grounded electrode at a distance of $L_{Gr}$, Fig. 1.3a. Once an electric potential is applied to the tip of the nozzle, an external electric field is induced between the nozzle and plate. At the tip, this electric force pulls the liquid outward of the meniscus and changes its shape. Once the electrostatic pressure overcomes the surface tension, small droplets, ligaments, or fine spray(s) are ejected (depending on the solution properties and the electric field conditions) [6]–[11].

Sir Geoffrey Taylor [17] investigated a case, both theoretically and experimentally, where the surface tension and the electrostatic pressures are in a balance. Operating in the cone jet mode, he showed that the liquid at the meniscus takes a conical shape [17]. As shown in Fig. 1.3b, an electrical double layer forms at the liquid surface at the tip, due to the different migration rate of ions [18]. The thickness of this layer can be found using an excessive amount of ions with high mobility [3]. At the apex of the cone, so called “Taylor cone”, the electric field has its highest value. Therefore, an electrified jet is emerged from the apex, to satisfy the mass continuity. The induced electric field at the tip of a capillary, $E_c$, can be approximated with [19]:

![Figure 1.3](image_url)
\[ E_c = \frac{2V_c}{r_c \ln(4L_{Gr}/r_c)} \]  

(1-1)

where \( V_c \) and \( r_c \) are the applied voltage to the tip and capillary’s outer radius, respectively. Smith [18] derived the onset electric field at the nozzle tip, \( E_{on} \), for the cone jet mode:

\[ E_{on} \approx \left( \frac{2\sigma \cos \theta}{\varepsilon_0 r_c} \right)^{1/2} \]  

(1-2)

where \( \sigma \), \( \theta \), and \( \varepsilon_0 \) are the surface tension of the solution, the half angle of Taylor cone, and the permittivity of vacuum, \( \varepsilon_0 = 8.8 \times 10^{-12} \text{ J}^{-1}\text{C}^2\text{m}^{-1} \), respectively. Substituting Eq. 1-1 in Eq. 1-2, gives the onset voltage for the cone jet mode:

\[ V_{on} \approx \left( \frac{r_c \sigma \cos \theta}{2\varepsilon_0} \right)^{1/2} \ln(4L_{Gr}/r_c) \]  

(1-3)

Replacing \( \theta = 49.3^\circ \), from Taylor’s theoretical derivations, Eq. 1-3 becomes:

\[ V_{on} = 2 \times 10^5 (r_c \sigma)^{1/2} \ln(4L_{Gr}/r_c) \]  

(1-4)

According to this equation, as the surface tension increases, a higher potential for the operation of ES in the cone jet mode is required. But, high electric fields may diffuse the surrounding air and lead to electric discharge to the air. This phenomenon disrupts the ES operation and can prevent the cone jet mode. In fact, the high surface tension of water is the main obstacle in its electrospraying process [20]. An ES can operate in both polarities; however, in the negative mode, the electron emission occurs, which causes electric or corona discharge more frequently [21].

1.1.3 Droplet Generation

In this section, the process of droplet generation by an ES is described. An inviscid liquid jet initially experiences instability and then breaks up into single sized droplets. Rayleigh examined the instability of cylindrical jets and their breakup under the action of surface tension [22], [23]. As shown in Fig. 1.4a, the jet surface experiences a sinusoidal disturbance with a wavelength, \( \lambda_j \), that has the maximum perturbation growth rate, \( \omega_{Max} \) [24]. The amplitude of oscillation, \( a_J \), grows exponentially, until the surface waves meet in the middle and a droplet pinches off. Therefore, the
volume of each droplet is approximately equal to the volume of a jet column with the height of one wavelength. Using Rayleigh’s analysis, the wavelength and droplet diameter are determined:

\[
\lambda_j = 4.5d_j 
\]

\[
d_d = 1.89d_j 
\]

where \(d_d\) and \(d_j\) are droplet and unperturbed jet diameters, respectively. The experiments on ESs have also shown the generation of tiny satellite droplets in the breakup process; however, the effect of these small droplets on the main droplet size is only become significant for highly viscous liquids [24].

**Figure 1.4** Left: geometry of a liquid jet due to Rayleigh instabilities; Middle: the emission of an electrified jet from the tip of Taylor cone and its breakup; Right: dispersion of the electrospayed droplets and plume formation

The breakup of charged liquid jets has also been studied, both theoretically and experimentally, by several researchers [25]–[29]. Cloupeau and Prunet-Foch [26] compared their electrospayed
droplet sizes with Eq. 1-5 and reported a good agreement. On the other hand, some researchers reported generation of smaller sizes, with electrified jets [27], [30], [31]. Huebner and Chu [31] employed small perturbation analysis to formulate Lagrangian differential equation for the electrified jet. They showed $\omega_{\text{Max}}$ increases from 0.69 to around 0.75 for an electrified jet. Thus, the perturbation wavelength and droplet size become:

$$\lambda_j \approx 4.2d_j \quad (1-7)$$

$$d_d \approx 1.76d_j \quad (1-8)$$

Based on the assumption that disturbance corresponds to $\omega_{\text{Max}}$, the oscillation amplitude is expected to grow exponentially with time. Thus, the length of an inviscid jet until it breaks is calculated as [32]:

$$\frac{L_j}{d_j} = 1.04C\sqrt{We_j} \quad (1-9)$$

where, $C$ is a constant estimated from experiments. $We_j$ is the Weber number of jet and is a measure for jet inertia over surface tension:

$$We_j = \frac{\rho_j u_j^2 d_j}{\sigma} \quad (1-10)$$

where, $\rho_j$, and $u_j$ are the density of working solution, and the velocity of the jet, respectively. In an uncharged jet, the experimental data of Grant and Middleman [33] shows a good agreement with the theoretical analysis once $C=13$. The jet viscosity plays a damping role on the jet perturbation and therefore increases the break up time and jet length [32]. In order to include the effect of viscosity, Eq. 1-9 can be refined with:

$$\frac{L_j}{d_j} = C\sqrt{We_j} \left( 1 + 3 \frac{\sqrt{We_j}}{Re_j} \right) = C\sqrt{We_j}(1 + 3 \text{Oh}) \quad (1-11)$$

where, $Re_j$, and $Oh$ are the Reynolds number of jet and Ohnesorge number, respectively. $Re_j$ gives the ratio of inertia over viscous forces and $Oh$ relates the viscous forces to the surface tension and inertial forces:
\[ \text{Re}_j = \frac{\rho_j u_j d_j}{\mu_j} \]  
\[ \text{Oh} = \frac{\mu_j}{\sqrt{\rho_j \sigma d_j}} \]  

(1-12)  
(1-13)

where, \( \mu_j \) is the viscosity of working solution. One should note that the length of emitted jet in ESs, depends on the conductivity of the operating solution as well [34].

In the cone jet mode, the generated charged droplets from the emitting electrified jet, form a plume. This plume is significantly larger in comparison to the emitting jet. This process is illustrated in Fig. 1.4b-c. Figure 1.5 shows the results of a recent experimental study on the generated droplet size with an ES [25], which are consistent with Eq. 1-8.

![Figure 1.5 Diameter of electrosprayed droplets versus their electrified jet diameter](image)

**Figure 1.5 Diameter of electrosprayed droplets versus their electrified jet diameter**

The charge of a generated droplet, \( q_d \), has a great influence on its motion in an established electric field. Different suggestions have been proposed to estimate the charge, or the charge to mass ratio of droplets, \( \left( \frac{q}{m} \right)_d \), which will be presented in §1.1.5. Similar to the droplet size analysis, we assume the charge on a droplet is equal to the charge of the jet on any given undulation of
wavelength, $\lambda_j$. This assumption is true if the charge relaxation time on the jet is smaller than the droplet generation time, i.e. the charge transfers faster than the liquid [27]. Thus, the surface charge density of a jet can be represented as:

$$\sigma_j = \frac{q_d}{\pi d_j \lambda_j} = \frac{0.076 q_d}{d_j^2}$$  \hspace{0.5cm} (1-14)$$

$$\sigma_j = 0.075 \rho_j d_d \left( \frac{q}{m} \right)_d$$  \hspace{0.5cm} (1-15)$$

One should note that the generation of satellite droplets among main droplet, or during the jet breakup, can appreciably reduce the transferred charge on the main droplets [35].

1.1.4 Coulombic Fission

Generated droplets experience evaporation during their traveling time in the air. The emission of ions from the solution to the gas phase is highly endoergic; therefore, droplets do not lose the charge during the vaporization [36]. As a result, the surface charge density increases for the shrinking droplets. At a certain size, the charge repulsion on the surface of an evaporating droplet exceeds the surface tension and makes the droplet unstable. The charge in which a single droplet loses its stability was calculated theoretically by Lord Rayleigh [37]. Assuming the surface tension and electric pressure are equal at this diameter, the maximum charge on a stable droplet, so called Rayleigh limit, is estimated with:

$$q_{RL} = 2\sqrt{2}\pi \varepsilon_0 \sigma d_d^3 \frac{1}{2}$$  \hspace{0.5cm} (1-16)$$

As shown in Fig. 1.6, once the charge repulsion overcomes the surface tension, the droplet surface instantaneously deforms to a conical shape and a stream of finer droplets are emitted. This process is called coulombic fission. Recently, Duft et al. [38] showed that this fission occurs exactly at the Rayleigh limit. According to Tang and Gomez [39], fission leads to the loss of 2% of mass and 15% of charge of the mother droplet. As a result, the residue droplet has a lower charge density. The evaporation and fission process continue for the mother and the daughter droplets until the gas phase ions are produced [36]. The ion generation theories will be discussed in §1.2.2.
1.1.5 Droplet Charge

The initial charge of droplets is crucial for the prediction of coulombic fission and droplet motion. De la Mora and Loscertales [41] suggested the following equations for the current, droplet radius, and charge, respectively, based on the experimental results and theoretical reasoning:

\[
I = f\left(\frac{\varepsilon}{\varepsilon_0}\right)\left(\sigma\kappa_{sol}\frac{\varepsilon}{\varepsilon_0}\right)^{1/2}
\]

(1-17)

\[
d_d \approx (Q_{sol}\varepsilon/8\kappa)^{1/3}
\]

(1-18)

\[
q_d \approx 0.7q_{RL} = 0.7\left[2\sqrt{2}\pi(\varepsilon_0\sigma d_d^3)^{1/2}\right]
\]

(1-19)
where, $\varepsilon$, $\kappa$, and $Q_{\text{sol}}$ are the electric permittivity, conductivity, and volumetric flow rate of the working solution, respectively. The value of the numerical function $f(\varepsilon/\varepsilon_0)$ is approximately 18, when the solution dielectric constant, $\varepsilon/\varepsilon_0$, is greater than 40.

Many authors have found relationships for the charge to mass ratio of the electrohydrodynamically produced droplets; instead of a correlation for charge. Among them, suggestions of Vonnegut and Neubauer [42], and Jones and Thong [19] have become more popular:

$$\left(\frac{q}{m}\right)_d = \begin{cases} 
\frac{6\sqrt{2}\varepsilon_0\sigma}{\rho_d d_d^{1.5}} & \quad [\text{Vonnegut and Neubauer}] \\
\frac{27\sqrt{2}\varepsilon_0 E_c}{2 \rho_d d_d} & \quad [\text{Jones and Thong}] 
\end{cases}$$  \hspace{2cm} (1-20)

1.1.6 Droplet Evaporation

In this section, the droplet evaporation process is introduced and its evaporation rate is evaluated. A similar approach to Fuchs [43], based on Maxwell’s equation is taken here. Maxwell [44] considered a stationary spherical droplet in a still, uniform, and infinite medium. The rate of diffusion across the droplet is expressed as:

$$\dot{m} = 4\pi r^2 \frac{dc}{dr} D$$  \hspace{2cm} (1-22)

in which $r$, $c$, and $D$ are the distance from the center of the droplet, vapor concentration, and vapor diffusion coefficient, respectively. Integrating Eq. 1-22 with respect to $c$ and $r$, and applying the concentration boundary conditions, gives Maxwell’s equation:

$$\dot{m} = \dot{m}_0 = -4\pi R_d D (c_0 - c_\infty)$$  \hspace{2cm} (1-23)

where, $c_0$, and $c_\infty$ are vapor concentration values at droplet surface, and far from the surface, respectively. Maxwell assumed the vapor concentration at the surface is equal to its equilibrium concentration. Using $\dot{m}_0$ in this equation emphasizes that the diffusion rate for a stationary droplet evaporation is constant and the negative sign shows the mass loss during the evaporation. Rewriting Eq. 1-23 at the droplet’s surface with time, $t$, results in:
\[
\frac{dR_d^2}{dt} = -\frac{2D}{\rho_d} (c_0 - c_\infty)
\]  \hspace{1cm} (1-24)

\[
R_0^2 - R_d^2 = \frac{2D}{\rho_d} (c_0 - c_\infty) t
\]  \hspace{1cm} (1-25)

\[
S_0 - S = \frac{8\pi D}{\rho_d} (c_0 - c_\infty) t
\]  \hspace{1cm} (1-26)

where, \(R_0\), \(S_0\), and \(S\) are initial droplet radius, initial and instantaneous droplet surface area, respectively. Assuming the vapor obeys the ideal gas law, the vapor concentration becomes:

\[
c = \frac{P_v M_v}{\gamma R T}
\]  \hspace{1cm} (1-27)

where, \(M_v\), \(P_v\), \(\gamma\), and \(T\) are molecular weight, partial vapor pressure, ideal gas constant, and temperature, respectively. Applying Eq. 1-27 in Eq. 1-25 gives:

\[
R_0^2 - R_d^2 = \frac{2DM_v}{\gamma R \rho_d} \left(\frac{P_0}{T_0} - \frac{P_\infty}{T_\infty}\right) t
\]  \hspace{1cm} (1-28)

Considering the temperature of droplet is constant, the relationship between radius squared and time is linear. Besides, the time for complete evaporation of droplet becomes proportional to its initial radius squared, or the initial surface area. The rate of evaporation is slow in the beginning and increases as the droplet shrinks. This equation is fairly precise for large droplets and shows a good agreement with experimental data [43]. One should notice that the assumptions made by Maxwell are valid for droplets significantly larger than the mean free path of the vapor molecules. For very small droplets, the equation should be treated carefully and errors and suitable corrections needs to be considered. To improve the Maxwell’s equation, some other effects and corrections can be considered. These are: temperature depression, Kelvin effect, Fuchs effect, Stefan flow, and wind factors. The description of these effects is presented in Appendix A.

### 1.2 Electrospray in Mass Spectrometry

At 1967, Erwin Neher discussed various methods, including ES, for the generation of macromolecules aerosol as the source for MS [45]. The first combination of ES ion source and MS
was performed by Dole et al. [46], which showed molecules as heavy as 51000 Daltons can be electrospayed. The work that turned the electrospray ionization (ESI) to a recognized technique for MS was reported at Yale by Yamashita and Fenn [47] in 1984. Their developed ES ion source was used with a quadrupole mass spectrometer. At the same time at USSR, Aleksandrov et al. also developed and reported the operation of an ES ion source with a magnetic sector mass spectrometer [12]. Soon enough, ESI replaced the other ionization methods such as fast atom bombardment and plasma desorption, which needed high energies. ESI is operated in atmospheric pressure, gives higher sensitivity in comparison with the previous methods, and has overcome the problems in analyzing the high molecular weight compounds. The development of ESI for the analysis of biological macromolecules was rewarded with a quarter of Nobel Prize in Chemistry to John Bennett Fenn in 2002 [48].

In ESI-MS, the ultimate goal is to bring single ions to the detector, through a mass spectrometer. A conventional ESI source consists of two separate but interdependent parts; namely: the atmospheric region and vacuum interface. The first region includes the ES nozzle and supplementary components. The latter usually includes set of skimmers, vacuum levels, and a Radio Frequency (RF) ion guide. These component provide a means for ion introduction into the mass spectrometer. In this study we focus on the atmospheric region, and prediction of the best operating conditions.

One of the key factors in MS is the size of generated ions (charged particles). Generally, the smaller the droplets the higher the sensitivity, because the evaporation of the solution and generation of gas phase ions become faster. The method of introducing the ions into the mass spectrometer also plays an important role. Different ways of guiding the ions to the inlet, such as vacuum layers [12], Differential Mobility Analyzer (DMA) [49], coaxial gas or liquid flow [50], [51], have been investigated and resulted in improvements in the sensitivity and stability of detections. Recently, a novel device has been built by Jolliffe et al. [52] and has made further improvements in ESI-MS in different aspects. More details on this device will be provided in §1.3.3. In the next section, detailed discussion on the generation of single ions, their path toward the detector of a mass spectrometer, and other involved phenomena, are provided.
1.2.1 Ions: From ES Nozzle to Mass Spectrometer Detector

The term “ion” is used for a charged particle, either it is made of one or more charged molecules, e.g. the charged droplets sometimes are called ions. Here we use “single ion” in order to specifically denote a single charged molecule. A better detection can be delivered in MS with arrival of as many as single gas phase ions to the detector of the mass spectrometer. Once the charged droplets are produced by the ES, the goal is to transport desolvated ions into the analyzer. In this process, the ions should be sampled by an orifice inside the ESI source and be driven into the analyzer. Figure 1.7 depicts an example of ions mobilization from an ES capillary to the detector, through a triple stage quadrupole mass spectrometer (TQMS).

1.2.1.1 Ions inside an ESI Source

As mentioned before, an ESI source includes both the ion generator at the atmospheric pressure, and the ion sampling orifice at vacuum. The way of introducing ions from the ES nozzle to the sampling section, plays an important role in the detected sensitivity, stability, and signal to noise ratio (SNR). One of the important parameters is the positioning of the ES capillary with respect to the sampling orifice and spectrometer’s inlet. In fact, the designers of ion-sampling orifices and vacuum systems for atmospheric pressure ionization (API) and ESI-MS systems, need to overcome two issues: 1- the transport of ions from the atmospheric region into the vacuum system of the mass spectrometer, 2- the condensation of solvent vapors during the expansion in the vacuum [36]. Yamashita and Fenn [47], located the nozzle at the center in front of the sampling orifice. Later
on, other investigators studied the change of angle and location of the nozzle, resulting in better detection rates. Complete droplet desolvation is more likely to happen at the perimeter of the plume and not in the core region. Therefore, off-axis positioning of the spray with respect to the sampling orifice can improve the results by introducing the ions from the plume periphery. A diagonal positioning with the spray aimed at one centimeter offset of the orifice, reduces the chance of droplets entering directly to the mass spectrometer. In other words, the larger droplets have less chance to enter the analyzer and only the smaller ones are sucked in by the vacuum, due to their lower inertia. In this case, the detected stability is improved without losing the sensitivity. It is worth mentioning that this positioning is more effective for ESs with pneumatic and ultrasonic assistance. For µESs, the capillary is located exactly on the axis with few millimeters distance from the sampling orifice. The distance between the sprayer and the orifice for a regular ES and a pneumatically assisted ES are usually around 1 and 2 cm, respectively. The extreme case of angled positioning is the orthogonal configuration, as shown in Fig. 1.7. For a thorough literature review on the positioning and geometry of ion sources, the reader is referred to [36], [51], [54].

To overcome sampling issues, a system, called Hot Source Induced Desolvation (HSID) interface, has been developed by IONICS that does not sample ions in free expansion [55]. This device is located between the spray and the mass spectrometer. Free jet expansion of ion flow is decreased in HSID as laminar and turbulent flows and high temperatures are adopted. Also the special geometry of HSID reduces ion dispersion and, therefore, the ion loss.

1.2.1.2 Mass Spectrometers

A mass spectrometer, or analyzer, is a device that determines the molecular mass of the single ions. Once the ions enter the spectrometer, the single gas phase ions should be separated and guided to the detectors for the mass analysis. In this section of the thesis, a popular type of analyzer is introduced and its working procedure is described. For more information on some other types of mass spectrometers, see Appendix B. One should note that each type of mass analyzers has its own benefit and should be selected based on the application.

1.2.1.2.1 Quadrupole Mass Spectrometer

As the name suggests, the quadrupole consists of four parallel metal rods. The ions travel between these rods. Each opposing pair of rods is connected electrically, and a radio frequency (RF) voltage is applied between the two pairs. A direct current voltage is then superimposed on the RF voltage.
The quadrupole uses the stability of ion trajectories in an oscillating electric field to separate ions based on their mass to charge ratio, m/z [56]. In other words, only the ions with a specific range of m/z can travel between the rods, where the rest deflect and move out of this path. The equations of motion in Cartesian coordinates between quadrupoles and along its axial direction are:

\[
\frac{d^2x}{dt^2} + \frac{2ze}{m r_{qd}^2} (V_{\text{Dir}} - V_{\text{RF}} \cos \omega t) x = 0 \\
\frac{d^2y}{dt^2} + \frac{2ze}{m r_{qd}^2} (V_{\text{Dir}} - V_{\text{RF}} \cos \omega t) y = 0
\]

(1-29) (1-30)

in which \(z\), \(e\), \(r_{qd}\), \(V_{\text{Dir}}\), \(V_{\text{RF}}\), and \(\omega\) are the charge on the ion, elementary charge, half of the distance between opposing rods, direct potential, zero to peak amplitude of RF voltage, and the angular frequency of RF, respectively. Single quadrupole mass spectrometers have been used more widely than the others for ESI. Their advantage is the low cost and relative reliability, although it gives low resolution results. To improve the results and structural analysis, a TQMS can be adopted. This spectrometer has been used for the majority of quantitative analysis with ESI-MS [12]. According to Fig. 1.7, the three stages in TQMS are: a first stage quadrupole for precursor ion selection, a RF-only quadrupole as a collision region, and a second stage quadrupole for product ion analysis. The survived ions hit the detectors and produce a distribution for mass to charge ratio. Using the given spectrum, the molecular weight of the sample is calculated [12], [36].

1.2.2 Ion Generation Theories

In this section the suggested processes for the generation of single gas phase ions are explained in more details. As a charged droplet evaporates, Coulombic fission repeats for the parent, residue and child droplets, until the gas phase ions are produced. There are two well-known mechanisms describing formation of gas phase ions, Fig. 1.8; namely: Charged Residue Method (CRM), and Ion Evaporation Model (IEM). In the former, proposed by Dole [46], charged droplets experience consecutive Coulombic fissions until a droplet contains only one ion; hence the solution of the droplet evaporates, and a single gas phase ion remains. In the second mechanism, introduced by Iribarne and Thomson [57], [58], droplets undergo fission until reaching a specific radius, ~10 nm. Below this size, the evaporation of the ions from the surface becomes dominant over the solution evaporation. In other words, at these sizes, the required energy for the escape of a single ion from
the surface is less than the required energy for the solution evaporation. It is worth mentioning that formation of macroions cannot be well described with the latter mechanism. During the evaporation of the solvent, the large size of single macroions makes their escape from the surface of nanometric droplets hard. Therefore, it is more probable that these ions undergo CRM mechanism. Due to very small size of the droplets during the production of gas phase ions, no experimental observation has been performed to support any of the models. Therefore, both of these mechanisms are accepted to some extent, based on the other measurements and captured evidence. More discussion on this topic can be found in [36], [59].

1.2.3 Corona Discharge

Corona discharge takes place, when the potential at the nozzle tip is too high and exceeds the permittivity of the surrounding medium, e.g. air. This electric discharge results in the detection of products of ion-molecule reactions in the spectrum. At the same time many existing ions in the
solution cannot be detected. Besides, during a discharge both positive and negative ions are generated and will recombine with the droplets holding the opposite charge [36]. These droplets will have smaller charges, and will not undergo coulombic fission. Thus smaller number of ions will reach the detector of the mass spectrometer, resulting in a lower sensitivity.

Electrospraying can be disturbed by corona discharges in both polarities; however, due to field emission of electrons from a sharp point, it happens easier and in lower potential if the ES needle operates at the negative polarity [36]. To reduce the chance of discharge, our ES is operated at the positive ion mode. Usually, current measurements above 1 µA indicate the presence of electric discharge. When spontaneous corona discharges are initiated at the outlet of the capillary, they reduce the electric field and generally establish a spurious phenomenon [26]:

i- If they occur before the onset voltage for the cone jet mode is achieved, they prevent the establishment of this mode. This phenomenon occurs especially with liquids having a high surface tension.

ii- If they occur once the cone jet mode has been established, fluctuations in the discharge current often prevent the conservation of steady-state conditions. However, if the voltage is increased, the discharge current can become regular and the stable cone jet mode can reappear as a result of the reduction of the field due to the space charges.

Rousse [60] investigated the onset electric field for discharge, $E_{\text{dis}}$, using different wire sizes and suggested the following relations [61]:

$$E_{\text{dis}} = \begin{cases} 3 \times 10^6 \left(1 + \frac{0.03}{r_c^{0.5}}\right) & [r_c > 100 \ \mu\text{m}] \\ 6.27 \times 10^6 + \frac{5502}{r_c^{0.75}} & [15 \ \mu\text{m} < r_c < 100 \ \mu\text{m}] \end{cases} \quad (1-32)$$

$$E_{\text{dis}} = \begin{cases} 3 \times 10^6 \left(1 + \frac{0.03}{r_c^{0.5}}\right) & [r_c > 100 \ \mu\text{m}] \\ 6.27 \times 10^6 + \frac{5502}{r_c^{0.75}} & [15 \ \mu\text{m} < r_c < 100 \ \mu\text{m}] \end{cases} \quad (1-33)$$

1.3 Interaction of Electrospray and Gas Flow

In this section, a literature review on ESs coupled with gas flows, with a higher emphasis on the visual investigations, is provided. The effects of the air crossflow on the ordinary sprays and liquid jets are explained as well.
1.3.1 Background

Visual studies on ES plume are limited, in comparison to the amount of research on the topic. Besides, most of the investigations have been performed without any airflows. Park et al. [62] visualized the effect of different solution flow rates and guard plates on the plume angle and the onset voltage for cone jet mode, with a CCD camera and an Argon ion laser sheet. Independent of the assembled guard plates, they reported similar electric field at the nozzle tip for the cone jet mode; but different plume dispersion angles were observed, as different guard plates induce different electric fields in the space. In addition, using the conductive guard plate gave a bigger range of the onset voltages. Wang et al. [34] visualized the effect of surface tension and ionic strength of the spraying solution on the plume angle and jet breakup length, using a high speed camera. The results showed good agreement with their derived theoretical correlations.

One of the recent studies on the interaction between air and ES, was performed in our group. This study illustrated the role of nebulizing or coaxial air flow in an ES performance in the spindle, cone jet and unstable modes [25]. Images were captured with a DSLR camera, and a nanoflash light. Spray characteristics such as size and velocity were analyzed, using a PDPA system, at both no air and with air conditions. With the nebulizing air, the droplets (specially the smaller ones) experience higher axial velocity and lower radial velocity, which is equivalent to less dispersion and more confinement. A slight shift toward the larger sizes were recorded in the cone jet and spindle modes. This shift was attributed to the pressure of air around the Taylor cone leading to a thicker jet emission from the cone. On the other hand, higher number of smaller droplets were generated due to the suppression of whipping motion by the coaxial air. Savtchenko et al. [63] numerically compared the traveling path and other characteristics of the droplets, including desolvation gas with or without swirl. The droplets were produced by an ES or Atmospheric Pressure Chemical Ionization (APCI) nebulizer spray. The simulated ion source had three coaxial channels, designed for: the spraying liquid, a nebulizer gas at room temperature, and a high temperature desolvation gas, respectively from the center. It was shown that the swirl helps the droplets to penetrate more in the axial direction, with increasing the confinement. Also, adding the swirl increases the temperature in the inner region and, thus, larger droplets evaporate faster than the no swirl case.
Wang et al. [64] studied the effect of high speed nebulizer gas, varying from subsonic to supersonic, on electrosonic spray ionization (ESSI) using ESSI-MS. For a neutral solution with low flow rates, the increase of the air velocity only accelerated the droplets; however, for high sample flow rates, droplets experienced breakups. They also simulated the flow pattern of the nebulizing air with respect to the ES plume and theoretically discussed the droplet acceleration and breakup conditions. Fomina et al. [14] developed a polycapillary ES source with nebulizing air to produce and transport charged droplets at high liquid flow rates. This source can be applied for detection of toxic material. In order to find the required crossflowing air to transport the droplets out of the field region, the influence of electric mobility and airflow on the velocity of charged droplets was estimated; but no images were captured to evaluate the behavior of the plumes.

1.3.2 Spray, Jet, or Droplet in Crossflow

Although we could not find any investigations on the interaction of an ES and a gas crossflow, many studies have focused on the behavior of liquid spray and jet in crossflow (JICF), mostly in combustion field. Similar to JICF, we adopt the term “ESICF” for “ES In CrossFlow”. Amighi et al. [65], [66] captured images of the atomization process and the dynamic of different liquid jets in high temperature and high pressure air crossflows and derived correlations for the trajectories, with image processing techniques. Mashayek and Ashgriz [67] derived a simple motion, or trajectory, equation for a jet introduced orthogonal into the gas crossflow. Their method was based on the force balance on an element of jet, resulted the following:

\[
\left( \frac{y}{d_j} \right) = \frac{u_j}{u_g} \sqrt{\frac{\pi \rho_j}{C_D \rho_g}} \left( \frac{x}{d_j} \right) \quad (1-34)
\]

where, \( u_g \), \( \rho_g \), and \( C_D \) are crossflow velocity, gas density, and drag coefficient, respectively.

Bai et al. [68], [69] visualized the mixing and velocity distribution of droplets, generated by one and two centrifugal nozzles, in the crossflow. They used PIV and photography to capture the spray behavior along the test section and also in different cross sections. Ghosh and Hunt [70] studied the interaction of the weak to moderate crossflows on the spray, considering the induced airflow by the spray. Depending on the crossflow velocity, different theoretical models for the behavior of the spray in crossflow were developed. Deshpande et al. [71] simulated the hollow cone sprays in
crossflow. Similar to Ghosh and Hunt, they discussed the spray’s behavior with respect to its distance from the emitter. The entrained air by spray can change the crossflow pattern, especially in the region close to the nozzle tip [70]. Tang and Gomez [72] measured the gas velocity for an ES operating at quiescent air. The measured values were less than 35% of the droplet velocity, for the average droplet size of larger than 10 µm. The induced airflow by the spray depends on the liquid flow rate (or velocity) and droplet sizes [70]. The effect of ES droplets and plume on the crossflow pattern, at low solution flow rate and small droplet sizes, is usually negligible. Therefore, the closest case to the ESICF is “spray in strong crossflow”. In this case, spray cannot entrain into the crossflow and therefore the leeward side of spray is deflected directly by the crossflow.

ESs have three main differences with the jets and sprays in the literature:

i- In an ES, the liquid flow rate and generated droplet sizes are usually much lower;

ii- The spray profiles and droplet size distributions are not alike, because the atomization processes are completely different;

iii- Besides the air drag, the external electric field and coulomb repulsion forces affect the motion of electrosprayed charged droplets.

Considering these points, the study on the ESICF is missed in the literature.

1.3.3 Electrospray Ion Desolvation Vessel

As mentioned earlier, the number of single ions carried to the mass spectrometer’s detector signifies the detection intensity. Jolliffe et al. [52] developed a chamber to inject the ES and allow the droplets to dissolve and evaporate before entering the mass spectrometer. As shown in Fig. 1.9, it includes: a chamber (II), a gas inlet into the chamber (I), an inlet for the ES nozzle at the top to introduce the ions (IV), and a converging outlet for the crossflowing gas to carry the generated ions to the analyzer (III). The chamber is made of conductive material and is grounded. The ES nozzle is fixed and operates inside this chamber and air flow carries the generated ions to the mass spectrometer through the outlet. The advantages of this ion source over the sources that adopt coaxial gas flow, are the ease in coupling with the sampling orifice of the mass spectrometer and better ion desolvation. In the other sources, the location of ES with respect to the sampling orifice affects the SNR, sensitivity, and stability [51]. Besides, these sources usually need additional position adjustments and ions do not dissolve completely at the spectrometer inlet, due to
insufficient droplet flight time. The desolvation vessel, because of its geometry, does not need additional adjustments and keeps the ions focused at its outlet. It also buys enough time for the generated charged droplets to dissolve completely into ions, before entering the analyzer. This device can be also coupled with HSID for further improvement of detection.

1.4 Objectives and Outline of the Current Study

A similar apparatus to the dissolvation vessel was built in order to investigate the performance of an ESICF inside the chamber. The main goal of our study is to determine the conditions that most ions are transported out of the vessel, toward the sampling orifice. The deformation of ES plume in air crossflow and inside the apparatus is investigated experimentally (Chapter 3). The effects of crossflow on the cone jet is also visualized. The theoretical prediction of the emitting electrified jet trajectory under the effect of a crossflow is another objective of our study. A 2D analytical solution for the trajectory is presented in chapter 4. Simulating and predicting the paths of ES plume and ions in the chamber is the other aim, which will help the users to find the proper conditions and geometries for ES operation. A numerical model is introduced for this purpose in chapter 5. Finally, the new findings, highlights, and suggestions of the current investigation are summarized in chapter 6. To the best of our knowledge, this is the first study on ESICF, which includes the effects of a gas crossflow on an ES plume, an electrified jet, the trajectories, and Taylor cone. In the next chapter, the experimental setup, and operating conditions is described.

Figure 1.9 An illustration of the desolvation vessel
Chapter 2

2 Experimental Setup and Procedure

An experimental setup was built to visualize the ES performance inside a test section. In this chapter, the design of test section is presented. Then, adopted components and their arrangements in order to run and record the experiments are shown. The test cases are presented and the image processing procedure is described.

2.1 Test Section

2.1.1 Design and Fabrication

The test section is a model of the desolvation chamber introduces in §1.3.3. To have a visual access and investigate the behavior of an ES inside the chamber, transparent materials were used. The model apparatus, Fig.2.1, was laser cut and machined at the original design size (10 × 10 × 19 mm³). The rectangular chamber of the model versus the circular cross section of original device was the only geometrical difference. As the cross section of the vessel is square shaped, its hydraulic diameter is 10 mm. Clear polycarbonate sheets were used as the body of the vessel and acrylic blocks were drilled for the gas inlet and outlet of the device. The rectangular design minimized the light deflection and gave us the ability to see the process, and capture images with proper lighting. The inlet and outlet diameters are 2.3 mm and 2.4 mm, respectively. The tapered outlet angle is 45° and the ES capillary was located at ~4 mm from the left wall. The apparatus, especially the windows, were replaced frequently, in order to keep the test section clean and sealed. To increase the speed of fabrication, an already existing clear box (16 × 16 × 19 mm³) was used as the body of the chamber. The original device is made of metal and is electrically grounded for ES operation. In our model, instead of grounding the body, a thin copper plate was glued to the bottom of the chamber and operated as the counter electrode.
As shown in Fig. 2.1, the air undergoes a sudden expansion at the entrance and a smoother tapered contraction at the outlet of vessel. The fabricated model has a long entrance channel, 60 mm; therefore, we can assume the air velocity profile at the inlet is fully developed [73]. In the abrupt expansion of a pipe, the inlet flow detaches from the wall. Due to the lower pressure next to the expansion steps, recirculation regions are generated, Fig. 2.2. According to experimental velocity profiles in the expanded part, the recirculation zone introduces a flow at the opposite direction of the main flow [74]. As we move in the downstream direction, the profile of this opposite airflow shrinks and its value decreases [74]. The recirculation region elongates up to the point that the main flow occupies the entire cross section and reattaches to the wall.
Figure 2.2 Top: a schematic illustration of sudden expansion process; Bottom: experimental results for velocity profiles at different cross sections [75]

The recirculation length depends on the inlet Reynolds number, expansion ratio, step height, $h_{\text{step}}$, and the length of the expanded chamber. In our tests, the Reynolds number of inlet air, based on the inlet velocity and diameter, was above 500. For Reynolds above this point, the ratio of the reattachment length to the step size has a minimum value of around 6 [74], [75]. The lengths of our vessels are shorter than 6 times of step height, for both of the model dimensions: $L_v/h_{\text{step}} = 19/3.85 \sim 5$, and $19/6.85 \sim 3$. In other words, the air reattachment takes place during the flow contraction at the tapered outlet and the recirculation region spreads along the whole length of vessel. Forrester and Evans [76] numerically investigated the effect of different geometrical
parameters on the airflow characteristics, in turbulent regime, inside a mixing reactor. Their reactor consists of a sudden expansion and a tapered contraction. Those results are consistent with our conclusion on the reattachment location. The ES nozzle itself might change the flow pattern at the higher half of the vessel, i.e. by introducing a wake region behind the nozzle. However, the imaged area of nozzle with respect to the chamber cross section is small and its effect on the air flow is most probably negligible.

### 2.2 Setup Components and Arrangements

Fig. 2.3 depicts the arrangement of electrical, optical and flow control systems. A platform was designed and built with extruded aluminum profiles (BOSCH Rexroth) and everything except the air flow panel and electrical system was kept on it for a better control of the optics and the ease in transporting the whole setup.

![Figure 2.3 A schematic illustration of the experimental setup](image)

#### 2.2.1 Liquid Spraying System

As shown in Fig. 2.4, the ES source includes two coaxial stainless steel tubes (Turbo Ion Sciex). The outer tube has been designed for a nebulizing gas, but no coaxial gas flow was used in this study. The ES source was connected to the platform, above the vessel, and its distance from the
centerline of the chamber was adjusted with a microscrew. A syringe pump (Series 74900 Cole Parmer) operating between 0.01 and 210 ml/hr with 0.01 ml/hr precision, supplied the liquid to the inner capillary of the sprayer, 150 µm ID and 300 µm OD.

A high voltage DC power supply (Series ER, Glassman High Voltage Inc.) applied the required potential to the ES emitter, up to +10 kV. A high voltage probe with the conversion factor of 1000 was built to measure the voltage. The electrical diagram of the fabricated probe is shown at Fig. 2.5. It consists of five 10 MΩ and one 50 kΩ resistors, soldered in series. Two ends of the resistors are connected to the tip at high voltage and the ground. The voltage difference between two sides of the 50 kΩ resistor is measured with a multimeter (GDM8145 Instek). The voltage reading precision was measured using a second multimeter (3435A Hewlett-Packard) and a HV Supply (Model 677B Trek), up to 2000 V. The error turned to be 2%, at the worst case.

![Figure 2.4 The geometry and dimensions of ion source tip](image)

![Figure 2.5 The electrical diagram of fabricated high voltage probe](image)
2.2.2 Air Control Panel

The air control panel consists of a pressure regulator, a filter, two rotameters for two different ranges of airflow (0-20 cfh King and 0-60 lpm Cole Parmer), and a miniature pressure gauge (0-30 Psi Noshok) to measure the outlet pressure of the operating rotameter. The rotameters were verified with an air flow calibrator (Definer220 DryCal) and the reading error turned to be less than 5%. This flow system supplies the carrier air to the inlet of the vessel. The regulator’s pressure was set to 20 Psig in all of the tests for consistency.

As listed in Table 2.1, the crossflowing air is divided into three categories based on the flow rate. This table also shows the operating flow rates, the outlet pressure of the rotameters, inlet velocities, and inlet Reynolds numbers. The standard flow rates were calculated with:

\[
Q_{\text{stp}} = Q_{\text{ind}} \left( \frac{\rho_g}{\rho_{\text{stp}}} \right)^{1/2} = Q_{\text{ind}} \left( \frac{\rho_g}{\rho_{\text{stp}}} \times \frac{T_{\text{stp}}}{T_g} \right)^{1/2}
\]

(2-1)

where \( Q, \rho, P, \) and \( T \) are flow rate, density, pressure, and temperature, respectively, and subscripts, stp, ind, and g, represent the standard conditions, rotameter’s indicator reading, and the flowing air, respectively [77]. The temperature of the air was measured in different tests and it was close to the standard value, 22 ± 3 ℃; therefore, the effect of temperature on the flow rate was neglected.

<table>
<thead>
<tr>
<th>Crossflow Air</th>
<th>Flow Rate [Cfh]</th>
<th>Pressure(^1) [Psig]</th>
<th>Flow Rate [Scfh]</th>
<th>Flow Rate [Slpm]</th>
<th>Velocity(^2) [m/s]</th>
<th>Reynolds(^2)</th>
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<tbody>
<tr>
<td>Low</td>
<td>2 - 10</td>
<td>0</td>
<td>2 - 10</td>
<td>0.95 - 4.72</td>
<td>3.8 -18.9</td>
<td>576 - 2882</td>
</tr>
<tr>
<td>Medium</td>
<td>10 - 20</td>
<td>0</td>
<td>10 - 20</td>
<td>4.72 - 9.44</td>
<td>18.9-37.9</td>
<td>2882 - 5764</td>
</tr>
<tr>
<td>High</td>
<td>&gt;20</td>
<td>&gt;0</td>
<td>&gt;20</td>
<td>&gt;9.44</td>
<td>&gt;37.9</td>
<td>&gt;5764</td>
</tr>
</tbody>
</table>

\(^1\) Room pressure: 14.4 ± 0.2 Psia

\(^2\) Calculated based on standard values and inlet diameter
2.2.3 Imaging Systems

A 13.5 Megapixels DSLR camera (D300 Nikon) with two different imaging systems was used to capture the ES plume and tip images, separately. At least two sets of six images were captured for each condition, at 6fps, using a wireless remote trigger. The second set was shot with a time delay, e.g. 1 min, to check the stability or repeatability of the results with time.

![Image of imaging and lighting systems]

**Figure 2.6 The configuration of imaging and lighting systems**

For the plume photography, a macro lens (AF Micro 60 mm Nikkor) coupled with 64 mm long extension tubes were used. As shown in Fig. 2.6a, a laser sheet was generated with passing a green laser beam (532 nm-50mw Intelite) through a cylindrical lens. In this arrangement, the laser plane and the camera view were perpendicular. A black metal plate was placed behind the test section as the background of plume images.

For the imaging of the capillary tip, Fig. 2.6b, a stereo microscope (SMZ-10 Nikon) and a camera flash (S13900 Nikon) with the flash duration of ~1 μs were adopted. The flash was located at the opposite side of the camera at 30° to 60° angle with respect to the viewing axis. The camera was operating at 2-2.5 μs shutter speed.

2.3 Experiment Cases and Operating Conditions

A JICF test was performed with a water jet inside the $10 \times 10 \times 19$ mm$^3$ vessel and images were captured with the nozzle tip located 3 mm above the centerline (see Appendix D). For the liquid
jet test, a 120 µm ID nozzle was adopted to run a water jet. Distilled water at 2 ml/min, equivalent to jet speed of 2.95 m/s, was used. This flow rate is three orders higher than the operating solution rates for the ES.

The behavior of ES plume was investigated at two different tip distances from the centerline: capillary 0.1 mm and 2.75 mm above the centerline. A 75/25 volumetric solution of methanol/water was chosen as the ES operating liquid. All of the operating modes, including the cone jet mode, could be captured with this solution. For dilute solutions, with less than 50% methanol, the steady plume was not observed due to high surface tension. The operating flow rates for the ES were kept at 1-2 µL/min. The air crossflow was varied from low to high airflows for all the cases (see Table 2.1).

The properties of the working solution have been listed in Table 2.2. The density of solution was calculated based on each component’s density and their ratio in the solution. The change of volume, due to mixing of two different soluble liquids, was neglected. Viscosities were measured with a Cannon-Fenske viscometer (Size #25). The measurement error of viscometer was less than 1%. As shown in Table 2.2, the viscosity of solution is higher than both pure components. The viscosity variation trend has been reported in the literature with measuring it at different methanol and water portions and temperatures [78]. This means that the intermolecular forces of the solution is stronger than its pure components, which prevents the sliding of molecules past each other and results in a more viscous fluid. The surface tension was calculated based on a proposed model by Chunxi et al. [79]. The reported electrical conductivity and permittivity values are the approximate values for pure water and methanol measured by different investigators [80], [81]. The conductivity is a measure of total released or existing ions inside a liquid; H⁺ and OH⁻ for water, CH₃⁺ and OH⁻ for methanol. Considering the portion of the released ions in the solution by each liquid is proportional to the molar fraction, the conductivity of solution can be approximated using their volumetric mixing percentage. The electric permittivity is a measure of the effect of an electric field on a medium. In other words, it indicates the polarization of material and the degree of response of molecules to the presence of an electric field. Considering a linear relationship based on the molar portion of each liquid in the solution, the permittivity can roughly be estimated with volumetric percentages of liquids. The property measurement results and calculations are provided in Appendix C.
Table 2.2 Properties of water (W), methanol (M), and 75% M-25% W volumetric mixture

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Density ρ [kg/m³]</th>
<th>Viscosity μ [Pa s]</th>
<th>Surface Tension σ [N/m]</th>
<th>Electrical Conductivity κ × 10⁴ [S/m]</th>
<th>Electrical Permittivity ε × 10¹⁰ [F/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>998.2</td>
<td>0.00108</td>
<td>0.07225</td>
<td>~0.54</td>
<td>~7.09</td>
</tr>
<tr>
<td>Methanol</td>
<td>792.1</td>
<td>0.00062</td>
<td>0.02295</td>
<td>~4</td>
<td>~2.66</td>
</tr>
<tr>
<td>75% M-25% W</td>
<td>843.6</td>
<td>0.00136</td>
<td>0.02544</td>
<td>~3.1</td>
<td>~3.77</td>
</tr>
</tbody>
</table>

The charge mobility and droplet breakup times in the operation of ES can be discussed based on the estimated properties of the solution. For a jet diameter of 3 microns, we have:

\[
\begin{align*}
    t_r &= \frac{\varepsilon}{\kappa} \sim 1.22 \mu\text{sec} \\
    t_c &= \sqrt{\frac{\rho d_j^2}{4\sigma}} \sim 270 \mu\text{sec}
\end{align*}
\]

where \( t_r \) and \( t_c \) are charge relaxation and jet collapsing time scales, respectively [29]. As the relaxation time is two orders of magnitude shorter, the charge and ions have enough time to settle on the surface of droplet, before the jet pinches off to form the droplet.

Based on our observation, in order to capture the cone jet mode, it is easier to first run the solution flow, and then increase the voltage to the onset value. Once the plume is achieved, the air crossflow can be added. We believe the wetting of the tip is one of the important parameters in ES performance and we will talk about it in Chapter 3. One of our test factors is the input sequence of voltage, solution flow, and air crossflow. Table 2.3 presents the order of applying these parameters in each sequence and the values of the mentioned parameters.
Table 2.3 List of tested input sequences for ESICF and their operating values

<table>
<thead>
<tr>
<th>#</th>
<th>Input Sequence</th>
<th>Voltage [kV]</th>
<th>Solution Flow Rate [μL/min]</th>
<th>Air Flow Rate [Slpm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Solution-Voltage-Crossflow</td>
<td>0-6</td>
<td>1-2</td>
<td>0-77</td>
</tr>
<tr>
<td>2</td>
<td>Voltage-Solution-Crossflow</td>
<td>2.81</td>
<td>2</td>
<td>0-77</td>
</tr>
<tr>
<td>3</td>
<td>Solution-Crossflow-Voltage</td>
<td>0-4.5</td>
<td>1</td>
<td>~4.7</td>
</tr>
</tbody>
</table>

2.4 Image Processing

The image processing was performed with an open source software, called ImageJ [82]. Before running the ES, background images were taken. In the beginning of post processing, these images were subtracted from the plume images to reduce the background noise. For a few sets, e.g. JICF case, the background was removed digitally by ImageJ. The adopted plugin called, “Rolling Ball Background Subtraction”. This plugin tries to correct uneven background by using a "rolling ball" algorithm. A local background value is determined for every pixel by averaging over a very large ball around the pixel. This value is hereafter subtracted from the original image. After the background removal, the brightness and contrast were adjusted automatically. This process is performed with setting the highest pixel intensity of the subtracted image to the highest value, e.g. 255 for an 8bit file. The other pixel intensities are also modified with respect to the mentioned adjustment.

The tip images of ESICF (Taylor cone and emitting jet) were also modified with only changing the brightness and the contrast. This process helped us to appreciate the cone angle and jet emission differences from one condition to the other.

The extraction of data from the experiments were performed with the help of another open source software, called Web Plot Digitizer [83]. The captured images first were scaled with ImageJ and then the data points were selected manually using the second program.
Chapter 3

3 Experiments on the Behavior of an ESICF

In this chapter we will discuss the interaction between the air crossflow (carrier gas) and the ES, based on the visualization results inside the test apparatus. The ES sprayer was operated inside the chamber to study the trajectory and deformation of plume at different carrier gas flow rates. The results of two different tip to vessel centerline distances are reported. The influence of crossflow on the cone deformation and jet bending is also discussed. Effective parameters on the operation of ESICF are identified. The best conditions for the operation of the ES are identified and compared with the MS results.

3.1 Effect of Carrier Gas on Bending and Plume Angles

Figure 3.1 shows a schematic of the ES capillary, with the flow pattern inside the vessel. In the first set of experiments, the tip of the ES nozzle is located on the chamber centerline and 4 mm from the gas inlet. In this case the applied voltage and the liquid flow rate are kept at 3 kV and 1.167 µL/min, respectively. Figure 3.2 shows this set, where the ES is operated in the stable cone jet mode using low crossflows. With no airflow, a symmetric conical plume is generated, as shown in Fig 3.1a. With a crossflow, both the leeward and windward boundaries bend toward the flow, as observed in Figs 3.1b-f. The bending angle increases with increase in the crossflow. Above 10 Scfh, i.e. 18.9 m/s, the plume was not stable and repeatedly disappeared and regenerated.
Figure 3.2 The ES operating at the stable cone jet mode inside the vessel with different air crossflows - tip located at the vessel centerline (the solid and dashed yellow lines show the vessel’s inlet diameter and the vessel centerline, respectively)

This ESICF has certain characteristics, which are shown in Fig. 3.3 and are discussed below:

**Jet Angle:** The jet emitting from the Taylor cone may have an angle with respect to the vertical axis, $\alpha_1$. The measured angle is essentially the angle of the straight line, which connects the jet emission point to the plume formation location, and the vertical axis. When there is no crossflow, the jet is vertical and the jet angle is zero. The jet angle increases with increasing the crossflow velocity; as shown in Fig. 3.3 with a black dashed line. This angle increases from 13° at 2 Scfh to 20° and to 31° at 6 Scfh and 10 Scfh, respectively.

**Initial Plume Angle:** The generated droplets by the jet slightly disperse shortly after breakup, forming a plume with an initial plume angle of $\alpha_2$. This angle reduces with increasing the crossflow. As shown in Fig. 3.3 (solid black line), the initial plume angle decreases from 44° at 2 Scfh to 24° at 10 Scfh. This reduction is mainly due to a higher effect of the crossflow on the windward plume boundary as compared to the leeward boundary. Thus, the windward side bends more toward the flow, reducing the initial plume angle.
Figure 3.3 Top: schematic illustrations and the guide for the defined bending and plume angles; Bottom: the characteristics of the ES plume in different crossflows inside the vessel (the nozzle tip located approximately at the centerline)
**Dispersed Bending Angle:** In addition to the initial plume angle, we have defined a bending angle for the plume, $\alpha_3$, as plotted by a dashed red line in Fig 3.3. This angle is defined as the angle between the centerline of the plume and the vertical axis. Centerline of the plume is drawn at half angle of the initial plume angle. This bending angle also increases with the flow, changing from 18° at 2 Scfh to 44° at 10 Scfh. The plume bending angle is slightly more than the jet angle for each crossflow condition (approximately 13° for flows between 4 and 10 Scfh).

**Dispersed Plume Angle:** Because the flow field inside the chamber has a recirculation zone below the main crossflow, and because there is a downward electric field, the plume disperses asymmetrically. The windward trajectory passes the central zone earlier, and bends back sharply toward the ground electrode. On the other hand, the leeward trajectory travels more in the central region. With increasing the air, the leeward trajectory moves even more than the windward side in flow direction; therefore, the plume opens up and spreads more. In order to characterize this plume dispersion in the vessel, a dispersed plume angle, $\alpha_4$, is defined. It is the angle between the downstream windward and leeward boundaries of the plume. The dispersed plume angle, shown with a solid red line in Fig. 3.3, is much larger than the initial plume angle, which indicates a significant dispersion. The angle changes from 61° at 2 Scfh to 82° at 10 Scfh.

The aforementioned angles were measured and averaged with six images in order to reduce the measurement errors. The dispersion of measurements from the averaged value is less than 4° and 2° for the plume, and the bending angles, respectively. The electrospayed droplets disperse, evaporate and undergo breakups. Due to these phenomena the plume image fades away and cannot be followed after some point at the downstream. At around 10 Scfh, the plume behavior becomes slightly dynamic but still stable. However, the captured images at medium to high crossflows show the generation of unstable cone jet mode and plume. These observations are provided and discussed in Appendix D.

### 3.2 Effect of Tip to Centerline Distance

The main objective of introducing an ES in crossflow is to carry the ions toward the entrance of mass spectrometer. Since the chamber has a complicated internal flow, the injection point of the ES makes a large difference in the final droplet trajectories.
In the previous section, §3.1, the ES nozzle was located at the crossflow centerline. In this section, we present results for a case in which the nozzle tip is located at approximately 2.75 mm above the flow centerline. The applied voltage and liquid flow rate are 3.4 kV and 1 µL/min, respectively.

When the nozzle is located at the centerline of the flow, droplets quickly pass through the high velocity crossflow and enter in either the low velocity crossflow or the returned flow at the recirculation zone. Such droplets, i.e. ions, will not leave the vessel and may collide with the walls. In order to prevent this ion loss and increase the number of ions leaving the vessel, the ES capillary is lifted upwards by 2.75 mm.

Figure 3.4 shows the ES plume for this condition and for different crossflow velocities. At no crossflow, a relatively symmetric plume is formed (Fig. 3.4a). As the crossflow is increased, the plume is bent but it is mainly confined and captured in the main crossflow zone, as shown in Fig. 3.4c-e. As the flow is increased to 14 Scfh, i.e. 26.5 m/s, the droplets are dispersed so rapidly and it is difficult to see the plume, Fig. 3.4f. At this crossflow, the Reynolds number is ~4100, indicating turbulent condition inside the vessel, which enhances the dispersion.

![Figure 3.4](image)

**Figure 3.4** The ES operating at the stable cone jet mode inside the vessel with different air crossflows - tip located ~2.75 mm above the vessel centerline (the yellow lines show the chamber’s inlet diameter)
The breakup of emitting jet takes place at some axial distance from the tip. When the nozzle is located well above the centerline, the droplets are also generated above the centerline. As shown in Fig. 3.5, when the droplets are above the centerline, they experience more flight distance and time in the main crossflow. As a result, once the air flow is sufficient, they receive a sufficient momentum from the air in the horizontal direction and are dragged by the air path. Besides, a high electric force is applied over the generated charged droplets when they are at the vicinity of the needle tip. This force is induced by both the columbic repulsion between droplets and the external electric field. The generated droplets are very close to each other initially and repel each other in two opposite directions, in and against the crossflow direction. For the case of tip on the centerline, the electric force on droplets is still significant in comparison to the drag force of the central zone. This electric force can push the ions off the central zone and bend the plume back downwards.

Park et al. [62] showed when the induced electric field at the tip are similar, the applied voltage, itself, does not influence the operation mode. Considering the other parameters, e.g. surface tension, are similar for the centered and off-centered nozzle locations, the electric field at the tip determines the jet or droplet emission velocity. Using Eq. 1-1, the calculated electric fields at the
tip are 7.46 and 8.01 MV/m for the centered and off-centered cases, respectively. Therefore, the difference in the initial droplet velocity between these two sets should not have a vital role in the observed change of behavior. In addition, droplets are more dispersed in the off-centered case, and are expected to have lower inertia when they reach the centerline. Therefore, the drag force can dominate the motion of the droplets even at low flow rates and bend both the windward and leeward boundaries toward the centerline.

Another important attribute of locating ES above the flow centerline is that only higher crossflows than 14 Scfh can cause disruption in the plume generation. This value was 10 Scfh for the nozzle located at the centerline. In the off-centered case, the ES nozzle is located at a lower local flow velocity condition, therefore, ES is more stable than the centered configuration. From this observation, we noted that high velocity crossflows cause destabilizations at the Taylor cone, which will be discussed later.

![Figure 3.6 The detected intensity of a mass spectrometer versus the inlet airflow rate of vessel](image-url)
Figure 3.6 compares the ESICF images with the detected intensities of a mass spectrometer (performed and provided by IONICS Inc.). In their test, a $10^{-7}$ Molality Reserpin solution at the flow rate of 1 µL/min was run through an emitter with 100 µm ID. Up to around 8 Scfh, the increase of crossflow rate enhances the detection rate fast. This is compatible with the visual observations, indicating that low air flows cannot bend the plume sufficiently; therefore, many ions hit the walls and are lost. With increasing the airflow, the plume is dragged closer to the centerline and more ions can exit the vessel. In a range of airflow, 8-12 Scfh, the detected intensity is at the peak. We believe the peak is detected once the generated droplets in the stable plume is carried by the crossflow and reach the spectrometer’s inlet. Above this optimum flow rates, the effect of plume dispersion is also well matched with the intensity results. The detection rate decreases moderately with further increase of crossflow, because the droplets disperse inside the vessel and the air cannot carry some of them, leading to ion loss. Similar behavior was observed for a liquid JICF. The discussion on the JICF inside the vessel is provided in Appendix D. The disruption in the generation of a stable plume at higher air crossflows also can lead to a lower ion emission and detection.

### 3.3 Cone Jet in Crossflow

A cone jet in stagnant air is typically a symmetric cone, formed on a capillary, with a single liquid jet emitting from the tip of the cone, as shown in Fig. 3.7a. This case shows a cone jet at the liquid flow rate of 2 µL/min and applied voltage of 3.05 kV.

As a crossflow is imposed on the cone jet, it deforms the Taylor cone in addition to bending the jet. At relatively lower crossflows, i.e. 4 and 8 Scfh, the Taylor cone is bent and the cone tip is shifted to the right side (see Fig. 3.7b-c). In these conditions, the cone jet is still stable.

The crossflow makes the cone boundary curved and its apex pointier. These higher curved boundaries are attributed to a higher local air pressure due to introducing the air flow. Pantano et al. [84] numerically discussed the shape of Taylor cone with respect to the pressure difference between the liquid and the surrounding air. Three groups of shapes were discussed: conical, curved toward the axis and curved away from the axis, for no pressure difference, higher, and lower liquid pressure, respectively [85]. At Fig. 3.7d-e, the cone shape looks similar to the lower liquid pressure case. These observation is also consistent with the discussion of Gubarenko et al. [86]. In addition, the direct interaction of air with the cone can mechanically change the shape of the cone.
Figure 3.7 Close up illustrations of ES and cone jet performance with different crossflows inside the vessel - applied voltages: [a-f] 3.05 kV; [g-m] 3.35 kV
When the crossflow is increased to 12 Scfh, 22.7 m/s, the air flow becomes so large that the Taylor cone becomes unstable. Figure 3.7d-e shows the unstable behavior of the emitting jet at this crossflow at different instants. The shape and size of meniscus change constantly and jet emission happens from different spots, one at a time and intermittently. In our tests we observed that better plumes and jets can be captured at higher voltages (see Appendix D). This is attributed to a higher outward electric pressure on the meniscus, which can compensate the increase of the local air pressure. We increase the voltage from 3.05 kV to 3.35 kV at 16 Scfh, i.e. 30.3 m/s. A stable cone jet was observed at this condition, as shown in Fig. 3.7g. It is observed that the size of the cone reduces with the voltage. Further increase in crossflow to 20 Scfh, i.e. 37.9 m/s, makes the cone jet to move and, although it is formed steadily, the location and bending is not constant (see Fig. 3.7h-i). We refer to this as a dynamic cone jet.

Figure 3.7j-k shows the ES operating at high airflow of ~48 Scfh (~91 m/s) and 3.35 kV. In this condition the electrospraying mode is unstable cone jet and the Taylor cone appears much rarely. The emission of jet only occurs when the fluid can form an instantaneous cone. In these instants, the jet has a short time to emit, before the airflow ruins the instantaneous balance between the electric, surface tension, and the pressure difference at the liquid/air interface. With further increase of the airflow to ~77 Scfh (~145 m/s), Fig. 3.7l-m, the liquid at the tip is washed, sheared, and dispersed by the air. Almost all of the liquid is inside the capillary and sometimes cloud-like pulsations emit from the existing liquid at the tip.

Up to this point, the voltages were kept below 4 kV. Another set of images, provided in Appendix D, was captured to investigate the behavior of ES at ~48 Scfh (~91 m/s), and relatively high voltages, 4.4-5.2 kV. The highest frequency and multiple number of jets was captured at 4.6-4.8 kV, where the ES was operated in either the unstable cone jet, or the unstable multi-jet mode, Fig. 3.8. We expect the highest spectrometer’s detection rate in this voltage range. This prediction is simply because the emission of jets is at its maximum level, which should lead to the highest ion generation. The intensity results of spectrometer versus the voltage was reported using a 64 Scfh crossflow and a Reserpine solution [87]. The ion detection rate enhances with voltage and reaches the maximum between 4.5 and 5.5 kV. Although the operational conditions are not exactly the same for these cases, the reported voltage ranges show a fairly good agreement. A better understanding on ESs operating at high air crossflows requires further investigation.
3.4 Effect of Input Sequence on the ES Performance

In our experiments, we realized the sequence of applying voltage, solution flow, and air crossflow can significantly influence the ES operation and its characteristics, such as emitting jet angle. The discussion in this section is based on a case where the capillary tip is located at the centerline of the vessel, i.e. tip to counter electrode distance was set at 5 mm. Three different input orders are (1) Solution-Voltage-Crossflow, (2) Voltage-Solution-Crossflow, and (3) Solution-Crossflow-Voltage. In all of the previous cases, the solution flow was set initially; then, the voltage was modified to capture the cone jet mode, and at the end crossflow was added in order to study the behavior of an ESICF (Sequence 1). The second and the third sequences are discussed in this section (for images see Appendix D).

The “Sequence 2” was performed with initially increasing the applied voltage to 2.81 kV. Before running the solution, all the liquid at the tip was ejected due to the applied voltage. The solution at 2 µL/min was introduced and, once the stable jet was formed, the air crossflow was added. Without any crossflow, an asymmetric steady cone was formed at the right half of the nozzle tip and a bended jet emitted toward the right. This cone was much smaller than the ones in typical cone jets, in which a cone symmetrically covers all the tip surface. With the addition of crossflow, the ES underwent the following stages: more bending to the right; dynamic behavior; unstable jet emission; and no jet emissions. These steps are qualitatively similar to the first sequence. During the running the ES with no emissions, the liquid spread and reached the whole tip surface. After this point, the crossflow was closed and the ES performance became similar to the Sequence 1. Enhancing the crossflow after this point, gave a similar behavior as Sequence 1.
The operation of an ES with a similar sequence, but without the crossflow, was discussed by Chiarot et al. [88]. They studied the transient response of the liquid interface when the voltage was applied before the liquid. A smooth symmetrical transition to the formation of a steady and symmetrical cone jet was captured. The initial asymmetry of our cone jet is purely attributed to the local wetting of the tip. A system acts transient for a period of time before reaching the steady state conditions. In an ES, different initial and boundary conditions can change the transient process, and resulting in different steady cone jets. Therefore, the first input sequence is preferred over the second one from the practical point of view in ESI-MS.

In “Sequence 3”, 1 µL/min solution was introduced initially, then the air was set to the constant low flow of ~4.7 Scfh (~9 m/s), and at last, the voltage was increased to 3 kV. Below this voltage, the cone jet mode was not observed. The operation mode at 3 kV was pulsating, where the meniscus elongates in the axial direction, a jet or a ligament is ejected, and the meniscus returns to the cusp shape. Increasing the voltage up to 3.5 kV, pushed the ES to the unstable or droplet ejection mode, where the liquid can eject in bulks or droplets. Returning to 3.38 kV resulted in the pulsating mode with more variation in ejection. Further efforts to achieve a cone jet were not successful either. At the end, when the crossflowing air was closed and the voltage was decreased to 3.25 kV, the ES operation mode became the stable cone jet. The stable cone jet mode is achievable using the first sequence and similar solution flow, crossflow, and voltages.

Considering the meniscus as a control system, it works in the cone jet mode whenever the applied forces reach a balance in a quasi-equilibrium state, either steadily or for a short time. We think the inability to form a stable cone jet with Sequence 3, is due to the perturbations caused initially on the surface of meniscus by the crossflow. In other words, the system operates in a highly transient and unstable way and the liquid instabilities on the liquid surface are too high that the electric force cannot overcome them. Therefore, a steady cone jet does not form. At Sequence 1, the liquid at the tip is initially stationary and ES initially operates in a steady cone jet mode. Therefore, when the crossflow is added, the system can stand the air effect and operate in the stable manner. With the first sequence, the ES operates at the cone jet mode up to some crossflow rate. Once the air flow is increased and the flow pressure exceeds a value, strong fluctuations are introduced to the liquid surface, which disrupt the balance of the system.
3.5 Electrohydrodynamic (EHD) Hysteresis in ESICF

A parameter affecting the ES operation is identified as the trend of voltage variation, i.e. increasing or decreasing. Figures 3.9a-d and 3.9e-h illustrate the ES performance at 20 Scfh (37.8 m/s), with increasing the voltage up to 3.4 kV, and decreasing it down to the same potential, respectively. The four panels in each case show different instants of the ES operation in crossflow, all four in the mentioned conditions. The decreasing trend resulted in a more stable and frequent plume appearance than the enhancing case. This behavior was observed repeatedly with different input conditions.

Figure 3.9 ES performance and plume formation with increasing and decreasing the applied voltage; air crossflow: 20 Scfh (37.8 m/s)
At the first glance, this behavior may be interpreted as a spray current hysteresis phenomenon, between the cone jet and the pulsating modes; similar to the report of Chen et al. [89], and Noymer and Garel [90]. One should note that in the stable cone jet mode, the operation of ES and Taylor cone is stable, which is not the case in the unstable cone jet mode in a crossflow. Marginean et al. [91], referred to the standing waves as the reason of periodic liquid ejection in the pulsating mode. In another paper, Marginean et al. [92] stated that the hysteresis between the cone jet and the pulsating modes can be attributed to the stationary behavior of the liquid at the meniscus. In other words, in order to ES fall back into the pulsating mode, a mechanical fluctuation must initiate the instability to the liquid surface. Therefore, as long as this fluctuation does not arise, the standing waves are not generated and the stable cone jet can operate below the onset voltage. Having this in mind, the plume and Taylor cone in our case are highly affected by the crossflow and are not stationary; therefore, our observed phenomenon is not the discussed hysteresis in the literature.

We think the physics behind this phenomenon is the variation of the boundary conditions, by increasing the voltage above 3.4 kV (in this specific case) and returning it back to this value. The effective boundary conditions on the cone can be listed as: the geometry of cone, the space charge of droplets, and the wetting of capillary tip. We call our observation EHD hysteresis as its source is believed to be the liquid condition at the capillary tip, under the effect of electric field and air crossflow. Operation of the ES with EHD hysteresis, Fig.3.9e-h, is expected to result in a better ion detection in a mass spectrometer, due to better plume and ion generations. Detailed investigations on the current hysteresis and this new observation are still necessary, but they are beyond the scope of this thesis.

In general, to predict the exact behavior of the ES, knowing the final voltage and air crossflow is necessary, but not enough. We believe the main reasons of unpredictable ES behavior in the medium-high crossflows, are the changes in the tip wetting, i.e. the shape and fluid dynamics of meniscus, which leads to the variation of boundary conditions. This effect is a serious obstacle for the repeatability, quantifying, and prediction of the exact results; however, the qualitative behavior can be justified and predicted. Understanding the physics of tip wetting and its relation with operational parameters, such as airflow and voltage, will lead to a new approach on ESICF, and its existing and possible applications. The analysis of the transient behaviors of an ESICF using an equilibrium model, similar to [88], [86], can be highly beneficiary. It is also required to study the other types of capillaries and nozzles under the effect of crossflow.
An ideal solution to overcome the prediction issue of ES in the medium-high crossflows, is to monitor the ES performance when it is coupled with a mass spectrometer. An automated control system based on image processing techniques, similar to [93], can be adopted to identify the operation mode. Thus, a software can control the sufficient air crossflow based on the live imaging of ES, which will result in the improvement of ion intensity detection.
4 Electrified Jet Trajectory in Crossflow (Theoretical Analysis)

4.1 Approach

The emitting jet from a Taylor cone is essentially an electrified micro jet. In this chapter, theoretical models for the trajectory of an Electrified Jet In CrossFlow (EJICF) are suggested. Initially, the applied forces on an emitting electrified jet from the Taylor cone are discussed. Then, the force balance equations are solved and the equations of motion in 2D are derived. Finally, the results of the analytical solutions are analyzed and compared with some of the experimental cases discussed earlier.

![Figure 4.1 Schematics of orthogonal EJICF and uniform electric fields in 2D](image)

The simplest form of EJICF is when we consider the jet is emitted perpendicularly to a uniform gas flow. However, as shown in the previous chapter, the cone shape and jet emission angle are
affected by the crossflow. Theoretical analysis will be presented for both orthogonal and angled cases. The theoretical analysis of the angled case will be presented later.

Figure 4.1 shows the schematic of an orthogonal EJICF and the geometry of the problem. The diameter of jet is considered constant from its emission point to the breakup location. We assume the jet is made of a stack of small cylinders. In order to forecast the jet trajectory, one of these cylindrical elements is followed and, based on the applied forces, its projectile is predicted. This element has the same diameter as jet diameter, \( d_j \), and an infinitesimal height, \( h \). In the next section, the applied forces on this element will be analyzed for the orthogonal configuration.

4.2 Applied Forces

4.2.1 Drag Force

The drag force is a result of relative velocity between the air and the liquid jet, \( U_{rel} \):

\[
U_{rel} = \sqrt{\left( u_{gx} - \frac{dx}{dt} \right)^2 + \left( u_{gy} - \frac{dy}{dt} \right)^2}
\]

The normal component of \( U_{rel} \) to the jet causes the drag force. The component of relative velocity in jet direction results in a shear force on the surface. In the orthogonal EJICF, the drag force is only defined in the x direction, as the interaction of air and jet in the y direction is mostly based on shear. In other words, we assume the jet velocity is always in its initial emission direction. This assumption is justifiable, if the jet does not bend so much [68]. The crossflowing air velocity, \( u_g \), is assumed to be uniform and constant. The drag force is calculated as:

\[
F_D = \frac{1}{2} C_D \rho_g \left( u_g - \frac{dx}{dt} \right)\left| u_g - \frac{dx}{dt} \right| A_{Fr}
\]

where, \( C_D \) is the drag coefficient and \( A_{Fr} \) is the frontal area of the cylinder. For the orthogonal configuration, the frontal area is a rectangle, \( h \times d_j \).

Considering a cylindrical jet, the drag coefficient should be calculated for a flow past a cylinder. Lamb [94] derived an approximate analytical solution of drag of a viscous flow over a cylinder:
\[ C_D = \frac{8\pi}{Re_{cyl}(2.002 - \ln(Re_{cyl}))} \]  

where, \( Re_{cyl} = \frac{\rho g U_{rel} d_{cyl}}{\mu_g} \). This equation shows a good agreement with experimental results for Reynolds smaller than 1. Wieselsberger [95], Finn [96], and Tritton [97] provided experimental data for the drag coefficient at different ranges of Reynolds number and cylinder diameter. Based on these experiments [95]–[97], we suggest the following correlation for the drag coefficient of a flow passing over a cylinder:

\[ C_D = \frac{10}{\sqrt{Re_{cyl}}} \]  

Figure 4.2 illustrates the agreement between the experiments and the suggested correlation, especially at \( 0.5 < Re_{cyl} < 100 \).
As mentioned in chapter one, when a flow undergoes a sudden expansion, a main flow at the central zone and recirculation flows next to the expansion steps are generated. At the downstream of the main flow the velocity reduces. In order to simplify and compare our test results with the theoretical correlations, three assumptions are added:

i- An average uniform velocity is considered for the crossflow, i.e. no change in the y direction. (This simplification is only applied for analytical analysis)

ii- The magnitude of this average velocity was calculated based on the expanded area at the ES nozzle location and the inlet velocity.

iii- The effect of radial velocity on the trajectory is neglected. (Due to its small value)

![Figure 4.3 Recirculation length over step height in sudden expansion versus Reynolds](image)

**Figure 4.3 Recirculation length over step height in sudden expansion versus Reynolds**

An important parameter in sudden expansions is the length of recirculation zone, $L_{RE}$. Here, we adopt a symmetric velocity profile in the vessel and use Back and Roschke’s experimental measurements [75]. Figure 4.3 shows the length of the recirculation zone over the step size, $L_{RE}/h_{Step}$, based on the inlet Reynolds. $L_{RE}/h_{Step}$ first increases in the laminar regime, up to ~25 at $Re_{in}$~300 (not shown), and then decreases until it reaches ~6 at $Re_{in}$~1000. Above this Reynolds and in the turbulent inlet, the ratio increases again up to a constant value around 8.5.
Our operational inlet Reynolds number is always above 500. The following third order polynomial fit to the experimental data gives less than 7% discrepancy from the experimental data:

\[
\frac{L_{RE}}{h_{step}} = \begin{cases} 
-1.85 \times 10^{-8}Re_{in}^3 + 7 \times 10^{-5}Re_{in}^2 - 8.29 \times 10^{-2}Re_{in} + 37.57 \\ 8.5 
\end{cases} 
\quad [400 \leq Re_{in} \leq 1600] 
\quad [Re_{in} > 1600] 
\quad (4-5)
\]

![Diagram of vessel geometry and expansion parameters](image)

**Figure 4.4 Geometry and expansion parameters inside the vessel**

The next unknown is the flow expansion shape. Theoretical and experimental results have shown that the flow in sudden expansion initially experiences a linear development and then bends more [75]. As our vessel length is short, we approximate a linear expansion, similar to Fig. 4.4. Thus:

\[
r_{Ex}(x) = \frac{d_{in}}{2} + \frac{x + L_{tip-in}}{L_{RE}} \times h_{step} 
\quad (4-6)
\]

where \(L_{tip-in}\) and \(d_{in}\) are the distance between the vessel inlet and the nozzle and the inlet diameter for airflow, respectively. \(r_{Ex}\) is the expanding radius of the flow, i.e. the distance between the centerline of vessel and the boundary of negative and positive air flows. Assuming the volumetric flow rate in the main flow in each cross section is the same as the inlet, the average velocity, \(U_{Avg}\), can be expressed based on the average inlet velocity, \(U_{in}\):

\[
U_{Avg}(x) = U_{in} \times \left(\frac{d_{in}}{2r_{Ex}}\right)^2 
\quad (4-7)
\]
4.2.2 External Electric Force

In an electrospaying process, the external electric field applies an electric force on the charged jet. The applied electric force on the cylindrical element can be simply calculated in two directions by:

\[ F_{E,x} = \sigma_i A_{\text{surf}} E_x \] (4-8)

\[ F_{E,y} = \sigma_i A_{\text{surf}} E_y \] (4-9)

where \( E_x, E_y \), and \( A_{\text{surf}} \) are electric fields in \( x \) and \( y \) directions, and the surface area of the element, i.e. \( \pi d_j h \), respectively. The surface charge density, \( \sigma_i \), is calculated using Eq. 1-15. The charge to mass ratio of droplets in this equation is determined by Eqs. 1-20 and 1-21.

The adopted electric field in the majority of numerical studies on ESs is based on the needle-plate configuration. In order to derive the external electric field for this configuration, the image charge method is adopted in axisymmetric cylindrical coordinates [19]:

**Figure 4.5** Left: cylindrical coordinates at needle-plate configuration; Right: Cartesian coordinates on a close up image of the Taylor cone in crossflow
\[ E_r = \frac{\sigma_c}{4\pi\varepsilon_0 r} \left( \frac{2L_{Gr} - z}{\{r^2 + (2L_{Gr} - z)^2\}^{1/2}} - \frac{z}{\{r^2 + z^2\}^{1/2}} \right) \] (4-10)

\[ E_z = \frac{\sigma_c}{4\pi\varepsilon_0} \left( \frac{1}{\{r^2 + (2L_{Gr} - z)^2\}^{1/2}} + \frac{1}{\{r^2 + z^2\}^{1/2}} \right) \] (4-11)

where, \( \sigma_c \) is the charge per unit length of capillary and is calculated by:

\[ \sigma_c = \frac{4\pi\varepsilon_0 V_{on}}{\ln(4L_{Gr}/r_c)} \] (4-12)

In this chapter, the apex of Taylor cone is selected as the origin, Fig. 4.5b. As observed in chapter 3, the apex has offsets from the center of capillary tip in both \( x \) and \( y \) directions. Considering the offset lengths, the electric fields in a 2D Cartesian system become:

\[ E_x = \frac{\sigma_c}{4\pi\varepsilon_0 (x + L_{off})} \left( \frac{2L_{Gr} - y - L_{Apex}}{\{(x + L_{off})^2 + (2L_{Gr} - y - L_{Apex})^2\}^{1/2}} \right. \\
- \left. \frac{y + L_{Apex}}{\{(x + L_{off})^2 + (y + L_{Apex})^2\}^{1/2}} \right) \] (4-13)

\[ E_y = \frac{\sigma_c}{4\pi\varepsilon_0} \left( \frac{1}{\{(x + L_{off})^2 + (2L_{Gr} - y - L_{Apex})^2\}^{1/2}} + \frac{1}{\{(x + L_{off})^2 + (y + L_{Apex})^2\}^{1/2}} \right) \] (4-14)

Unfortunately, Eqs. 4-13 and 4-14 make the equations of force balance too complicated to solve. Even their geometrically simplified equations do not result in an analytical solution for jet trajectory and requires numerical computations (see Appendix E). In our analysis, the electric field is averaged and considered constant in the \( x \) and \( y \) directions. The average values will be calculated in §4.4.
4.2.3 Gravity

The mass of element applies a downwards force, in the $y$ direction:

$$F_{g,y} = \rho_j A_c h g = \frac{\pi d_j^2 h \rho_j}{4} g \quad (4-15)$$

$$F_{g,x} = 0 \quad (4-16)$$

4.2.4 Shear Force

The shear force appears when a flow passes over a surface and a velocity gradient and, therefore, a boundary layer is formed. For a moving cylindrical jet in a stilled medium, this force appears in the opposite direction of jet velocity. In the orthogonal EJICF case, the shear force is applied upward, in the $y$ direction. The amount of shear force in this case can be estimated based on the velocity gradient at jet surface:

$$F_{\text{Shear},y} = -\pi d_j h \mu g \left( \frac{\partial u_{gy}}{\partial x} \right)_{\text{surf}} \quad (4-17)$$

$$F_{\text{Shear},x} = 0 \quad (4-18)$$

4.3 Electrified Liquid Jet in Crossflow

In this section, the force balance equations in two directions are written; then, the equations of motion are derived. Two solutions are proposed in the jet direction based on the significance of electric field. The equation of motion in the normal direction to the jet is the same.

If the electric force in the jet direction is low, the acceleration is considered negligible. In this case, the jet diameter should remain constant. In other words, if the jet experiences acceleration in its emission direction, the change of diameter is the only way that both continuity and force balance equations can be satisfied.

For a high electric field, the jet is expected to accelerate in the $y$ direction, decreasing its diameter. In the experiments, the diameter variation was not detectable with our optical system. Therefore, we discuss both situations considering constant jet diameter. The space charge of plume over the jet is neglected for all of the cases.
4.3.1 Orthogonal EJICF – Low Electric Fields

In this model, the trajectory of an electrified jet perpendicular to the gas crossflow, is determined. The force balance in the y direction is:

\[
\Sigma F_y = \left( \rho_j \frac{\pi d_j^2 h}{4} \right) \frac{d^2 y}{dt^2} = \sigma_j A_{surf} E_y - \pi d_j L_j \mu_g \left( \frac{\partial u_y}{\partial x} \right)_{surf} + \frac{\pi d_j^2 h \rho_j}{4} g
\]  

(4-19)

where first, second, and third terms in the RHS are electric force, shear force, and gravity, respectively. The gravity and shear forces are negligible (see Appendix E). In this model, no acceleration is considered in the y direction, as the electric field is low. Integrating Eq. 4-19 gives us the relationship between y and time:

\[
y = u_j t
\]  

(4-20)

In the x direction, drag and external electric forces are applied on the droplet:

\[
\Sigma F_x = \left( \rho_j \frac{\pi d_j^2 h}{4} \right) \frac{d^2 x}{dt^2} = \frac{1}{2} C_D \rho_g \left( u_g - \frac{dx}{dt} \right) |u_g - \frac{dx}{dt}| A_{Fr,x} + \sigma_j A_{surf} E_x
\]  

(4-21)

\[
\frac{d^2 x}{dt^2} = \frac{2 C_D \rho_g}{\pi \rho_j d_j} \left( u_g - \frac{dx}{dt} \right) |u_g - \frac{dx}{dt}| + \frac{4 \sigma_j E_x}{\rho_j d_j}
\]  

(4-22)

where the first and second term in the RHS of Eq. 4-22 are the accelerations applied by drag and electric forces, respectively. For the analytical solution, this equation should be split into two: one for the gas velocity higher than the jet velocity in the x direction, Eq. 4-23, and the other for the lower case, Eq. 4-24:

\[
\frac{d^2 x}{dt^2} = \begin{cases} 
    a \left( b - \frac{dx}{dt} \right)^2 + c, & \text{if } u_g \geq \frac{dx}{dt} \\
    -a \left( b - \frac{dx}{dt} \right)^2 + c, & \text{if } u_g \leq \frac{dx}{dt}
\end{cases}
\]  

(4-23)

(4-24)

where the coefficients are:

\[
a = \frac{2 C_D \rho_g}{\pi d_j \rho_j}, \quad b = u_g, \quad c = \frac{4 \sigma_j E_x}{\rho_j d_j}
\]  

(4-25)
The constants a and b are positive; but depending on the electric force direction, c can be either positive or negative. These equations are second order autonomous nonlinear differential equations. A differential equation or system of ordinary differential equations is called autonomous if it does not explicitly contain the independent variable, t; i.e. if the equation can take this general form:

\[ f(r, r', r'') = 0 \]  

(4-26)

A common way to solve a second order autonomous equation, is to use a substitute variable and reduce its order to one. The solution of Eqs. 4-23 and 24 are provided in the table below.

### Table 4.1 The analytical solution for equations of motion in positive low electric fields

<table>
<thead>
<tr>
<th>IF [ u_g \geq \frac{dx}{dt} &amp; c &gt; 0 ] THEN</th>
<th>IF [ u_g \leq \frac{dx}{dt} &amp; c &gt; 0 ] THEN</th>
</tr>
</thead>
</table>
| \[
\frac{d^2x}{dt^2} = a \left( b - \frac{dx}{dt} \right)^2 + c
\] | \[
\frac{d^2x}{dt^2} = -a \left( b - \frac{dx}{dt} \right)^2 + c
\] |
| \[
\frac{dx}{dt} = v \quad \frac{d^2x}{dt^2} = \frac{dv}{dt}
\] | \[
\frac{dx}{dt} = v \quad \frac{d^2x}{dt^2} = \frac{dv}{dt}
\] |
| \[
\frac{dv}{dt} = a(b - v)^2 + c
\] | \[
\frac{dv}{dt} = -a(b - v)^2 + c
\] |
| \[
\frac{dv}{a(b - v)^2 + c} = dt
\] | \[
\frac{dv}{-a(b - v)^2 + c} = dt
\] |
| \[
\tan^{-1} \left( \sqrt{\frac{b}{c}} \left( v - b \right) \right) = t + k_1
\] | \[
\tanh^{-1} \left( \sqrt{\frac{b}{c}} \left( v - b \right) \right) = t + k_3
\] |
| \[
v = b + \sqrt{\frac{c}{a}} \tan \left( \sqrt{ac} t + k_1 \right)
\] | \[
v = b + \sqrt{\frac{c}{a}} \tanh \left( \sqrt{ac} t + k_3 \right)
\] |
| \[
dx = \left( b + \sqrt{\frac{c}{a}} \tan \left( \sqrt{ac} t + k_1 \right) \right) dt
\] | \[
dx = \left( b + \sqrt{\frac{c}{a}} \tanh \left( \sqrt{ac} t + k_3 \right) \right) dt
\] |
where, $k_1, k_2, k_3,$ and $k_4$ are integration constants and are found based on the initial conditions:

$$x(0) = 0, \quad \dot{x}(0) = 0$$  \quad (4-29)

The initial position and the velocity in the x directions are zero. Thus, the values of the integration constants become:

$$k_1 = \tan^{-1}\left[-\frac{b}{\sqrt{ac}}\right], \quad k_2 = \frac{\ln(\cos[k_1])}{a}$$  \quad (4-30)

$$k_3 = \tanh^{-1}\left[-\frac{b}{\sqrt{ac}}\right], \quad k_4 = -\frac{\ln(\cosh[k_3])}{a}$$  \quad (4-31)

Note that $\tanh^{-1}\left[\frac{a}{c}(\frac{dx}{dt} - b)\right]$ has an answer when $\left|\frac{a}{c}(\frac{dx}{dt} - b)\right| < 1$. This condition is satisfied when the value of the drag force is smaller than the electric force. If the drag force is larger than the electric force, i.e. $\left|\frac{a}{c}(\frac{dx}{dt} - b)\right| > 1$, the solution of $x(t)$ changes into the form of $\ln|\sinh|$, instead of $\ln(\cosh)$. In the same manner, the position and velocity boundary conditions take the form of $\coth^{-1}$ and $\ln|\sinh|$, respectively. Table 4.2 provides the solution of Eqs. 4-23 and 24 when the negative electric field is applied in the x direction.

### Table 4.2 The analytical solution for equations of motion in negative low electric fields

<table>
<thead>
<tr>
<th>IF $u_g \geq \frac{dx}{dt} &amp; c &lt; 0$ THEN</th>
<th>IF $u_g \leq \frac{dx}{dt} &amp; c &lt; 0$ THEN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{d^2x}{dt^2} = a\left(b - \frac{dx}{dt}\right)^2 + c$</td>
<td>$\frac{d^2x}{dt^2} = -a\left(b - \frac{dx}{dt}\right)^2 + c$</td>
</tr>
<tr>
<td>$\frac{dx}{dt} = b - \sqrt{c} \frac{a}{\tanh\left[\sqrt{ac} t + k_5\right]}$</td>
<td>$\frac{dx}{dt} = b - \sqrt{c} \frac{a}{\tan\left[\sqrt{ac} t + k_7\right]}$</td>
</tr>
</tbody>
</table>
\[
\begin{align*}
\text{(4-32)} & \quad x = bt - \frac{1}{a} \ln(\cosh\left[\sqrt{ac} t + k_5\right]) + k_6 \\
\text{(4-33)} & \quad x = bt + \frac{1}{a} \ln(\cos\left[\sqrt{ac} t + k_7\right]) + k_8
\end{align*}
\]

where integration constants are:

\[
\begin{align*}
k_5 &= \tanh^{-1} \left[ b \frac{\sqrt{a}}{-c} \right], & k_6 &= \frac{\ln(\cosh[k_5])}{a} \\
k_7 &= \tan^{-1} \left[ b \frac{\sqrt{a}}{-c} \right], & k_8 &= -\frac{\ln(\cos[k_7])}{a}
\end{align*}
\]

As shown in Eqs. 4-28 and 32, the solution of \( x \) becomes hyperbolic when the drag force and electric force are applied in the opposite directions. Replacing the integral coefficients into the equations of motion (Eqs. 4-27, 28, 32, and 33) results in the following:

\[
\begin{align*}
x(t) &= bt - \frac{1}{a} \ln \left( \cos \left( \sqrt{ac} t + \tan^{-1} \left[ -b \frac{\sqrt{a}}{\sqrt{-c}} \right] \right) \right) + \ln \left( \cos \left( \tan^{-1} \left[ -b \frac{\sqrt{a}}{\sqrt{-c}} \right] \right) \right) \\
\text{For } & \quad u_g \geq \frac{dx}{dt} & c > 0
\end{align*}
\]

\[
\begin{align*}
x(t) &= bt + \frac{1}{a} \ln \left( \cosh \left( \sqrt{ac} t + \tan^{-1} \left[ -b \frac{\sqrt{a}}{\sqrt{-c}} \right] \right) \right) - \ln \left( \cosh \left( \tan^{-1} \left[ -b \frac{\sqrt{a}}{\sqrt{-c}} \right] \right) \right) \\
\text{For } & \quad u_g \leq \frac{dx}{dt} & c > 0
\end{align*}
\]

\[
\begin{align*}
x(t) &= bt - \frac{1}{a} \ln \left( \cosh \left( \sqrt{-ac} t + \tan^{-1} \left[ b \frac{\sqrt{a}}{\sqrt{-c}} \right] \right) \right) + \ln \left( \cosh \left( \tan^{-1} \left[ b \frac{\sqrt{a}}{\sqrt{-c}} \right] \right) \right) \\
\text{For } & \quad u_g \geq \frac{dx}{dt} & c < 0
\end{align*}
\]
\[ x(t) = bt + \frac{1}{a} \ln \left( \cos \left[ \sqrt{-ac} \ t + \tan^{-1} \left( \frac{a}{\sqrt{-c}} \right) \right] \right) - \frac{\ln \left( \cos \left[ \tan^{-1} \left( \frac{a}{\sqrt{-c}} \right) \right] \right)}{a} \]  \tag{4-39}

For \( u_g \leq \frac{dx}{dt} \) & \( c < 0 \)

4.3.1.1 Non-Dimensional Formats

In order to identify the effective parameters on the jet trajectory, Buckingham’s \( \pi \) theorem is used and the non-dimensional forms of Eqs. 4-36 to 4-39 are derived. The parameters and variables in these equations are listed in Table 4.3.

<table>
<thead>
<tr>
<th>Table 4.3 Variables and Parameters in the Equations of Motion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length Parameters</td>
</tr>
<tr>
<td>( d_j ) [m]</td>
</tr>
<tr>
<td>( L_j ) [m]</td>
</tr>
<tr>
<td>( )</td>
</tr>
</tbody>
</table>

Having 9 parameters and 4 dimensional quantities, indicates that we need to define 9-4=5 non-dimensional numbers. Three of these numbers are selected to be the ratios of the velocities, the densities, and the jet diameter to its length:

\[
\pi_1 = \frac{d_j}{L_j}, \quad \pi_2 = \frac{u_j}{u_g}, \quad \pi_3 = \frac{\rho_j}{\rho_g} \quad (4-40)
\]

The last two numbers is selected in a way that cancels out the dimension of electric field:

\[
\pi_4, \pi_5 = E \sigma_j^a \rho_j^b u_j^c L_j^d
\]
To find the powers of each parameter, a system of four equations and four unknowns is solved, which gives the fourth and fifth non-dimensional numbers:

$$
\varepsilon_{i,x} = \frac{E_x \sigma_j}{\rho_j u_j^2}, \quad \varepsilon_{i,y} = \frac{E_y \sigma_j}{\rho_j u_j^2}
$$

(4-41)

As these numbers represent the ratio of the induced electric force over the inertia, we call them “$\varepsilon_i$”. One may use the ratio of induced electric momentum to the gas inertia, as we will see it appears in the trajectory equations. The relations become:

$$
\varepsilon_{i,g,x} = \frac{E_x \sigma_j}{\rho_g u_g^2}, \quad \varepsilon_{i,g,y} = \frac{E_y \sigma_j}{\rho_g u_g^2}
$$

(4-42)

Applying the non-dimensional variables and parameters into Eqs. 4-36 to 4-39 gives:

$$
x^*(t^*) = \left(\frac{u_g}{u_j}\right) t^* + \frac{\pi}{2C_{D,x}} \left(\frac{\rho_j}{\rho_g}\right) \left(\frac{d_j}{L_j}\right) \cos \left[ t^* + \tan^{-1} \left( -\frac{C_{D,x}}{2\pi \varepsilon_{i,g,x}} \right) \right] \ln \left( \cos \left( \frac{L_j}{d_j} \frac{\rho_g}{\rho_j} \frac{8C_{D,x} \varepsilon_{i,j,x}}{\pi} \right) \right) \left( -\frac{C_{D,x}}{2\pi \varepsilon_{i,g,x}} \right)
$$

(4-43)

For $\left[ \frac{u_g}{u_j} \geq \frac{dx^*}{dt^*} \right. \text{ & } \varepsilon_{i,x} > 0$

$$
x^*(t^*) = \left(\frac{u_g}{u_j}\right) t^* - \frac{\pi}{2C_{D,x}} \left(\frac{\rho_j}{\rho_g}\right) \left(\frac{d_j}{L_j}\right) \cosh \left[ t^* + \tanh^{-1} \left( -\frac{C_{D,x}}{2\pi \varepsilon_{i,g,x}} \right) \right] \ln \left( \cosh \left( \frac{L_j}{d_j} \frac{\rho_g}{\rho_j} \frac{8C_{D,x} \varepsilon_{i,j,x}}{\pi} \right) \right) \left( -\frac{C_{D,x}}{2\pi \varepsilon_{i,g,x}} \right)
$$

(4-44)

For $\left[ \frac{u_g}{u_j} \leq \frac{dx^*}{dt^*} \right. \text{ & } \varepsilon_{i,x} > 0$
\[ x^*(t^*) = \left( \frac{u_g}{u_j} \right) t^* + \frac{\pi}{2C_{D,x}} \frac{\rho_i}{\rho_g} \left( \frac{d_j}{L_j} \right) \]

\[ \times \ln \left( \frac{\cosh \left( \frac{l_j}{d_j} \sqrt{- \frac{\rho_g}{\rho_i} \frac{8C_{D,x}\xi_{i,x}}{\pi} t^* + \tanh^{-1} \sqrt{- \frac{C_{D,x}}{2\pi \xi_{i,g,x}}} \right)}}{\cosh \left( \frac{l_j}{d_j} \sqrt{- \frac{\rho_g}{\rho_i} \frac{8C_{D,x}\xi_{i,x}}{\pi} t^* + \tanh^{-1} \sqrt{- \frac{C_{D,x}}{2\pi \xi_{i,g,x}}} \right)} \right) \]  \hspace{1cm} (4-45)

For \[ \frac{u_g}{u_j} \geq \frac{dx^*}{dt^*} \text{ & } \xi_{i,x} < 0 \]

\[ x^*(t^*) = \left( \frac{u_g}{u_j} \right) t^* - \frac{\pi}{2C_{D,x}} \frac{\rho_i}{\rho_g} \left( \frac{d_j}{L_j} \right) \]

\[ \times \ln \left( \frac{\cos \left( \frac{l_j}{d_j} \sqrt{- \frac{\rho_g}{\rho_i} \frac{8C_{D,x}\xi_{i,x}}{\pi} t^* + \tan^{-1} \sqrt{- \frac{C_{D,x}}{2\pi \xi_{i,g,x}}} \right)}}{\cos \left( \frac{l_j}{d_j} \sqrt{- \frac{\rho_g}{\rho_i} \frac{8C_{D,x}\xi_{i,x}}{\pi} t^* + \tan^{-1} \sqrt{- \frac{C_{D,x}}{2\pi \xi_{i,g,x}}} \right)} \right) \]  \hspace{1cm} (4-46)

For \[ \frac{u_g}{u_j} \leq \frac{dx^*}{dt^*} \text{ & } \xi_{i,x} < 0 \]

The term \( \frac{C_{D,x}}{2\pi \xi_{i,g,x}} \) in the RHS of these equations is essentially the ratio of initial drag force to the electric force, \( F \). This number is introduced to the equations by the initial velocity condition. The non-dimensional velocity and acceleration equations in the x direction are found similarly (see Appendix E).

The non-dimensional form of the equation of motion in the y direction, Eq. 4-20, becomes:

\[ y^* = t^* \]  \hspace{1cm} (4-47)

The difference in the forms of trajectory equations indicates the importance of drag and electric force directions and the dominance of one on the other. The average electric field is a constant value; however, the change of drag direction before the jet breaks is possible. In order to realize
whether the relative velocity changes its direction, one should find the real answers for the times that velocity equation becomes equal to gas velocity:

\[ \frac{dx}{dt} = u_g \]  

(4-48)

The difference in the forms of velocity equations show that the change of the drag direction is highly case dependent. In some cases and conditions, the relative velocity may be predicted to change its direction multiple times. This behavior of velocity can result in an oscillatory trajectory in a steady jet. We will not discuss the conditions for these cases here, as they are not in the scope of this study.

### 4.3.2 Orthogonal Electrified JICF – High Electric Fields

So far we have considered that the jet does not experience acceleration in its emission direction; but this may not be the case, especially when a high electric force is applied to the jet. In the present model, the equation of motion of the jet in the x direction is exactly the same as the lower electric field model, i.e. Eqs. 4-43 to 4-46. However, the electric force is dominant over shear and gravity forces in the y direction (see Appendix E). Therefore, Eq. 4-19 becomes:

\[ \Sigma F_y = \left( \rho_j \frac{\pi d_j^2 h}{4} \right) \frac{d^2 y}{dt^2} = \sigma_j A_{surf} E_y \]  

(4-49)

\[ \frac{d^2 y}{dt^2} = \frac{4 \sigma_j E_y}{\rho_j d_j} \]  

(4-50)

To find the trajectory of a jet with variable diameter, either:

1- The Eqs. 4-450 and 4-22 should be coupled and solved numerically; or

2- \( d_j \) should be expressed as a function of \( y \).

We do not have a relating equation between \( y \) and \( d_j \), and according to our observations, we consider a negligible diameter variation. Although this assumption does not satisfy the continuity equation, it can be treated as an extreme case for trajectory prediction. We will discuss this idea in §4.4. As the right hand side of Eq. 4-49 is constant, the equations of velocity and motion in the y direction are expressed with:
\[ \frac{dy}{dt} = \left( \frac{4 \sigma_j E_y}{\rho_j d_j} \right) t + k_9 \]  
\[ y = \left( \frac{2 \sigma_j E_y}{\rho_j d_j} \right) t^2 + k_9 t + k_{10} \]  

(4-51)  
(4-52)

The initial location and velocity in the y axis are zero and \( u_j \), respectively. Then:

\[ k_9 = u_j, \quad k_{10} = 0 \]  

(4-53)

The non-dimensional form of Eq. 4-52 is:

\[ y^* = 2 \left( \frac{L_j}{d_j} \right) \xi_{i,y} t^2 + t^* \]  

(4-54)

Solving this equation for \( t^* \) gives us two answer, in which the positive values are acceptable:

\[
t^* = \begin{cases} 
-1 + \sqrt{1 + 8 \left( \frac{L_j}{d_j} \right) \xi_{i,y} y^*} \\
\xi_{i,y} \left( \frac{L_j}{d_j} \right) 
\end{cases} [\xi_{i,y} > 0] \quad (4-55) \\
-1 - \sqrt{1 + 8 \left( \frac{L_j}{d_j} \right) \xi_{i,y} y^*} \\
4\xi_{i,y} \left( \frac{L_j}{d_j} \right) \quad [\xi_{i,y} < 0] \quad (4-56) 
\]

In the low electric field model, \( \xi_{i,y} \) is small, or zero, and Eq. 4-54 reduces to Eq. 4-47. This means, one can consider the low electric field model as an especial case of the high electric field model. We differentiate these two models, to highlight the importance of the effective electric force in the y direction. Analysis on the predicted trajectories by these models and the comparison between them will be provided and discussed in §4.4.1.
4.3.3 Angled EJICF (Electrosprayed JICF) – Low Electric Fields

In this part the equation of motion is derived for the case of an emitting jet with an angle of $\beta_0$ with respect to the y axis, under the influence of a crossflow in the x direction. As shown in the previous chapter, the crossflow adds an initial angle to the emitting jet from the cone; therefore, one can call the angled case an "Electrosprayed jet in crossflow". One should note that $\beta_0$ is different than the $\alpha_1$ introduced in §3.1. $\beta_0$ is the initial jet emission angle; where $\alpha_1$ is the average deflection angle and its value is larger. Similar to §4.3.1, the acceleration in the jet direction is neglected initially. Solving the force balance in the x-y coordinates needs a coupling, as the applied forces in each direction have both x and y parameters. In order to avoid the coupling, the coordinates are rotated to eliminate the dependence of force balance equations. As illustrated in Fig. 4.6, the direction of jet can be set on the y' axis with rotating the coordinates for $\beta_0$ degrees, counter clockwise. In a similar manner to the orthogonal EJICF, the velocity in the y' direction is considered constant and equals to $u_j$; therefore:

$$y' = u_j t$$  \hspace{1cm} (4-57)
The force balance in the $x'$ direction becomes:

$$\frac{d^2 x'}{dt^2} = \begin{cases} 
  a \left( b - \frac{dx'}{dt} \right)^2 + c & \left[ u_g \cos \beta_0 \geq \frac{dx'}{dt} \right] \\
  -a \left( b - \frac{dx'}{dt} \right)^2 + c & \left[ u_g \cos \beta_0 \leq \frac{dx'}{dt} \right] 
\end{cases}$$

(4-58) (4-59)

The solution of Eqs. 4-58 and 59 are similar to the orthogonal EJICF cases; however, one should note the adjustment in the coefficients:

$$a = \frac{2C_{D,x'} \rho_g}{\pi d_j \rho_j}, \quad b = u_g \cos \beta_0, \quad c = \frac{4\sigma_j E_{x'}}{\rho_j d_j}$$

(4-60)

$$E_{x'} = E_x \cos \beta_0 - E_y \sin \beta_0$$

(4-61)

This change of electric field should be implemented in $\mathcal{E}_i$ calculations as well:

$$\mathcal{E}_{i\,x'} = \frac{E_{x'} \sigma_j}{\rho_j u_j^2} = \frac{(E_x \cos \beta_0 - E_y \sin \beta_0) \sigma_j}{\rho_j u_j^2}$$

(4-62)

$$\mathcal{E}_{i\,g\,x'} = \frac{E_{x'} \sigma_j}{\rho_g u_g^2} = \frac{(E_x \cos \beta_0 - E_y \sin \beta_0) \sigma_j}{\rho_g u_g^2}$$

(4-63)

The non-dimensional trajectory equations in the $x'$ direction for the four combinations of positive or negative electric fields and drag forces are provided in the following:

$$x' (t^*) = \left( \frac{u_g \cos \beta_0}{u_j} \right) t^* + \frac{\pi}{2C_{D,x'}} \left( \frac{\rho_j}{\rho_g} \right) \left( \frac{d_j}{L_j} \right)$$

$$\times \ln \left( \cos \left[ \tan^{-1} \left[ \cos \beta_0 \frac{C_{D,x'}}{2\pi \mathcal{E}_{i\,g\,x'}} \right] \right] \right)$$

(4-64)

For $$\frac{u_g \cos \beta_0}{u_j} \geq \frac{dx'}{dt^*} \quad \& \quad \mathcal{E}_{i\,x'} > 0$$
\[ x^* (t^*) = \left( \frac{u_g \cos \beta_0}{u_j} \right) t^* - \frac{\pi}{2C_{D,x'}} \left( \frac{\rho_j}{\rho_g} \right) \left( \frac{d_i}{L_i} \right) \times \ln \left( \frac{\cosh \left[ \tanh^{-1} \left( \cos \beta_0 \sqrt{\frac{C_{D,x'}}{2\pi \xi_{g,x'}}} \right) \right]}{\cosh \left[ \left( \frac{L_i}{d_i} \right) \sqrt{\frac{8C_{D,x'} \xi_{g,x'}^2}{\pi}} t^* + \tanh^{-1} \left( \cos \beta_0 \sqrt{\frac{C_{D,x'}}{2\pi \xi_{g,x'}}} \right) \right]} \right) \]  

(4-65)

For \[ \left[ \frac{u_g \cos \beta_0}{u_j} \leq \frac{dx^*}{dt^*} \& \xi_{x,x'} > 0 \right] \]

\[ x^* (t^*) = \left( \frac{u_g \cos \beta_0}{u_j} \right) t^* + \frac{\pi}{2C_{D,x'}} \left( \frac{\rho_j}{\rho_g} \right) \left( \frac{d_i}{L_i} \right) \times \ln \left( \frac{\cosh \left[ \tanh^{-1} \left( \cos \beta_0 \sqrt{\frac{C_{D,x'}}{2\pi \xi_{g,x'}}} \right) \right]}{\cosh \left[ \left( \frac{L_i}{d_i} \right) \sqrt{\frac{8C_{D,x'} \xi_{g,x'}^2}{\pi}} t^* + \tanh^{-1} \left( \cos \beta_0 \sqrt{\frac{C_{D,x'}}{2\pi \xi_{g,x'}}} \right) \right]} \right) \]  

(4-66)

For \[ \left[ \frac{u_g \cos \beta_0}{u_j} \geq \frac{dx^*}{dt^*} \& \xi_{x,x'} < 0 \right] \]

\[ x^* (t^*) = \left( \frac{u_g \cos \beta_0}{u_j} \right) t^* - \frac{\pi}{2C_{D,x'}} \left( \frac{\rho_j}{\rho_g} \right) \left( \frac{d_i}{L_i} \right) \times \ln \left( \frac{\cosh \left[ \tanh^{-1} \left( \cos \beta_0 \sqrt{\frac{C_{D,x'}}{2\pi \xi_{g,x'}}} \right) \right]}{\cosh \left[ \left( \frac{L_i}{d_i} \right) \sqrt{\frac{8C_{D,x'} \xi_{g,x'}^2}{\pi}} t^* + \tanh^{-1} \left( \cos \beta_0 \sqrt{\frac{C_{D,x'}}{2\pi \xi_{g,x'}}} \right) \right]} \right) \]  

(4-67)

For \[ \left[ \frac{u_g \cos \beta_0}{u_j} \leq \frac{dx^*}{dt^*} \& \xi_{x,x'} < 0 \right] \]
From Eq. 4.57, the non-dimensional form of time can be replaced with:

\[ t^* = y'' \]  

(4-68)

In these equations, all the coefficients are found and replaced using the input parameters. To find and plot the jet trajectory in the x-y coordinates, one need to rotate the coordinates back. For this purpose, \( x' \) and \( y' \) need to be replaced using the following rotation matrix:

\[
\begin{bmatrix}
  x' \\
  y'
\end{bmatrix} =
\begin{bmatrix}
  \cos \beta_0 & \sin \beta_0 \\
  -\sin \beta_0 & \cos \beta_0
\end{bmatrix}
\begin{bmatrix}
  x \\
  y
\end{bmatrix}
\]

(4-69)

For simplicity, this rotation is applied with the location values, after the calculations of jet trajectory are completed.

### 4.3.4 Angled EJICF (Electrosprayed JICF) – High Electric Fields

For high electric fields, the equation of motion in the \( x' \) direction is similar to the low field case, Eqs. 4-64 to 4-67. In the \( y' \) direction, according to Fig. 4.4, the electric field is expressed as:

\[ E_{y'} = E_x \sin \beta_0 + E_y \cos \beta_0 \]  

(4-70)

If the electric field is dominant with respect to shear, as brought up in §4.3.2, the force balance in \( y' \) becomes:

\[
\frac{d^2 y'}{dt^2} = \frac{4 \sigma_j E_{y'}}{\rho_j d_j} \]  

(4-71)

The non-dimensional forms of location in the \( y' \) direction is represented as:

\[ y'' = 2 \left( \frac{L_j}{d_j} \right) \varepsilon_{i,y} t'^2 + t^* \]  

(4-72)

Thus, the non-dimensional time for positive and negative electric field in the \( y' \) direction, respectively, become:
Two other models for high electric fields are also presented in Appendix E. These models are different with the current model in the decoupling assumptions and drag calculation.

4.4 Results

4.4.1 Model Analysis

In this section, the effective parameters and the general forms of jet trajectory equations in high and low electric fields are discussed. In here, we only analyze the orthogonal EJICF cases and the jet velocity in the x direction is always smaller than the gas velocity and the electric field is applied in the positive direction. The trajectory equation for this condition, Eq. 4-43, is rewritten in a non-dimensionalized form with using $d_j$ as the characteristic length, instead of $L_j$. Thus this equation becomes:

$$x^*(t^*) = \left(\frac{u_g}{u_j}\right) t^* + \frac{\pi}{2C_{D,x}} \left(\frac{\rho_j}{\rho_g}\right) \times \ln \left( \cos \left( \tan^{-1} \left[ -\frac{C_{D,x}}{2\pi q\varepsilon_i_{j,x}} \right] \right) \right)$$

$$x^*(t^*) = \left\{ \begin{array}{ll}
-1 + \sqrt{1 + 8 \left(\frac{L_j}{d_j}\right) \varepsilon_{i,y} y'^*} & [\varepsilon_{i,y} > 0] \\
4\varepsilon_{i,y,j} \left(\frac{L_j}{d_j}\right) & \\
-1 - \sqrt{1 + 8 \left(\frac{L_j}{d_j}\right) \varepsilon_{i,y} y'^*} & [\varepsilon_{i,y} < 0]
\end{array} \right. \quad (4-73)$$

$$t^* = \frac{4\varepsilon_{i,y,j} \left(\frac{L_j}{d_j}\right)}{4\varepsilon_{i,y,j} \left(\frac{L_j}{d_j}\right)} \quad (4-74)$$
where q is the ratio of jet inertia to the crossflow inertia:

\[ q = \frac{\rho_j u_j^2}{\rho_g u_g^2} \]  

(4-76)

This parameter is the most important factor affecting the trajectory of an ordinary (not electrified) JICF [67]. As we eliminated \( L_j \), the three independent parameters affecting the motion of an EJICF in the x direction are \( \frac{\rho_j}{\rho_g}, \frac{u_j}{u_g}, \mathcal{E}_{i,ij} \). In the low electric field model, according to Eq. 4-47, the non-dimensional y and time are equal. For the high electric field model, the non-dimensional form of Eq. 4-54, with using \( d_j \) instead of \( L_j \), becomes:

\[ y^* = 2\mathcal{E}_{i,y}t^* + t^* \]  

(4-77)

The only parameter changing the trajectory in the y direction is \( \mathcal{E}_{i,j,y} \). An electrified methanol jet is used for the analysis. The considered jet diameter, emission velocity, density, and surface charge are 5 \( \mu \)m, 10 m/s, 792.1 kg/m\(^3\), and \( 10^{-4} \) C/m\(^2\), respectively. The density and viscosity of air crossflow are 1.173 kg/m\(^3\) and 18.1\( \times \)10\(^{-6} \) kg/(m s), respectively. Table 4.4 lists the adopted gas flow inputs to the models for our analysis. Table 4.5 lists the used electric field parameters for both x and y directions.

### Table 4.4 Adopted air flow inputs for the model analysis

<table>
<thead>
<tr>
<th>( u_g ) [m/s]</th>
<th>25</th>
<th>50</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>q</td>
<td>108</td>
<td>27</td>
<td>6.75</td>
</tr>
<tr>
<td>Re</td>
<td>8.1</td>
<td>16.2</td>
<td>32.4</td>
</tr>
<tr>
<td>( C_{D,x} )</td>
<td>3.51</td>
<td>2.48</td>
<td>1.76</td>
</tr>
</tbody>
</table>

### Table 4.5 Adopted electric field inputs for the model analysis

<table>
<thead>
<tr>
<th>( E_x, E_y ) [V/m]</th>
<th>1</th>
<th>( 10^4 )</th>
<th>( 10^6 )</th>
<th>( 10^7 )</th>
<th>( 10^8 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mathcal{E}<em>{i,x} ), ( \mathcal{E}</em>{i,y} )</td>
<td>( 1.25 \times 10^{-9} )</td>
<td>( 1.25 \times 10^{-5} )</td>
<td>( 1.25 \times 10^{-3} )</td>
<td>( 1.25 \times 10^{-2} )</td>
<td>( 1.25 \times 10^{-1} )</td>
</tr>
</tbody>
</table>
Figure 4. The non-dimensional jet trajectory prediction at $\varepsilon_i = 1.25 \times 10^{-3}$, $\rho_j/\rho_g = 675$, and different $\varepsilon_{i,y}$ and $q$s

Figure 4.7 shows the trajectory predictions at $\varepsilon_{i,x} = 1.25 \times 10^{-3}$ at different $q$ and $\varepsilon_{i,y}$ values. The jet trajectories are shown up to the point where the jet velocity in the $x$ direction becomes equal to the crossflow velocity. Once the jet velocity exceeds the gas velocity, Eq. 4-28 with new initial conditions should be adopted in order to continue the trajectory prediction. The initial velocity for this equation is the new relative velocity between the jet and crossflow, which is equal to zero. The initial location should be implemented from the calculated value by the previous equation.
As shown in Fig. 4.7, the increase of $q$ decreases the trajectory bending in the flow direction, independent from $\mathcal{E}$. This is due to the increase of jet velocity and inertia in comparison to the applied inertia by the gas. The $\mathcal{E}_{i,j}=0$ is the low electric filed case in which the bending in the flow direction is the highest. This is because there is no extra force to pull the jet in the $y$ direction. In this case, the slope of trajectory decreases as moving to the downstream. Usually a penetration length for a jet or a spray is defined for the fuel mixing and combustion applications. Above the penetration length, the jet does not travel significantly in the $y$ direction.

![Figure 4.8 The non-dimensional jet trajectory prediction with low electric field model, $\rho_j/\rho_g = 675$, $q = 6.75$, and different $\mathcal{E}_{i,j}$s](image-url)
At low $\mathcal{E}_{ij}$, the jet trajectories overlap the no electric or the low electric field model results. As $\mathcal{E}_{ij}$ increases, the jet bends more in the y direction. Above a specific value of $\mathcal{E}_{ij}$, which depends on the other independent parameters, the slope of trajectory increases at downstream. This means the jet tends to move in the y direction infinitely. The motion in the x direction, Eq. 4-74, is of the first order with an oscillatory term. The motion in the y direction with an electric force, Eq. 4-76, is a second order parabola. This is the reason that the jet with a constant acceleration term in the y direction tends to penetrate in this direction.

Figure 4.8 shows the trajectory prediction with the low electric field model at $q$ of 6.75 and different $\mathcal{E}_{ij}$s. At high electric fields in the x direction, the jet bends so much. As the electric field decreases, the trajectory bending decreases and, therefore, the penetration length increases. Below a certain value of $\mathcal{E}_{ij}$ (~$10^{-5}$), the trajectory does not change noticeably, e.g. the trajectories at 1 V/m and $10^4$ V/m are almost identical.

4.4.2 Comparison of the Model with Experiments

In this part, the experimental results are compared with the theoretical outcomes for the deflections of an electrosprayed jet in 4 and 8 Scfh air crossflows, equivalent to 6.96 and 13.91 m/s inlet velocities, respectively. Experimental data of each case was derived by extracting jet trajectory for at least 10 images, and then averaging them.

4.4.2.1 Input Conditions

The inputs of the proposed models are according to two experimental cases. In these cases, the ES was operating at 3.05 kV and 2 µL/min. Adopting Eqs. 4-5 to 4-7, the average crossflow velocities at the jet location become 4 and 9.12 m/s, for 4 and 8 Scfh cases, respectively. The initial jet angles were approximately $\pi/10$, and $\pi/8$, respectively. The jet diameter was approximated using the high speed flash images, Fig. 1.3, captured at similar operating conditions, but without the air crossflow. The density and viscosity of air, at standard room temperature and pressure, are 1.173 kg/m$^3$ and $18.1 \times 10^{-6}$ kg/(m s), respectively.

The jet velocity is calculated with the continuity equation for the incompressible liquid:

$$u_j = \frac{4Q_{sol}}{\pi d_j^2} \quad (4-78)$$
where, $Q_{sol}$ is the volumetric flow rate of the working liquid. The measured average diameter of the generated main droplets was approximately 5 μm. Based on Eqs. 1-8 and 4-78 the jet diameter and velocity are 2.85 μm and 5.25 m/s, respectively. Having these known parameters, one can calculate the gas Reynolds number over the jet and then the drag coefficients by Eq. 4-4. For the calculation of $C_{D,x'}$ the initial relative velocity in the $x'$ direction is used.

### Table 4.6 Trajectory prediction cases and inputs of the derive equations for an EJICF

<table>
<thead>
<tr>
<th>Case #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crossflow [Scfh]</td>
<td>4</td>
<td>4</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>$q/m$ [C/kg]</td>
<td>J and T</td>
<td>V and N</td>
<td>J and T</td>
<td>V and N</td>
</tr>
<tr>
<td>$\beta_0$ [Rad]</td>
<td>$\pi/10$</td>
<td>$\pi/10$</td>
<td>$\pi/8$</td>
<td>$\pi/8$</td>
</tr>
<tr>
<td>$d_j / L_j$</td>
<td>0.0233</td>
<td>0.0233</td>
<td>0.0233</td>
<td>0.0233</td>
</tr>
<tr>
<td>$u_g / u_j$</td>
<td>0.76</td>
<td>0.76</td>
<td>1.73</td>
<td>1.73</td>
</tr>
<tr>
<td>$\rho_g / \rho_j$</td>
<td>$1.39 \times 10^{-3}$</td>
<td>$1.39 \times 10^{-3}$</td>
<td>$1.39 \times 10^{-3}$</td>
<td>$1.39 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\mathcal{E}_{i,j,x'}$</td>
<td>$-6.95 \times 10^{-4}$</td>
<td>$-1.26 \times 10^{-3}$</td>
<td>$-2.13 \times 10^{-3}$</td>
<td>$-3.86 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\mathcal{E}_{i,g,x'}$</td>
<td>$-8.65 \times 10^{-1}$</td>
<td>$-1.57$</td>
<td>$-5.10 \times 10^{-1}$</td>
<td>$-9.24 \times 10^{-1}$</td>
</tr>
<tr>
<td>$\mathcal{E}_{i,j,y'}$</td>
<td>$-1.93 \times 10^{-2}$</td>
<td>$-3.49 \times 10^{-2}$</td>
<td>$-1.85 \times 10^{-2}$</td>
<td>$-3.35 \times 10^{-2}$</td>
</tr>
<tr>
<td>$Re_{x'}$</td>
<td>0.7</td>
<td>0.7</td>
<td>1.55</td>
<td>1.55</td>
</tr>
<tr>
<td>$C_{D,x'}$</td>
<td>12.0</td>
<td>12.0</td>
<td>8.03</td>
<td>8.03</td>
</tr>
</tbody>
</table>

In order to determine the ratio between the jet diameter and length, we used a set of images taken with the high speed flash. The jet length was 122±6 μm, giving the jet length to diameter ratio of ~43. Comparing this value with Eq. 1-11, the constant in this equation for our electospraying
condition is approximately 20. The discrepancy of this value from Grant and Middleman [33] is related to the role of electrical conductivity of working solution in electrosprayed jets.

The jet surface charge was calculated with Vonnegut and Neubauer [42], and Jones and Thong [19] correlations; $2.21 \times 10^{-4}$, and $1.22 \times 10^{-4}$ C/m², respectively. The constant values of $E_x$ and $E_y$ are estimated with the average of electric fields on the jet, between the cone apex and the break up point of the jet (i.e. $0 < x'/L_j < 1$ & $y' = 0$). Once the averaged values are found, $\mathcal{E}$is are calculated with Eqs. 4-41, 4-42, 4-62, and 4-63. Based on the air crossflow and the surface charge correlations, four cases are separated and discussed. Table 4.6 lists the input values of the derived trajectory equations for these cases.

### 4.4.2.2 Trajectory Prediction and Analysis

The trajectory results of listed cases are illustrated and compared in Figs. 4.9 to 4.12. We first compare the results for different surface charges. Then, the predictions of low electric field model (LE) and high electric field model (HE) are discussed.

In the prediction of cases #2 and #4, Figs. 4-10 and 4-12, both of the models show a smaller deflection in contrast to cases #1 and #3, Figs. 4-9 and 4-11, respectively. This observation is related to the electric charge correlations. Vonnegut and Neubauer’s model predicts a higher surface charge. According to Eqs. 4-8 and 4-9, the electric force and then $\mathcal{E}i$ take larger negative values using this correlation. In LE, the electric field is only defined normal to the jet direction. The larger the $\mathcal{E}i$, the larger the electric force toward the left in the $x'$ direction; thus, the smaller the bending. In HE solution, the $\mathcal{E}i$ is defined in 2D and the increase of surface charge increases the electric force in both $x$ and $y$ directions, with the same proportion. As the deflection of jet depends on the total forces in each direction, the magnitude of drag force comes into the play as well. In other words, using the HE approach, the variation of jet deflection with surface charge is case dependent. In our cases, Figs. 4.9 to 4.12, it is apparent that the increase of surface charge changes the total force in the $x$ direction more than the $y$ direction. With a similar reasoning, the influence of surface charge on LE is more than HE.
Figure 4.9 The non-dimensional trajectory of the electrospayed JICF; Case #1: 4 Scfh (7.6 m/s) crossflow and Jones and Thong’s correlation for surface charge prediction ($\beta_0: \pi/10$)

The LE model with Vonnegut and Neubuer’s correlation shows a good agreement with the experimental results. On the other hand, the trajectory in case #3, i.e. with Jones and Thong’s correlation, is highly overpredicted by LE. One may conclude the surface charge of our jet is closer to the former. This conclusion seems consistent with Pfeifer and Hendricks [98], and Ogata et al. [99], [100], who discussed the droplet specific charge versus its diameter. However, we stay
doubtful about this conclusion at this point of time, as there are many simplifying assumptions which can affect the results.

Figure 4.10 The non-dimensional trajectory of the electrospayed JICF; Case #2: 4 Scfh (7.6 m/s) crossflow and Vonnegut and Neubuer’s correlation for surface charge prediction ($\beta_0: \pi/10$)
Figure 4.11 The non-dimensional trajectory of the electrosprayed JICF; Case #3: 8 Scfh (15.1 m/s) crossflow and Jones and Thong’s correlation for surface charge prediction ($\beta_0: \pi/8$)

In all of the shown cases, the LE model bends toward the right side of the initial slope. This means that the positive drag force is larger than the negative electric force in the normal direction to jet. Besides, LE predicts a larger bend than HE. This observation is expected, as the HE has an extra accelerating force, applied in the jet flow direction; therefore, this model forecasts more movement
in the jet direction. If the electric force was decelerating, i.e. against the jet flow, the HE prediction would show a higher deflection toward the right, with respect to the LE.

Figure 4.12 The non-dimensional trajectory of the electrospayed JICF; Case #4: 8 Scfh (15.1 m/s) crossflow and Vonnegut and Neubuer’s correlation for surface charge prediction ($\beta_0 : \pi/8$)
In an EJICF, the effective electric force on the dynamic of jet can be smaller than the multiplication of the electric field by the charge. The reason is the interaction among the charged molecules inside the jet. The applied electric force may take the pressure form in the jet. This means, not all the applied electric force is devoted to the increasing the velocity in the applied direction. Only a portion of the total electric force accelerates the jet. This is why the jet diameter variation is not noticeable as one may expect. The amount of effective force can be found by considering the continuity equation, measuring the diameter change, and calculating the acceleration.

The diameter of our electrosprayed jets are in the order of micron and we were not able to perform optical diameter measurements in order to implement it to our model. However, we conclude:

i- LE and HE models can be treated as the extreme cases, illustrating the range in which the electrified jet bends in a gas crossflow. In other words, the real trajectory of the jet falls between these two extremes.

ii- An exact prediction should be feasible with knowing the proportion of the effective electric force with respect to the total applied force.

These conclusions are observed in all the cases, as almost all the HE models underpredict the jet trajectory and, on the other hand, LE overpredicts it. This range becomes wider as the air crossflow increases and enhances the effect of drag.

At the time of writing this thesis, we were working on the experiments with larger electrified jets in different crossflows. This study should result in better understanding about the physics of the problem, in addition to stronger proofs and firm conclusions on the precision of our analytical models.
Chapter 5

5 Charged Droplets in Crossflow (Numerical Analysis)

5.1 Introduction

The prediction of plume trajectory is of a great importance in MS to control the traveling paths of ions. Our ultimate goal is to predict the trajectory of ES plume inside a chamber with a sudden expansion inlet and a tapered outlet. As shown in Fig. 5.1, a charged droplet starts its journey at the jet breakup location and travels under the influence of different forces. In our model, the equations of motion of a droplet are solved in 2D Cartesian coordinates on the central plane of the vessel. The drag and electric forces are estimated based on 3D axisymmetric models. The droplet evaporation is also considered. The properties of droplet are calculated in each time step.

Figure 5.1 Close up illustration of a generated charged droplet by ES inside the chamber
A Visual Basic for Applications (VBA) code integrated in Microsoft Excel is developed to estimate the trajectory of a single charged droplet inside the vessel. Multiple runs of this code with different initial inputs were computed in order to predict the plume trajectory. The designed Excel sheet has a user friendly environment. In order to run the program, one only needs to enter the initial and operating conditions. The time of a single run is in the order of 15 seconds for 100,000 time steps (with an Intel Premium CPU G620 @ 2.60GHz and 3.85 RAM). The results and corresponding graphs are recorded in the same file and can be observed and analyzed quickly.

In this chapter, the physics behind the trajectory simulation of a charged droplet inside the chamber is presented. The assumptions and input conditions are discussed. Then, the employed numerical methods and the procedure to solve the equations of droplet motion, size, and temperature are shown. Finally, the simulation results based on our experimental inputs from chapter 3, are presented and analyzed.

5.2 Theory

Applied forces, evaporation, and the temperature variation of the droplet are discussed in this section. Adopted correlations for the calculation of properties are also presented.

5.2.1 Drag Force

In order to calculate the applied drag force on the droplet, the air velocity profiles inside the vessel is implemented in the model. Existing analytical solutions for a sudden expansion can be derived for specific cases. For instance, the proposed similarity solution by Revuelta et al. [101] is true when the diameter of a laminar air jet is much smaller than the vessel diameter, or:

\[ \Re_{in} \times \frac{d_{in}}{d_v} \approx 1 \]  

(5-1)

In our tests, this value is at least 100 times larger than unity and this solution cannot be adopted. Therefore, we have approximated the air flow of the chamber with other known profiles, e.g. experimental results in the literature.
As mentioned before, in a sudden expansion, a main flow at the central zone of the chamber and a recirculation flow next to the expansion steps are generated, Fig. 5.2. The radial velocity of the air is neglected, due to its small value and simplicity of the solution. Similar to chapter 4, the
expansion is considered linear and the average velocity in each cross section is calculated using Eqs. 4-5 to 4-7. Based on this average velocity, two distributions are considered to predict the velocity profile of the main flow, namely: Laminar/Turbulent, and Gaussian. For the former, first, the regime of flow is identified using the inlet Reynolds. Then, one of the following equations is adopted in order to find the axial air velocity at different distances from centerline:

\[
u_g(X, r) = \begin{cases} 
2U_{Avg}(X) \times \left(1 - \frac{r^2}{r_{Ex}^2}\right) & \text{Laminar} \\
1.225U_{Avg}(X) \times \left(1 - \frac{r}{r_{Ex}}\right)^{1/7} & \text{Turbulent}
\end{cases}
\] (5-2)

Note that r-X represents a 2D cylindrical coordinate with the origin at the center of inlet pipe, Fig. 5.2. Albertson et al. [102] suggested a Gaussian velocity profile for a submerged jet expansion. Thus, in the second velocity profile, a Gaussian distribution with the standard deviation of \(r_{Ex}/3\) is considered:

\[
u_g(X, r) = 4.55U_{Avg}(X) \times e^{-4.5\left(\frac{r}{r_{Ex}}\right)^2}
\] (5-3)

The derivations of Eqs. 5-2 and 5-3 are shown in Appendix F.

For the negative flow, next to the walls, always the laminar profiles are used, as they look more compatible with the experimental results [75]. According to these experiments, the average velocity of the negative flow in a cross section is approximately one tenth of the main flow in that cross section. We assume the negative velocity is the maximum at the center of its profile, i.e. between the wall and the boundary of forward and returning flows. Therefore, for \(r > r_{Ex}\):

\[
u_g(X, r) = -0.2U_{Avg} \left(1 - \frac{r - \left[d_v/2 + r_{Ex}\right]}{d_v/2 - r_{Ex}}\right)^2
\] (5-4)

where, \(d_v\) is the inner diameter of the chamber. In order to adopt the drag force solution to our 2D Cartesian coordinates, r and X are replaced with \(|L_{tip-CL} - y|\), and \((x + L_{tip-in})\), respectively. \(L_{tip-CL}\) and \(L_{tip-in}\) are the distance of the capillary from the centerline and the gas inlet of the chamber, respectively.
The droplet is considered spherical at all times and its drag coefficient is calculated based on the Reynolds number using the relative velocity of the air [103]:

\[
C_D = \begin{cases} 
0 & \text{[Re}_d = 0] \\
\frac{24}{Re_d} \left(1 + \frac{Re_d^2}{6}\right) & \text{[Re}_d \leq 1000] \\
0.424 & \text{[Re}_d > 1000]
\end{cases} 
\]  

(5-5)

where,

\[
Re_d = \frac{\rho_g U_{rel} d_d}{\mu_g} 
\]  

(5-6)

The frontal area of a sphere is a circle with the droplet diameter:

\[
A_{Fr} = \frac{\pi d_d^2}{4} 
\]  

(5-7)

Now, the drag force can be calculated at each time step by:

\[
F_{Dx} = \frac{1}{2} C_D \rho_g A_{Fr} U_{rel} (u_g - u_d) 
\]  

(5-8)

\[
F_{Dy} = \frac{1}{2} C_D \rho_g A_{Fr} U_{rel} (w_g - w_d) 
\]  

(5-9)

where, \(u\), and \(w\) are instantaneous velocities in the x and y directions, respectively, and the relative velocity in each instant is defined as:

\[
U_{rel} = \sqrt{(u_g - u_d)^2 + (w_g - w_d)^2} 
\]  

(5-10)

5.2.2 External Electric Force

Needle-plate configuration is considered for the electric field calculations with Eqs. 4-10 and 4-11. Similar to the previous chapter, two correlations are used to calculate the amount of initial charge to mass ratio of the droplets, using Eqs. 1-20 and 1-21.
5.2.3 Image Charge Force

A charged particle near a conducting surface induces a surface charge with the opposite polarity. Therefore, an attractive force between the particle and the surface is induced. The amount of this force for a charged droplet and an infinite conductive plate is determined by [3]:

\[
F_{\text{image}} = -\frac{q_d^2}{16\pi\epsilon_0 L_{d-Gr}^2}
\]  

(5-11)

in which, \(L_{d-Gr}\) is the distance between the droplet and the plate. In our case, a downward image force is applied on the droplet from the ground plate. The amount of image force between a particle and a finite plate is lower than the calculated values by this equation; however, as we will see, the amount of this force becomes significant only when the droplets are very close to the plate, approximately 0.5 mm. At these distances the ground electrode can be considered infinite; therefore, Eq. 5-11 gives a good estimation of the image force.

5.2.4 Gravity

Gravity, or more precisely the buoyancy force, is calculated by:

\[
F_g = \frac{(\rho_g - \rho_d)\pi d^3 g}{6}
\]  

(5-12)

The amount of this force decreases, as the solution evaporates and droplet shrinks with time. The droplet density is higher than the density of medium, therefore the direction of gravity force is downwards.

5.2.5 Space Charge Force

As shown in Fig. 1.4, the electrosprayed droplets initially travel on a line. After ~0.5 mm, they start to deviate from this line and the space charge comes into play. Space charge forces become important at highly charged spray plumes. The repulsion forces among the droplets become significant, when the droplets are located very close to each other. In ESs, the direction of this force is radial and plays an important role in the beginning of the plume formation from the emitting jet. The repelling forces of charged drops on each other is more effective on smaller droplets and pushes them toward the edge of plume [25], [39]. From Sultan’s work [25], the planar
distribution of droplet diameters is illustrated in Fig. 5.3. Droplet sizes in the plume reduce almost linearly as the distance from the axis of the jet increases. As we have not considered the space charge force inside the plume, its segregation effect is not expected to be predicted by our model.

As moving downstream, the plume opens up, and droplets disperse more and more. Due to the increase of the distances among droplets, the space charge force diminishes significantly. In fact, the space charge force decreases with the distance from the breakup point. De la mora and Loscertales [41] showed that for electrospraying with a very conductive solution, where an axisymmetric plume is initiated from the apex of a Taylor cone, the space charge force is inversely proportional to the distance from the cone tip. They solved the Poisson equation in the spherical coordinates, considering a uniform charge density distribution for a conical plume. In the literature, many numerical studies have taken the space charge into account by including the repulsion of single droplets on each other, requiring relatively high processing times [15], [104]–[106]. On the other hand, some investigators have not considered the effect of repulsion between droplets [107].

![Figure 5.3](image.png)

**Figure 5.3** Droplet size distribution at the cone jet mode on X-Y plane, located 1.87 mm below the capillary tip; Sultan [25]
As our plume is deformed by air, determining a precise value for the space charge force and its effect on the droplets becomes even more complex. One may add an approximation of this force to the code with a two run trajectory calculation. In this case, first, the plume trajectory needs to be found without the space charge. Once the shape and deviation of plume are identified, the Poisson equation may be solvable analytically [41]. Then the plume trajectory can be computed again, including the derived solution for the force. In the present study, we neglect the space charge force. However, because the direction of this force inside the plume is outward, we expect to have a larger plume dispersion angle in reality, in comparison to our current predictions.

5.2.6 Evaporation

Some researchers have studied the droplet evaporation in ESs. Siu et al. [108] discussed the effect of evaporation in the mechanism of ESI-MS. They found that evaporation is not important due to the high vapor concentration in the plume, which reduces the evaporation significantly. On the other hand, Wilhelm et al. [15], [107] considered the droplet evaporation in their simulations of ES plume. They considered a background solution vapor concentration in their calculations. In our code, we take two extreme approaches for the evaporation:

1- Evaporation of a single droplet with zero solution vapor concentration in the surrounding medium;
2- No evaporation, i.e. the surrounding medium has been saturated with solution vapor.

The traveling path of a droplet in crossflow with a certain background vapor concentration, is expected to fall in between the trajectories of these two cases. Below is the description of the calculations for the first approach.

The evaporation problem is tackled with the calculation of mass loss rate at the surface of the droplet [109], [110]. The result gives a similar form to what was derived in chapter one:

\[ d_0^2 - d_i^2 = \lambda t \]  \hspace{1cm} (5-13)

\[ \lambda = \frac{8 \ln(1 + B_M) K_{Mix}}{\rho_{sol} C_{pMix}} \]  \hspace{1cm} (5-14)
where, $K_{\text{Mix}}$, $C_{p_{\text{Mix}}}$, and $B_{M}$ are thermal conductivity, the specific heat capacity of the vapor-air mixture film, and the Spalding mass transfer number, respectively. The derivative of Eq. 5-13 with respect to time, gives the rate of diameter change:

$$\frac{dd_d}{dt} = -\frac{8 \ln(1 + B_M) K_{\text{Mix}}}{2d_d \rho_{\text{sol}} C_{p_{\text{Mix}}}}$$ (5-15)

In order to calculate the unknown parameters of this equation, the mass fraction of vapor solution, $y_{vf}$, and air, $y_{gf}$, in the gaseous film mixture should be found first:

$$y_{vs} = \frac{m_{vs}}{m_{vs} + m_{gs}} = \frac{1}{1 + \frac{P_{gs} M_g}{P_{vs} M_v}}$$ (5-16)

Indices $g$, $v$, $s$, $f$, and $\infty$ represent the air, solution vapor, at the droplet surface, at the gas-vapor mixture film, and the surrounding medium, respectively. Using the Dalton’s law of gas partial pressures in a mixture, $P_\infty = P_{vs} + P_{gs}$, we have:

$$y_{vs} = \frac{1}{1 + \left(\frac{P_\infty}{P_{vs}} - 1\right) \left(\frac{M_g}{M_v}\right)}$$ (5-17)

The mass fraction of vapor in the film is averaged with giving a higher weight to the portion of vapor solution [111]:

$$y_{vf} = \frac{2}{3} y_{vs}$$ (5-18)

$$y_{gf} = 1 - y_{vf}$$ (5-19)

$$K_{\text{Mix}} = y_{vf} K_v + y_{gf} K_g$$ (5-20)

$$C_{p_{\text{Mix}}} = y_{vf} C_{p_v} + y_{gf} C_{p_g}$$ (5-21)

Thermal conductivity and specific heat values are calculated at a reference temperature (provided in §5.2.8). The Spalding mass transfer number is defined as:
\[ B_M = \frac{y_{vs} - y_{v∞}}{1 - y_{vs}} \]  \hspace{1cm} (5-22)

where, \( y_{v∞} \) is the mass fraction of vapor in the surrounding air. As our air crossflow was dry; thus \( y_{v∞} \) is zero and Spalding mass transfer number reduces to:

\[ B_M = \frac{y_{vs}}{1 - y_{vs}} \]  \hspace{1cm} (5-23)

Assuming that the liquid and vapor phases are in equilibrium at the evaporating solution surface, Antoine equation gives the following vapor pressure:

\[ P_{vs} = 10^{a - \frac{b}{T_s + c}} \]  \hspace{1cm} (5-24)

where a, b, and c are Antoine constants, calculated from the experimental results of vapor pressure [112]. The temperature and the pressure in this equation are in Celsius and millimeters of Mercury, respectively. These values for water and methanol are listed in the table below:

| Table 5.1 Antoine constants for water (W), methanol (M), and 75% M-25% W volumetric mixture |
|--------------------------------------|----|----|----|----|
| Temperature Range [°C]              | a  | b  | c  | Error % |
| Water                               | -17.3 ~ 100 | 7.52940 | 1435.264 | 208.302 | 1.79 |
| Methanol                            | 14.9 ~ 83.6 | 8.07919 | 1581.341 | 239.650 | 0.08 |
| 75% M-25% W                         | 14.9 ~ 83.6 | 8.012  | 1544.822 | 231.813 | 3.53 |

From combining Raoult’s Law [113], and Dalton’s Law, the vapor pressure of an ideal solution is determined by:

\[ P_{vs} = (P_{vs})_1x_1 + (P_{vs})_2x_2 \]  \hspace{1cm} (5-25)

where \( x_1 \), and \( x_2 \) are mole fraction of component 1 and 2 in the solution, respectively. A liquid mixture is called ideal when the polarities of the components are similar. According to Raoult’s Law, the ratio of the components in the liquid and gas phases are not the same as in the solution.
In other words, one component evaporates faster than the other, and as a result, the ratio of the solution varies with time. Although this effect can influence the evaporation rate, we treat the mixture as a pure liquid, assuming the ratio of water and methanol stays constant in the liquid phase. Besides, the methanol and water mixture is not really an ideal solution [114]. The vapor pressure of the mixture at different temperatures is calculated by Eq. 5-25. The Antoine constants of the mixture based on the calculated pressure values are listed in Table 5.1. In order to convert the pressure values to the SI unit, pascal, the result of Eq. 5-24 is multiplied by 133.32.

5.2.7 Droplet Temperature

Droplet evaporation and heat transfer with the surrounding changes the droplet temperature. In order to calculate the temperature variation, first we need to know the mass rate of droplet evaporation. This value can be found with the following equation [110]:

\[
\dot{m}_{evap} = \frac{\bar{h} \ln(1 + B_M)}{C_{p,Mix}} \times \pi d_d^2
\]  

(5-26)

where, \( \bar{h} \) is the convective heat transfer coefficient and can be calculated using the Nusselt number, \( \bar{Nu} \):

\[
\bar{h} = \frac{\bar{Nu} K_g}{d_d} = \frac{(2 + 0.6Re_d^{0.5}Pr_g^{0.33}) K_g}{d_d}
\]  

(5-27)

The temperature variation with time is computed with [115]:

\[
\frac{dT}{dt} = \frac{\dot{m}_l L_l \left( \frac{B_T}{B_M} - 1 \right)}{C_{p,sol} m_d}
\]  

(5-28)

where, the Spalding heat transfer number, \( B_T \), is defined as:

\[
B_T = \frac{C_{p,Mix}(T_{\infty} - T_s)}{L_{sol}}
\]  

(5-29)
5.2.8 Property Correlations

5.2.8.1 Properties of Solution and Its Vapor

The working solution influences the temperature variation, evaporation, and the amount of applied forces, and therefore the trajectory of the droplet. Here, we concentrate on the properties of the 75% Methanol-25% Water volumetric solution.

The temperature variation inside the droplet is neglected due to its small size and relatively high conductivity. Therefore, the properties of solution are determined at the surface temperature of droplet, \( T_s \). The properties of the solution vapor are calculated in an averaged reference temperature, \( T_{\text{ref}} \), between the surface and air temperature, using the one-third rule; recommended by Yuen and Chen [111]:

\[
T_{\text{ref}} = T_s + \frac{T_{\infty} - T_s}{3} \tag{5-30}
\]

The properties are computed in each time step with the following equations in KMS SI units. The derivation of these correlations, including their references, have been presented in Appendix C.

\[
\rho_{\text{sol}}(T_s) = -0.891 T_s + 1096.8 \tag{5-31}
\]

\[
K_v(T_{\text{ref}}) = -3.08 \times 10^{-9} T_{\text{ref}}^2 + 1.03 \times 10^{-4} T_{\text{ref}} - 0.0154 \tag{5-32}
\]

\[
L_{\text{sol}}(T_s) = 1943.2 \left( 1 - \frac{T_s}{546.5} \right)^{0.38} \tag{5-33}
\]

\[
C_{p_v}(T_{\text{ref}}) = 2.10 T_{\text{ref}} + 842 \tag{5-34}
\]

\[
C_{p_{\text{sol}}}(T_s) = 3.28 \times 10^{-2} T_s^2 - 14.5 T_s + 4200 \tag{5-35}
\]

The initial diameter, location and velocity of droplet in 2D Cartesian coordinates are also inputs to the code, which will be discussed later (see §5.4).
5.2.8.2 Air Properties

Similar to the solution vapor, the air properties are also computed at the reference temperature, at each time step:

\[
\rho_g(T_{\text{ref}}) = \frac{351.99}{T_{\text{ref}}} + \frac{344.84}{T_{\text{ref}}^2}
\]

\[ (5-36) \]

\[
\mu_g(T_{\text{ref}}) = \frac{1.4592 T_{\text{ref}}^{1.5}}{109.1 + T_{\text{ref}}} \times 10^{-6}
\]

\[ (5-37) \]

\[
K_g(T_{\text{ref}}) = \frac{2.3340 T_{\text{ref}}^{1.5}}{164.54 + T_{\text{ref}}} \times 10^{-3}
\]

\[ (5-38) \]

\[
C_{p_g}(T_{\text{ref}}) = 3.9734 \times 10^{-4} T_{\text{ref}}^2 - 0.19975 T_{\text{ref}} + 1030.5
\]

\[ (5-39) \]

Density and specific heat equations are from Hilsenrath et al. [116]. The relations of viscosity and thermal conductivity are from Reid et al. [117]. The Prandtl number is calculated with Eqs. 5-37 to 39.

5.3 Assumptions, Simplifications, and Other Effective Factors

In this section we explain the adopted considerations and simplifying assumptions in our code, as well as the effect of other parameters.

5.3.1 Symmetry of Sudden Expansion

Above a certain Reynolds number, the velocity profiles lose their symmetry during the expansion. Many researchers have reported the asymmetric flow expansion, in a symmetric geometry [118], [119]. This critical Reynolds is usually in the laminar range and depends on the geometry and flow parameters. For simplicity, this asymmetry is not included in the code.

5.3.2 Electric Field Assumptions

The adopted electric field expressions, Eqs. 4-10 and 11, have been derived for a capillary and an infinite plate. In our case, the ground plate has finite dimensions. In reality a finite plate induces a
smaller electric field than the former [3], [19]. Therefore, our code may overpredict the external electric field. This effect is compensated with the amount of the electric charge on the droplet. In addition, in the original geometry of the chamber, the whole body is grounded. This effect is neglected in order to prevent complexity.

5.3.3 Droplet Disintegration

It is well known that a droplet breaks into smaller droplets at high air velocities. This phenomenon occurs when the aerodynamic force overcomes the surface tension force, resulting into the deformation and disintegration of the droplet [120]. The parameter relating these two forces is the droplet weber number:

$$W_{ed} = \frac{\rho g d d U_{rel}^2}{\sigma_e}$$

(5-40)

where, $\sigma_e$ is the effective surface tension of a charged droplet [120]:

$$\sigma_e = \sigma - \frac{q_d^2}{8\varepsilon_0 \pi^2 d_d^2}$$

(5-41)

According to this equation, the applied electric force on the droplet works against the surface tension, which tends to hold the droplet as one. The critical weber for breakup is in the order of 10 [120]. For an extreme case ($U_{rel}=100$ m/s, and the charge to mass ratio estimated by the Vonnegut and Neubauer’s correlation), the calculated values of weber number vs droplet diameter are presented in Fig. 5.2. The effect of charge on surface tension is very small, therefore the relationship between the weber and diameter stays linear. Our operating droplet sizes are below 6 $\mu$m, equivalent to weber of ~3; therefore, we do not expect any aerodynamically droplet breakup.

The coulombic fission is another way of disintegration, in which the induced electric pressure overcomes the surface tension [37]. This phenomenon is not considered in the code, but the critical diameter is determined and the time of first fission is estimated (see §5.6). For generated submicron droplets, Gomez and Tang [39] suggested that, in principle, droplets reach the condition for desorption of field ions before experiencing intermediate Coulomb fissions.
5.3.4 Induced Air by Spray

As discussed in chapters 1, the spraying droplets can generate a downward airflow. This effect may deflect the crossflowing air, especially close to the tip. Neglecting this flow in the code is fair, as its size is at least one order of magnitude smaller than the crossflows used in this study [106].

5.3.5 Brownian Motion

When droplets are significantly small, their collisions with individual air molecules may displace the droplets by a measurable amount. The resulting random displacement by these collisions is called Brownian motion, which adds up to the main movement of a particle. As listed in table 5.2, these displacements, with respect to the induced movement by gravity, only become important when the droplets are in the submicron range [121]. Brownian motion is not included in the code, and its negligible effect will be observed in the analysis of results.
Table 5.2 Comparison of Brownian and gravitational settling displacements for air at 1atm and 21°C

<table>
<thead>
<tr>
<th>Droplet diameter [µm]</th>
<th>Due to Brownian motion [µm]</th>
<th>Due to gravitational settling [µm]</th>
<th>Brownian to gravitational displacement ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>29.4</td>
<td>1.73</td>
<td>16.99</td>
</tr>
<tr>
<td>0.25</td>
<td>14.2</td>
<td>6.3</td>
<td>2.25</td>
</tr>
<tr>
<td>0.50</td>
<td>8.92</td>
<td>19.9</td>
<td>0.45</td>
</tr>
<tr>
<td>1.0</td>
<td>5.91</td>
<td>69.6</td>
<td>0.085</td>
</tr>
<tr>
<td>2.5</td>
<td>3.58</td>
<td>400</td>
<td>0.009</td>
</tr>
<tr>
<td>10.0</td>
<td>1.75</td>
<td>1550</td>
<td>0.001</td>
</tr>
</tbody>
</table>

5.4 Imported and Exported Parameters

In this section initial assumptions, conditions and the inputs of the code are introduced.

5.4.1 Droplet Size

The initial diameter of droplet is probably the most important parameter. An ES, operating in the cone jet mode, generates a unimodal size distribution. The peak of this distribution are the droplets that their breakup follows the Rayleigh jet instability model (see chapter 1). Although the main size can be predicted based on jet the diameter, the plume includes droplets with a size range. For instance, some droplets are produced intermittently or between two main droplets. The width of distribution can vary for different ES systems and is usually determined experimentally. Fortunately, a thorough study on the planar size distribution has been performed in our group by Sultan, using the same system [25]. His measurements were made at the distance of 1.87 mm away from the tip. In the cone jet mode, he used the solution flow rate of 7 µL/min; versus 1-2 µL/min in ours. According to Eq. 1-18:
\[ d_{d_2} = d_{d_1} \left( \frac{Q_2}{Q_1} \right)^{1/3} \]  

(5-42)

where \( d_{d_1} \), and \( Q_1 \) are measured diameter and its flow rate, respectively; and \( d_{d_2} \), and \( Q_2 \) are the unknown diameter and its corresponding flow rate, respectively. One should note the diameters in Eq. 5-42 are the sizes right after the generation. Sultan’s measurements were approximately 1.5 mm below the jet’s breakup point. Due to the evaporation of droplets, the measured sizes are smaller than the droplet sizes at the generation location. Therefore, we first need to estimate the size distribution right after the jet breakup. Droplet evaporation is expressed with Eq. 5-13. Assuming \( \lambda \), and the traveling time from the breakup point to the measuring location are the same for all of the droplets:

\[ d_0^2 - d_d^2 = C \]  

(5-43)

where the constant \( C \) is determined based on the size variation of the main droplets. According to Sultan’s imaging results, the main droplet size when the jet breaks up is approximately 7 \( \mu \)m. His planar measurements showed the maximum count at 2.5 \( \mu \)m. We assume the main droplets in his tests has shrunk from 7 to 2.5 \( \mu \)m; thus, the constant \( C \) becomes -42.75. The summary of calculated size distributions, is presented in table 5.3. In order to confirm the estimations of 2 \( \mu \)L/min, we captured the images of ES tip with a 60 nsec flash light. The average generation size of droplets was around 5 \( \mu \)m, Fig. 1.4. Based on these visual results, the error of diameter estimation by the flow rates ratio, is approximately 8%.

According to the first row of table 5.3, for the ES operating at 2 \( \mu \)L/min, droplets below 4.30 \( \mu \)m, (e.g. satellite droplets) evaporate before reaching the measurement point. Therefore, we expect that they also evaporate quickly in our system and do not influence the captured trajectory of the plume. Considering the measurement errors, we select three droplet size classes representing the plume; 4, 5, and 6 \( \mu \)m.
Table 5.3 Calculated size distributions of electrosprayed droplets

<table>
<thead>
<tr>
<th>Diameter at 1.87 mm Q=7 µL/min</th>
<th>Normalized Count</th>
<th>Diameter at Breakup Point Q=7 µL/min</th>
<th>Diameter at Breakup Point Q=2 µL/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>6.54 &lt;</td>
<td>4.30 &lt;</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0167</td>
<td>6.55</td>
<td>4.32</td>
</tr>
<tr>
<td>1.5</td>
<td>0.2878</td>
<td>6.71</td>
<td>4.42</td>
</tr>
<tr>
<td>2.5</td>
<td>1</td>
<td>7</td>
<td>4.61</td>
</tr>
<tr>
<td>3.5</td>
<td>0.8539</td>
<td>7.42</td>
<td>4.89</td>
</tr>
<tr>
<td>4.5</td>
<td>0.1008</td>
<td>7.94</td>
<td>5.23</td>
</tr>
<tr>
<td>5.5</td>
<td>0.0027</td>
<td>8.55</td>
<td>5.63</td>
</tr>
</tbody>
</table>

Figure 5.5 Schematic illustration of initial location inputs of droplets to the code
5.4.2 Droplet Initial Location and Velocity

The droplets are generated at the jet breakup location. The jet breakup takes place at $122 \pm 6 \mu m$ away from the cone apex. For simplicity, the jet trajectory is considered a line, emitted with the measured initial angles from the experimental data. Small electrical instabilities in electrospraying process and the space charge can change the initial location of droplets, normal to the axial direction of jet. According to our captured images of droplet, this deviation is in the order of jet diameter. Positive and negative offsets with the value of $\pm 10 \mu m$, i.e. four times of jet diameter, are used in order to implement this effect in our analysis. The four corners as shown in Fig. 5.5 are the initial location inputs. The initial velocity of droplets is simply the jet velocity, calculated with the solution flow rate and the jet diameter.

5.4.3 Geometry, Electric, Mixture, and Air Flow Inputs

The important geometrical parameters are: inlet diameter, $d_{in}$, vessel diameter, $d_v$, vessel length, $L_v$, tip to inlet distance, $L_{tip-in}$, tip to centerline distance, $L_{tip-CL}$, and the outer diameter of ES capillary, $r_c$. The applied voltage is selected based on the experimental cases.

In the beginning, both the droplet and the crossflow air are considered to be at the room temperature. The solution and the air flow rates are two important parameters. We select their input values based on the experimental cases from §3.1. The air pressure can be entered based on the air pressure measurements, similar to table 2.1. The molecular weight of solution and air are 28.53 and 28.97 gr/mole, respectively.

5.5 Numerical Methodology

In this part the numerical method to find the droplet trajectory, including the equations that are solved at each time step, is shown.

The fourth-order Runge-Kutta method with Simpson’s one-third rule is used to solve the equations of motion of a droplet in each time step, through computing the location, velocity, diameter, and temperature. The general form of finding the new step condition based on the known values is expressed in 2D as [122]:

\[
\begin{align*}
\dot{f}(x, y, t) &= \frac{df(x, y, t)}{dt} \\
k_1 &= \Delta t \dot{f}(x, y, t) \\
k_2 &= \Delta t \dot{f}(x + \frac{k_1}{2}, y + \frac{h_1}{2}, t) \\
k_3 &= \Delta t \dot{f}(x + \frac{k_2}{2}, y + \frac{h_2}{2}, t) \\
k_4 &= \Delta t \dot{f}(x + k_3, y + h_3, t) \\
f_{(n+1)} &= f_{(n)} + \frac{k_1 + 2k_2 + 2k_3 + k_4}{6}
\end{align*}
\]

\[
\begin{align*}
\dot{g}(x, y, t) &= \frac{dg(x, y, t)}{dt} \\
h_1 &= \Delta t \dot{g}(x, y, t) \\
h_2 &= \Delta t \dot{g}(x + \frac{k_1}{2}, y + \frac{h_1}{2}, t) \\
h_3 &= \Delta t \dot{g}(x + \frac{k_2}{2}, y + \frac{h_2}{2}, t) \\
h_4 &= \Delta t \dot{g}(x + k_3, y + h_3, t) \\
g_{(n+1)} &= g_{(n)} + \frac{h_1 + 2h_2 + 2h_3 + h_4}{6}
\end{align*}
\]

where \(f\) and \(g\) are location or velocity components in the x and y directions, respectively. The subscripts \((n)\) and \((n+1)\) show the current and next time steps, respectively. The error of this method is in the order of \(O(\Delta t^5)\).

In order to calculate the parameters of the next time step, first, \(k_1\), and \(h_1\) are calculated for the location of droplet, based on the velocities in each direction. Then, in a similar way, \(k_4\) and \(h_4\) are computed for velocities with the acceleration values in two directions:

\[
\begin{align*}
\frac{dv}{dt} &= a_x = \frac{F_{D,x} + F_{E,x}}{m_d} \quad (5-46) \\
\frac{dw}{dt} &= a_y = \frac{F_{D,y} + F_{E,y} + F_{\text{image}} + F_g}{m_d} \quad (5-47)
\end{align*}
\]
Next one is the calculation of $k_1$, or $h_1$ for the droplet temperature and diameter, using Eqs. 5-28 and 5-15, respectively.

Once all $k_1$s, and $h_1$s are found for these six parameters, the accelerations, and the properties of the air, droplet, and the vapor-air film are calculated again with the newly calculated values. Similar steps are followed until all of the $k$s and $h$s are computed with Runge-Kutta equation sets, 5-44 and 45. This means the droplet location, velocity, diameter change, temperature variation, acceleration, and the liquid and the gas flow properties are calculated four times in each time step. These values are used to predict the next time step. For the very first step, the imported parameters and initial conditions are used.

The calculation will stop if:

1- the droplet evaporates completely;
2- the droplet reaches the outlet or hits the ground;
3- the number of imported calculation cycles is reached, before any of the former.

This code is solved for two cases and the results are presented and discussed in the next section.

5.6 Results

In this part, the simulated droplet trajectories are illustrated. The best matches with experiments are identified. The results of different velocity profile models, charge to mass ratio correlations, jet lengths and initial location are compared. Both the evaporative and non-evaporative assumptions are considered. First, the numerical results of plume trajectory are compared with their experimental pairs. Then, the effects of each model on the simulated trajectory are discussed.

Two experimental cases from §3.1 are selected to investigate the models in the code. The nozzle tip was located 0.1 mm above the centerline of chamber with the diameter of 16 mm. 4 and 8 Scfh air flow rates are used in here, i.e. equivalent to the inlet velocities of 7.6 and 15.1 m/s, respectively. The applied voltage for both cases is 3kV. The initial droplet velocity, based on 2 $\mu$L/min and jet diameter of 2.85 $\mu$m, is 5.25 m/s. The initial angles of the emitting droplets are 15° and 18° in 4 and 8 Scfh, respectively. Figure 5.6 shows the notations used in the graph titles and legends. Only the case of 4 Scfh is presented in this chapter for discussion and comparison between
the correlations; as the 8 Scfh show a similar behavior. The simulation results for 8 Scfh crossflow are provided in Appendix G.

5.6.1 Prediction of Plume Trajectory

In this section, an overall comparison of droplet trajectories with experimental results is presented initially. Then, the characteristics of each model and their influence on single droplet trajectories are discussed. Figures 5.7 and 5.8 show the simulation results for a laminar/turbulent velocity profile model (LT) and Vonnegut and Neubauer’s charge correlation (VN). The experimental results for the windward and the leeward boundary of plume are also plotted in the figures. The smaller the droplet, the smaller the inertia; therefore, as shown in Figs. 5.7 and 5.8, the air initially bends the small ones more toward the right than the larger ones. For the same reason, when a smaller droplet enters the reversed flow region, it bends back to the left with a higher slope, as some tend to fly to the left side of the large drops. An idea on the planar distribution of droplets will be discussed later, in §5.6.5. The evaporation does not have a significant effect on the overall trajectory of the predictions. Considering the evaporation, Fig. 5.8, the smaller droplets tend to move more toward the left side, once they enter the backward flow.
As mentioned earlier, the simulations do not include the repulsions between charged droplets. Therefore, our trajectory predictions are narrow and the boundaries fall inside the actual windward and leeward boundaries. If the predicted trajectories travel on the centerline of the plume, as shown in Fig. 5.7, we can say the predictions are accurate.

According to Figs. 5.9 and 5.10, the predicted trajectories with LT and Jones and Thong’s charge correlation (JT), still fall inside the experimental boundaries; however, they are much closer to the leeward side and would spread out of the boundary, if the effect of space charge was considered.
Figure 5.8 Plume trajectory prediction in 4 Scfh crossflow inside the vessel; adopted models in the run: laminar/turbulent velocity profile - Vonnegut and Neubauer’s charge correlation - evaporative droplets

Comparing the predicted plume trajectories at two charge correlations leads to the following conclusions for our cases:

1- Jones and Thong’s correlation overpredicts the central plume trajectory;
2- Vonnegut and Neubauer’s correlation gives a better approximation of the central plume trajectory, especially in the beginning.

These observations can be justified at both of 4 and 8 Scfh crossflows.
Figure 5.9 Plume trajectory prediction in 4 Scfh crossflow inside the vessel; adopted models in the run: laminar/turbulent velocity profile - Jones and Thong’s charge correlation - non-evaporative droplets

The droplet charge, at a specific diameter, with Vonnegut and Neubauer’s model is approximately twice the Jones and Thong’s correlation, which results in a higher external electric force. With the latter, the droplets travel more in the flow direction. In the needle-plate configuration, the electric force pulls the droplets toward the ground plate, and pushes them away from the capillary axis. This force is dominant in the y direction (at least in the beginning); on the other hand, the drag force plays an important role in the x direction. As a result, once the charge on a droplet is doubled, the total force in the y direction increases more than the one in the x axis. Therefore, with VN, the droplets experience an earlier bend toward the ground plate.
Figure 5.10 Plume trajectory prediction in 4 Scfh crossflow inside the vessel; adopted models in the run: laminar/turbulent velocity profile - Jones and Thong’s charge correlation - evaporative droplets

In fact, as shown in Figs. 5.7 and 5.8, the effect of electric field is very high, such that trajectories are kept close to each other and interfere. Figures 5.9 and 5.10 show that lower electric charge results in a better segregation between different sizes; e.g. the trajectories do not interfere as much. This differentiation with size is more obvious in the 8 Scfh crossflow, Figs. 7.21 and 7.22.

Another difference between the evaporative cases of VN and JT is the complete evaporation of 4 µm droplets when they gain a lower charge. This difference is related to the time that the droplet is carried by the air, so called “flight time”, and will be discussed in the next section.
Figure 5.11 Plume trajectory prediction in 4 Scfh crossflow inside the vessel; adopted models in the run: Gaussian velocity profile - Vonnegut and Neubauer’s charge correlation - non-evaporative droplets

Using the laminar/turbulent profile, the trajectories match and fall inside the experimental plume. In fact, it would be surprising if the Gaussian profile (G) was predicting better results, as the velocity profiles in the sudden expansion are more similar to LT.

According to Figs. 5.11-5.14, the Gaussian profile overpredicts the plume trajectory, especially in the beginning of the paths. Although we cross out the Gaussian profile as an erroneous profile for the vessel, the study of trajectories in this profile still can be beneficiary. This profile approximates the velocity profile of a developed free expanding air jet sufficiently [102]. By comparing G and LT graphs, we conclude: if one wants a steeper initial bend with the same flow rate, a free jet condition will be more satisfactory.
Figure 5.12 Plume trajectory prediction in 4 Scfh crossflow inside the vessel; adopted models in the run: Gaussian velocity profile - Vonnegut and Neubauer’s charge correlation - evaporative droplets

The initial location of the droplets is very close to the centerline of the vessel, where the maximum crossflow velocity is applied. For a specific air flow rate, the maximum velocity of Gaussian profile is approximately 2.3 and 3.7 times of laminar and turbulent velocities, respectively. This is essentially the main reason that droplets experience a higher drag and velocity than LT, in the beginning. Laminar and turbulent profiles have milder velocity variation in the y direction near the centerline. On the other hand, near the boundaries, their velocities have steeper variations than the Gaussian profile. Therefore, as shown in Figs. 5.9, 5.10, 7.21, and 7.22, the change in the droplet motion is also abrupt. From the shear stress point of view, Gaussian and laminar/turbulent profiles apply a higher shear in the centerline and the boundaries, respectively. These effects influence the
smaller droplets more, due to their lower inertia. In general, the aforementioned effects of Gaussian profile on the droplets results in a more penetration in the x direction. In the Gaussian profile, the droplets are being separated better once they gain a lower electric charge, Figs. 5.13 and 5.14.

Figure 5.13 Plume trajectory prediction in 4 Scfh crossflow inside the vessel; adopted models in the run: Gaussian velocity profile - Jones and Thong’s charge correlation - non-evaporative droplets
According to the discussed graphs, in all of the models, the variation of jet length does not really influence the trajectory of single droplets, i.e. the paths of droplets generated by different jet lengths almost overlap. The trajectory pairs that travel with a small distance from each other, e.g. the red and orange pair, are related to a specific diameter with ±10 µm offsets from the jet axis. As their paths are close, we select one of them in each diameter, in order to compare the predictions for different sizes. The case with 116 µm jet length and -10 µm offset is selected, which is the leftist droplet shown in Fig. 5.5. In the next section, the flight time and average velocity of single charged droplets in our expanding crossflow is discussed.

Figure 5.14 Plume trajectory prediction in 4 Scfh crossflow inside the vessel; adopted models in the run: Gaussian velocity profile - Jones and Thong’s charge correlation - evaporative droplets
5.6.2 Flight Time and Average Velocity Analysis

Flight time is defined as the time that a droplet travels from the generation point to the ground plate, or the time it takes for complete evaporation. The flight time of droplets in the vessel with the 4 Scfh crossflow are demonstrated in Figs. 5.15 and 5.16. The plots are separated based on the used charge correlation in the predictions. The results with the 8 Scfh air crossflow are provided in Appendix F.

According to Figs. 5.15 and 5.16, the smaller droplets take a longer time to reach the ground plate. Based on the trajectory observations, these droplets tend to deviate by the air more than the large ones and, therefore, have a longer path and longer flight time. The inertia of evaporative droplets keeps decreasing as it shrinks. Thus, the air can drag them for a longer time and path. This observation can be seen with comparing evaporative and non-evaporative cases in Figs. 5.15 and 5.16. The only exception is observed in the evaporative JT case, Fig. 5.15, where the 4 µm droplets evaporate completely, before they hit the ground plate.

Comparing the flight times of the droplets in the vessel at two charge correlations, Figs. 5.15 and 5.16, the droplets in the JT case have longer flight times. We can conclude that the longer the path, the later they hit the ground plate. Therefore, the smaller the droplet charge, the longer the flight time. Exceptions for this rule of thumb again occurs when an evaporating droplet is considered, and the flight time is long enough that droplet vaporizes completely, e.g. 4 µm droplets in JT cases. If the plume is non-evaporative, or solid charged particles are used, the flight time is expected to always increase for smaller droplets, as they bend back toward the ground plate. The ratio of this time between two charge correlations varies between two and three for 6 µm and 4 µm droplets, respectively.

Using the Gaussian profile, the droplets are expected to penetrate more in the x direction. This means a longer traveling path and time. According to Figs. 5.15 and 5.16, the difference between flight times with changing the velocity profile is not really significant. These time differences for the non-evaporative cases of 4Scfh-JT and 4Scfh-VN are 110-220 µs and 30-40 µs, respectively.
Figure 5.15 Predicted flight times at 4 Scfh crossflow with Jones and Thong’s correlation

Figure 5.16 Predicted flight times at 4 Scfh crossflow with Vonnegut and Neubauer’s correlation
Figures 5.17 and 5.18 show the average velocity of the droplets. This velocity is calculated as: the length of the flight path of a droplet divided by its flight time. The average velocity graphs for the 8 Scfh crossflow are provided in Appendix F.

According to Figs. 5.17 and 5.18, the smaller the droplets, the lower the average velocity. As the smaller droplets travel more and for a much longer time, their average velocity is smaller than the larger droplets. In these cases, the average velocity of evaporative droplets is even lower; because they experience longer flight times, due to the size shrinkage and less resistance against the main and counter flows. Comparing the average velocity between two charge correlations, Figs. 5.17 and 5.18, one can say the non-evaporative droplets with the higher charge (VN), are 1.5 to 2 times faster than the ones traveling with the lower charge (JT).

The average velocity of droplets with two different velocity profiles at 4 Scfh are almost identical. This is directly related to the slight variation of flight times with changing the velocity profile. A closer look into Figs. 5.17 and 5.18, shows that the laminar/turbulent flow pushes the droplets slightly faster.

Comparing 4 and 8 Scfh crossflows trajectory profiles, Figs. 5.7 and 5.25, the larger flow rate drags the droplets more. The discussed effects for 4 Scfh can be observed more clearly at 8 Scfh. For instance, in 8 Scfh, Figs. 7.29 and 7.30, the laminar/turbulent profile implies a higher average velocity, more significant than the case of 4 Scfh. The direct effect of flight time on the average velocity is more clear in 8 Scfh, Figs. 7.27 and 7.28. The flight times of droplets in 8 Scfh crossflow are 1.1 to 1.5 times of 4 Scfh ones. The higher difference in the flight times, i.e. 1.5 times, is related to the small droplets with the JT’s predicted charge, and the slight change, i.e. 1.1 times, happens for the large droplets with the VN’s charge.

The average velocity of droplets does not increase as much with doubling the inlet crossflow. The droplets accelerate in the main flow region, but once they enter the counter flow zone, they move slower. This deceleration continues until their direction changes and again acceleration takes place in the counter flow direction. The velocity in this region can go up to a value, which is one order of magnitude smaller than the main flow velocities. All the droplets with 4 and 8 Scfh crossflow experience these velocity variations and, therefore, their average velocity difference decreases.
Figure 5.17 Average velocities at 4 Scfh crossflow with Jones and Thong’s correlation

Figure 5.18 Average velocities at 4 Scfh crossflow with Vonnegut and Neubauer’s correlation
5.6.3 Droplet Temperature, Evaporation, and Fission

Figure 5.19 shows the droplet temperature versus time, for different initial diameters. In all of the cases, the temperature drops from 293K to 266.14K. However, the time that they reach this point depends on the droplet size. The smaller the diameter, the sooner the cooling. This observation qualitatively matches with the Eq. 5-28. If the droplet and vapor properties do not change dramatically, we can say:

\[
\frac{dT}{dt} \propto \frac{1}{d_d}
\]  

(5-48)

![Figure 5.19 Temperature of droplets with time](image)

Figure 5.20 shows the diameter squared versus time, for droplets with different initial sizes. Various models were selected and plotted in this graph. As expected, the variations are generally linear. The effect of temperature drop on the vaporization rate appears at the beginning. Figure 5.21 illustrates the steep change of diameter in the early moments of evaporation. This observation is justified with discussing the vapor pressure at the droplet surface. As we know, at higher solution temperatures, the surface can take a higher vapor pressure. This is why a liquid with higher
temperature evaporates faster. In our case, as the temperature drops, the amount of vapor that can equilibrate on the surface decreases. Due to this effect, the evaporation rate decreases rapidly in the beginning and once it reached the thermal equilibrium, follows the diameter squared rule.

Figure 5.20 Variation of droplet size with time

Figure 5.21 Initial non-linear variation of diameter squared
After the droplets reach the steady temperature, their properties become independent of the initial size, i.e. their $\lambda$s become identical. This is why the lines are parallel and mostly independent of the adopted velocity and charge models. In reality, due to the convective mass transfer, one would expect to have a higher evaporation rate at higher crossflows.

**Table 5.4 Relative final diameters, fission diameters and fission times of the electrospayed droplets in the vessel with the Gaussian velocity profile for crossflow**

<table>
<thead>
<tr>
<th>Diameter [µm]</th>
<th>Charge Model</th>
<th>Crossflow [Scfh]</th>
<th>Relative Final Diameter</th>
<th>Relative Fission Diameter</th>
<th>Relative Fission Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>JT</td>
<td>4</td>
<td>0*</td>
<td>0.3647</td>
<td>0.865</td>
</tr>
<tr>
<td>4</td>
<td>JT</td>
<td>8</td>
<td>0*</td>
<td>0.3647</td>
<td>0.865</td>
</tr>
<tr>
<td>4</td>
<td>VN</td>
<td>4</td>
<td>0.6445</td>
<td>0.6299</td>
<td>N/A</td>
</tr>
<tr>
<td>4</td>
<td>VN</td>
<td>8</td>
<td>0.5807</td>
<td>0.6299</td>
<td>0.908</td>
</tr>
<tr>
<td>5</td>
<td>JT</td>
<td>4</td>
<td>0.5237</td>
<td>0.3928</td>
<td>N/A</td>
</tr>
<tr>
<td>5</td>
<td>JT</td>
<td>8</td>
<td>0*</td>
<td>0.3928</td>
<td>0.844</td>
</tr>
<tr>
<td>5</td>
<td>VN</td>
<td>4</td>
<td>0.8242</td>
<td>0.6299</td>
<td>N/A</td>
</tr>
<tr>
<td>5</td>
<td>VN</td>
<td>8</td>
<td>0.8024</td>
<td>0.6299</td>
<td>N/A</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
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<td>0.8910</td>
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</tr>
<tr>
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<td>VN</td>
<td>8</td>
<td>0.8788</td>
<td>0.6299</td>
<td>N/A</td>
</tr>
</tbody>
</table>

* Droplet evaporates completely
Table 5.4 lists the relative final and fission diameters and fission times for different droplet sizes, crossflows, and charge models, in Gaussian velocity profile. The relative values were calculated based on the initial diameter and flight time of each droplet. In these cases, the majority of droplets do not reach the fission condition. Besides, the other ones that experience this type of fragmentation, have traveled 85% of their journey; therefore, the coulombic fission should not have a significant effect (at least in our cases). With the laminar/turbulent velocity profile, similar conclusions can be made. Lastly, Vonnegut and Neubauer’s model suggests that the relative fission diameter is independent of initial size; on the other hand, Jones and Thong’s correlation predicts larger relative fission diameters for larger droplets.

**Figure 5.22 Variation of applied forces on an evaporative 5 micron droplet at 4 Scfh crossflow (laminar/turbulent profile model and Vonnegut and Neubauer’s correlation)**

5.6.4 The Significance of Applied Forces on a Droplet

Figure 5.22 shows the variations of the applied forces on a single charged droplet in the crossflow. This case has been selected randomly only to give us an idea on the orders of magnitude of the forces. Applied forces in other cases have similar trends and orders of magnitude. The applied drag and electric forces on a micro size droplet are in the order of nanonewtons to the tens of
nanonewtons. Initially, the electric forces in both directions have high values; but they drop dramatically as the droplet flies away from the capillary tip. The drag forces usually have slightly lower value and may increase, as in the y direction, or change the applying direction, as observed in the x direction.

The gravity force is three to four orders of magnitude smaller than the drag and electric forces and negligible. As shown in the previous chapter, the Brownian motion effect on a droplet smaller than 100 nm is only one to two orders of magnitude bigger than gravity. Thus, neglecting the Brownian motion in our simulation is justified. The image force only becomes significant at the very last microseconds.

Figure 5.23 Effect of initial location on the trajectory of a single droplet under the induced electric field by needle-plate configuration
5.6.5 Effect of Space Charge

Figure 5.23 shows the droplet trajectories without the crossflow, starting from different initial locations. Once a droplet is located closer to the nozzle axis, it is being pulled highly toward the ground plate and is being pushed less toward the right side (the paths at the left). When it is farther from the axis, the downward electrical force is lower and the droplets can travel in the x direction more than the previous case. The role of the space charge in an ES plume is to initially push the droplets away from the plume’s axis, widening the plume with the help of external electric force.

Without the crossflow, the space charge segregates the droplets by size. Smaller droplets tend to travel closer to the boundaries and larger ones close to the axis [25]. Adding an air crossflow can change this configuration of droplets, as it is applied to the droplets, before the plume formation. The smaller droplets are dragged more toward the leeward boundary, whereas the larger droplets, due to their initial inertia, are less effected by the crossflow. The segregation effect was observed in Figs. 5.7-5.14. This segregation process by the crossflow can be enhanced by the repulsion effect among the droplets. As a result, the small droplets travel closer to the leeward side; whereas the larger ones stay in the left side of the plume axis and form the windward boundary, Fig. 5.24.

![Figure 5.24 A simplistic distribution of droplet size for an ES plume in crossflow; size classes: 4 μm (red) - 5 μm (green) - 6 μm (blue)](image-url)
The discussed VBA code can be applied to the ES ion sources in the desolvation chamber, helping the designers for further improvements. In addition, this code can be modified and expanded to other applications, where charged droplets are interacting with gas flows and electric fields. An existing application is differential mobility analyzers, developed by Fernandez de la Mora et al. [49], [123], in which the motion of ions in a crossflow is the base of the design and operation of these devices. The applications of ESICF and dynamics of charged particles in gas flows have not been explored very broadly. Besides, the difficulty of visual investigations in these topics hinders the progress. The efficient and reliable simulations, similar to what presented in this thesis, can help the innovators and inventors in various fields.
Chapter 6

6 Conclusions and Recommendations

6.1 Conclusions

The behavior of an electrospray (ES) in an air crossflow is studied (ESICF). Although, ES has been investigated extensively for decades, there has never been a study on the effect of a gaseous crossflow on the ES formation and its spray plume. Utilizing a gaseous crossflow together with an ES may allow a better control on the trajectory of the droplets and ions formed by the ES, which can then enhance the sensitivity of the next generation of mass spectrometers.

In the present study, an ES is placed inside a square test section (10 mm x 10 mm having a 19 mm length) that has a sudden expansion inlet (2.3 mm inlet diameter) and a tapered outlet (2.4 mm outlet diameter). The ES (ID = 150 µm and OD = 300 µm) is injected normal to the main airflow in the test section. The flow conditions are such that the recirculation zones are formed above and below the central crossflow and the ES plume. The liquid used in all the test comprised of 75% Methanol-25% Water volumetric solution. The following conclusions are made from the experimental, analytical, and numerical parts of this study.

6.1.1 Experiments on ESICF

The ES plume shape and the trajectory of the droplets depend on the flow structure inside the test chamber and the level of the electric field. Because of the specific geometry of the present chamber, the injection location of the ES can result in large changes in the ES plume behavior and structure.

When the tip of the ES nozzle is placed at the centerline of the crossflow, a stable plume is found for crossflows up to 18.9 m/s (10 Scfh) inlet velocities. In this configuration, the plume initially bends in the main flow direction. However, once the plume penetrates further into the chamber passing the central zone, it bends back toward the ground plate at the bottom of the chamber. Therefore, the generated ions may not exit the chamber. At medium crossflow inlet velocities, i.e. 18.9-37.8 m/s, the plume becomes unstable. The applied voltage to the ES has to be increased to obtain a stable ES.
When the tip of the ES nozzle is placed above the centerline (by 2.75 mm), a stable plume is found for cross flows up to 26.5 m/s (14 Scfh) inlet velocities. For crossflow velocities in the range of 15.1-22.7 m/s (8-12 Scfh), the plume bends sufficiently to direct the droplets towards the exit of the chamber. However, for inlet velocities below this range, the plume does not bend enough and the ions mostly collide with the ground plate. Above this range, the crossflow becomes highly turbulent, leading to dispersion and ion loss. These findings matched well with an actual intensity measurement by a MS system.

The general behavior of an ES in a crossflow can be described as follows:

As a crossflow is imposed on an ES cone jet, it deforms the Taylor cone and bends the emitting jet. The crossflow may make the cone boundary curved and its apex pointier, due to direct push of crossflow and applying a higher local pressure at the cone surface. Above a certain flow rate, the cone jet first becomes dynamic (moves on the surface of the cone) and later becomes unstable. Increasing the voltage may help the restoration of the stable cone. In the dynamic cone jet mode, the cone jet is still stable, but it deforms and moves continuously. In the unstable cone jet mode, the cone repeatedly forms and disappears and the jet emission occurs intermittently. In the stable cone jet mode, an increase in the voltage (in the onset voltage range) makes the cone and the plume angle smaller.

At high crossflows, e.g. above 90 m/s, the liquid at the meniscus is highly perturbed and washed. At high crossflows and relatively high voltages, e.g. 4.8 kV, instantaneous jet emissions occur. At some specific voltages multiple jets emit from the surface with relatively high frequencies.

The sequence of applying the voltage, starting the liquid solution flow, and starting the crossflow significantly influence the performance of the ES. The most stable and predictable plume was obtained by Solution-Voltage-Crossflow sequence. The ES performance with Voltage-Solution-Crossflow sequence depended highly on the tip boundary conditions and wetting. In the Crossflow-Solution-Voltage sequence, unlike the previous ones, the cone jet mode was not observed. This is attributed to the perturbations on the liquid surface induced by the air, which prevent the formation of the Taylor cone.

An EHD hysteresis phenomenon was observed at the crossflows in the medium crossflow range, i.e. 18.9-37.8 m/s, when the ES operated in the unstable cone jet mode. The plume generation in
this mode became more stable when the applied voltage was reduced to a target voltage from a higher value, in comparison to a case when the voltage was increased to the target voltage from a lower value. It is believed that the wetting of the ES nozzle tip coupled with the boundary conditions of the cone (voltage changes) cause this hysteresis. The temporary variation of inputs can change the boundary conditions at the tip and, therefore, the performance of an ESICF.

6.1.2 Analytical Model for EJICF

A 2D analytical model is derived for an electrified jet in crossflow (EJICF). In this model, the equations of force balance are solved separately in the x and y directions. The electric fields in the x and y directions are considered constant. The shear and gravity forces are negligible. For the drag force, the gas velocity is considered uniform and constant at the nozzle location. The following correlation is developed using prior published literature on the drag of a cylinder in a crossflow:

\[
C_D = \frac{10}{\sqrt{Re_{cyl}}}
\]

This correlation best fits for \(0.5 < Re_{cyl} < 100\), which is the range of Reynolds numbers used in the current study.

The following non-dimensional relation for the trajectory of an ESICF in the x direction is developed:

\[
x^* = Ay^* - B \ln(f(y^*)) + C
\]

The function \(f(y^*)\) is provided in the table below based on the directions and values of the applied drag and the electric forces:

<table>
<thead>
<tr>
<th>(f(y^*))</th>
<th>Directions</th>
<th>Dominant Force</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\cos[Dy^* + E])</td>
<td>Same</td>
<td>Electric or Drag</td>
</tr>
<tr>
<td>(\cosh[Dy^* + E])</td>
<td>Opposite</td>
<td>Electric</td>
</tr>
<tr>
<td>(\sinh[Dy^* + E])</td>
<td>Opposite</td>
<td>Drag</td>
</tr>
</tbody>
</table>
A new dimensionless parameter is defined which indicates the ratio of the induced momentum by electric field to the jet inertia:

$$\varepsilon_{i_{x_j}} = \frac{E_x \sigma_j}{\rho_j u_j^2}$$  \hspace{1cm} (6-3)

In Eq. 6-2, $C$ is a constant related to the initial location of the jet, and $E$ is a constant related to the initial velocity of the jet. These constants are also functions of the initial drag force over the applied electric force in the $x$ direction. The coefficient $A$ is the initial relative velocity between the jet and the crossflow. $B$ and $D$ depend on the ratio of densities and the drag coefficient, where $D$, in addition, is also a function of $\varepsilon_{i_{x_j}}$. The second term at the RHS of Eq. 6-2 can be oscillatory in some cases, depending on the input conditions.

The motion in the $y$ direction depends on the significance of the electric force. If the electric force in this direction is negligible, the motion is expected to be linear with time:

$$y = u_j t$$ \hspace{1cm} (6-4)

If the electric force is significant, the motion in the $y$ direction is predicted with a parabola:

$$y = \left(\frac{2\sigma_j E_y}{\rho_j d_j}\right) t^2 + u_j t$$ \hspace{1cm} (6-5)

The non-dimensional form of these equations is expressed as:

$$y^* = t^*$$ \hspace{1cm} (6-6)

$$y^* = 2\varepsilon_{i_{y_j}} t^* + t^*$$ \hspace{1cm} (6-7)

These models predict that an increase in the electric force in the $x$ and $y$ directions, increases and decreases the bending of the jet in the flow direction, respectively. Also, the increase in the jet inertia decreases the jet bending, similar to what is observed in JICF. At high electric fields, the jet tends to penetrate infinitely in the $y$ direction.

These models show a good agreement with the experimental results of our electrosprayed jets in crossflow. In reality, the effective electric force that accelerates the jet in the $y$ direction can be less than the applied electric force (or pressure). As the molecules inside the jet are charged, the
applied force can be converted to the random motion of the molecules and the pressure inside the jet. These motions result in a lower effective electric force on the jet acceleration in the y direction. The trajectory predictions by the low and high electric field models should be treated as two extremes, in which the true trajectory falls between them. By knowing the portion of effective electric force, one can predict the trajectory of an electrified jet more precisely.

6.1.3 Numerical Model for Plume in Crossflow

A numerical model to predict the trajectory of a charged droplet in a crossflow with an electric field is developed. The equations of the motion of a droplet are solved in 2D with considering the applied drag, electric, gravity, and image charge forces. The crossflow is considered to be a steady flow developed inside a chamber with a sudden expansion inlet, comprising of a core flow between recirculation zones. A simplified velocity variation inside the chamber is assumed. Two different velocity profiles are considered for the core flow: “Laminar/Turbulent” and “Gaussian” velocity distributions. The reverse flow in the recirculation zone is assumed to be laminar. The applied electric fields are assumed to be that of a needle-plate. Two different correlations are used for the calculation of the droplet initial change: “Jones and Thong” and “Vonnegut and Neubauer”.

The model also considers droplet evaporation. Instantaneous droplet temperature is calculated and the liquid, vapor, and air properties are found in each step.

A fourth-order Runge-Kutta method with Simpson’s one-third rule is used to solve the equations of motion in each time step. These equations require computation of the location, the velocity, the diameter, and the temperature of the droplet. Eight combinations of evaporation, velocity profile, and droplet charge correlations were used in order to determine the conditions that best matched the experimental results. Vonnegut and Neubauer’s charge correlation together with the laminar/turbulent velocity profile provided best prediction for the experiments. Droplet evaporation does not have a significant effect on the trajectory of the large droplets. It only becomes important when droplets evaporate or shrink significantly, which usually only occurs for small droplets.

The crossflow segregates the generated droplets by size: Smaller droplets should travel closer to the leeward boundary of the plume, and the larger ones travel near the windward boundary.
6.2 Suggestions for Future Research Work

- Correlate ES plume trajectory to the intensity level detected by a mass spectrometer. Although, some such comparison is provided in this thesis, it is recommended to extend this comparison to several other conditions, in order to improve the intensity. The suggested conditions are:
  i- adding a shielding plate close to the needle in order to protect the Taylor cone from the crossflow and to achieve a better plume establishment, and
  ii- adding a guard plate to increase the range of the onset voltage for the cone jet mode.
- Further study of the dynamic and unstable behavior of a Taylor cone in crossflow to understand the occurring processes from the equilibrium point of view, by determining the pressure at the liquid interface.
- Study the EHD hysteresis of the unstable Taylor cone and the appropriate boundary conditions at the tip for better cone jet generation.
- Experimental study of the trajectory of an “electrified jet” in crossflow. Although a model for the trajectory of an electrified jet in cross flow is developed, we do not have experiments to match it with. It is recommended to perform a set of experiments to obtain data on the jet trajectory to validate our model. Electrified jets can also be used in fuel injectors, in order to increase the penetration of a fuel in the crossflow, resulting in a better mixing.
- Perform a parametric study using the models provided here to determine an optimum chamber and crossflow design, as well as the location of an ion source in the chamber, to maximize the ion transfer and the detection intensity of mass spectrometer.
- Measure the droplet size distributions in an ESICF – currently there no such data.
- Development of a theoretical model or empirical correlations for space charge of an ES plume in crossflow.
References


2002.


7 Appendices

7.1 Appendix A: Neglected Effects in a Simple Evaporation Model

In this appendix, the additional factors for the presented droplet evaporation model in chapter 1 are discussed. These effects are namely: temperature depression, Kelvin effect, Fuchs effect, Stefan flow, and wind factors.

7.1.1 Temperature Depression

The liquid molecules need to gain the equivalent energy of the latent heat of evaporation from the liquid, in order to evaporate from the surface of a droplet. Therefore, the droplet usually experiences temperature depression during evaporation. This effect needs to be considered for volatile liquids, which have low saturation pressures. With writing energy balance for the droplet, an equilibrium droplet temperature can be calculated:

\[ 4\pi K_g R_d (T_\infty - T_0) = 4\pi R_d D(c_0 - c_\infty)L \]

The left hand side represents the heat gained from the surrounding, and the right hand side is the energy loss for vaporization. \(K_g\), \(D\), and \(L\) are the thermal conductivity of gas, diffusion coefficient, and the latent heat of evaporation, respectively. This effect is considered in the code (see §5.2.4).

7.1.2 Kelvin Effect

The equilibrium vapor pressure at the surface, during evaporation, is equal to the saturation vapor pressure. In this pressure the same number of molecules condenses as some molecules evaporate. This equilibrium pressure is defined for a flat liquid surface; however, highly curved surfaces, e.g. small droplets, need higher saturation pressure at the surface to stay in equilibrium. If the vapor pressure is less than this equilibrium pressure, the speed of evaporation will be higher than the speed of condensation and vice versa. In other words, very small droplets act more volatile in comparison to the larger droplets of the same liquid. The Kelvin equation shows the ratio of required equilibrium vapor pressure, \(P_{eq}\), and the saturation pressure for flat surfaces, \(P_{Sat}\):

\[ \frac{P_{eq}}{P_{Sat}} = \exp \left[ \frac{4\gamma M_v}{\rho_d R T d^*} \right] \]

(A-2)
where $\sigma$ and $d^*$ are surface tension and Kelvin diameter, respectively. The Kelvin diameter is the droplet diameter in which it is supposed to be in equilibrium. The Kelvin effect becomes important for droplets below 0.1 $\mu$m. This effect is not considered in our code, as the droplets are at least one order larger for the most of their travel time.

7.1.3 Fuchs Effect

According to Langmuir [124], there is a sudden change in the temperature gradient at a close distance to the droplet surface. This observation indicates the existence of a thin layer, in the order of gas mean free path, $\lambda$. Fuchs [43] used the analogy between conductivity and diffusion in gases and expanded the idea to the gradient of vapor concentration near the surface. Considering Maxwell’s equation, the evaporation rate, $\frac{dR_d}{dt}$, exceeds the theoretical maximum mass transfer rate in vacuum. To overcome this paradox, Fuchs reasoned that the vapor transports between the surface and an imaginary layer with the thickness of $\frac{4}{3}\lambda$, and is controlled by the kinetic theory of gases. This transportation is in series with the vapor diffusion outside the layer and as a result any of them can control the speed of evaporation. The correction including this effect gives the following expression:

$$\frac{dd_d}{dt} = \frac{4DM}{\mathcal{R}d_d} \rho_d \left( \frac{P_0}{T_0} - \frac{P_\infty}{T_\infty} \right) \left[ \frac{2\lambda + d_d}{d_d + \left( \frac{\lambda^2}{d_d} \right) + 3.42\lambda} \right]$$

(A-3)

The mean free path of air at 23°C and 1atm is ~65nm [125]. Fuchs effect becomes important once the sizes are very small, i.e. sub-micron droplets; therefore, it is not considered in our code.

7.1.4 Stefan Flow

The mass transfer of the vapor outside the kinetic layer, was considered only by diffusion so far. However, during the evaporation, a bulk motion of the vapor was identified by Stefan [126]. The vapor at the surface of the droplet flows away from the droplet as it is displaced by additional vapor evaporating from the droplet. This process also causes a hydrodynamic flow of medium gas away from the surface with a mean speed. The total dispersion flux of vapor is the sum of diffusion and this process. The corrected evaporation rate by the Stefan flow is calculated as following:
\[ \dot{m}_{st} \approx \dot{m}_0 \left( 1 + \frac{P_0 + P_\infty}{2P} \right) \]  \hspace{1cm} (A-4)

where, \( \dot{m}_0 \) is the rate of evaporation from Maxwell’s equation (Eq. 1-18) and \( P \) is the total pressure of the medium. For water droplets at 20°C and 1 atm, the correction is approximately 1%.

### 7.1.5 Wind Factors

All of the discussion until this point was for a stationary droplet in a still medium. Once we have a relative velocity between droplet and air, both the evaporation and rate of heat transfer to the drop increases. This effects results from the change in the ways of heat and mass transfer in the new conditions, i.e. both become convective, instead of conduction and diffusion, respectively. Due to complexity of the convective problems, wind factors are used to calculate the rate of evaporation and the droplet temperature. For steady state condition, these factors are Sherwood and Nusselt numbers:

\[ Sh = \frac{\dot{m}_c}{\dot{m}} = \frac{\dot{m}_c}{4\pi R_d D(c_0 - C_\infty)} \]  \hspace{1cm} (A-5)

\[ Nu = \frac{L \dot{m}_c}{4\pi R_d K_g (T_\infty - T_0)} \]  \hspace{1cm} (A-6)

where, \( \dot{m}_c \) is the convective evaporation mass rate. These non-dimensional numbers are the ratios of convective mass and heat transfer to diffusion and conduction, respectively. The wind factors can be estimated with:

\[ Sh = 1 + 0.276 Re^{1/2} Sc^{1/3} \]  \hspace{1cm} (A-7)

\[ Nu = 1 + 0.276 Re^{1/2} Pr^{1/3} \]  \hspace{1cm} (A-8)

\( Re, Sc \) and \( Pr \) are Reynolds, Schmidt, and Prandtl numbers, respectively.

\[ Re = \frac{\text{Inertia}}{\text{Momentum Diffusivity}} = \frac{U_{\text{rel}} d_d}{\nu} \]  \hspace{1cm} (A-9)

\[ Sc = \frac{\text{Momentum Diffusivity}}{\text{Diffusivity of Vapor Through Gas}} = \frac{\nu}{D} \]  \hspace{1cm} (A-10)
Pr = \frac{\text{Momentum Diffusivity}}{\text{Diffusivity of Heat Through Gas}} = \frac{u}{\kappa_g/(c_p \rho)} \quad (A-11)

where \( U_{rel}, d_d, \upsilon, \) and \( c_p \) are relative velocity, droplet diameter, kinematic viscosity of surrounding gas, and specific heat of liquid, respectively. For convective evaporation, Maxwell’s equation and temperature depression respectively become:

\[
\dot{m}_c = \frac{4\pi R_d M D M}{9 \kappa_g} \left( \frac{P_0}{T_0} - \frac{P_\infty}{T_\infty} \right) \left( 1 + 0.276 \text{Re}^{2/3} \text{Sc}^{1/3} \right) \quad (A-12)
\]

\[
T_\infty - T_0 = \frac{D M L}{9 \kappa_g} \left( \frac{P_0}{T_0} - \frac{P_\infty}{T_\infty} \right) \left( 1 + 0.276 \text{Re}^{2/3} \text{Sc}^{1/3} \right) \left( 1 + 0.276 \text{Pr}^{2/3} \right) \quad (A-13)
\]

where \( M \) is the molecular weight of the liquid. For a water droplet with \( d_d < 20 \mu m \), falling at its terminal velocity, the wind factors are close to unity.
Appendix B: Mass spectrometer Types

In this appendix, some types of mass spectrometers, their operation methods, and their relevant features to ESI is introduced briefly. One should note that each of the mass analyzers has its own benefit and should be selected based on the application. For a more detailed discussion on this device, the reader is referred to [36].

7.2.1 Magnetic Sector Mass Spectrometer

In this spectrometer, the ions pass through a magnetic sector in which the magnetic field is applied perpendicular to the direction of ion motion. When a magnetic field, \( B \), is applied perpendicular to the velocity vector of a charged object, its velocity remains constant, but travels in a circular path with radius \( r_{\text{ion}} \) [127]. Let us consider an ion with the mass, \( m \), and the charge, \( z \), accelerated in an ion source with the potential difference, \( V \). In this condition, the kinetic energy at the outlet of ion source becomes:

\[
\frac{mu_{\text{ion}}^2}{2} = zV
\]  

(B-1)

where \( u_{\text{ion}} \) is the ion velocity at the outlet. Because the ion follows a circular path, the centrifugal force equilibrates the magnetic force:

\[
z u_{\text{ion}} B = \frac{mu_{\text{ion}}^2}{r_{\text{ion}}}
\]

(B-2)

Substituting the velocity from Eq. B-1 into Eq. B-2 gives the following:

\[
\frac{m}{z} = \frac{r^2B^2}{2V} \quad \text{or} \quad r_{\text{ion}} = \frac{1}{B} \sqrt{\frac{2Vm}{z}}
\]

(B-3)

According to this equation, magnetic sector can separate the ions based on m/z; however, to achieve a better resolution by the detector, an electric sector is added in order to focus the ions according to their kinetic energy. The simplest mode of operation of a magnetic sector mass spectrometer, keeps the electric sector at a constant potential and changes the magnetic field. Ions that have a constant kinetic energy, but different mass-to-charge ratio, are brought into focus at a slit (called collector slit), with different magnetic field strengths. Depending on the application,
the slit width can be modified to capture different sensitivities and resolutions. The accelerating voltage, instead of magnetic field, is the other alternative for this purpose.

7.2.2 Time of Flight Mass Spectrometer

A time of flight (TOF) mass spectrometer measures the time that the ions with different masses travel from the ion source to the detector. Therefore, this type of mass analyzers requires a controlled pulsed ion formation, or ejection; unlike the aforementioned types that operate with continuous ion flows. In Eq. B-1, substituting the velocity with \( \frac{L_{fl}}{t} \), gives:

\[
\frac{m}{z} = \frac{2Vt^2}{L_{fl}^2} \quad \text{or} \quad t = L_{fl} \sqrt{\frac{m}{2Vz}} \quad (B-4)
\]

where, \( L_{fl} \) is the length of flight path. One should note that the ions leaving the ion source do not have exactly the same starting times and kinetic energies; however, various TOF spectrometer designs have been developed to compensate these differences.

7.2.3 Tandem Mass Spectrometer

Let us assume we want to analyze a mixture of components, where each component produces characteristic ion species. The mass spectrum of this mixture contains peaks of different compound ions in the mixture. In order to identify the fragment ions of one component, tandem mass spectrometers are adopted. Tandem analyzers essentially combine two mass spectrometers (MS/MS systems). The first spectrometer is used for precursor ion selection, to choose a specific analyte in a mixture, and the second one is for production analysis of produced fragment ions. TQMS is an example of a tandem system. Tandem systems provide exceptional resolving power but the size of device, the operational complexity and its high cost are the main limits for many researchers.


7.3 Appendix C: Solution Properties Calculations and Approximations

In this appendix, the properties of 75%Methanol-25%Water volumetric mixture is calculated. The results are being used in the theoretical analysis (chapter 4) and the trajectory prediction code (chapter 5).

7.3.1 Viscosity Measurement

Dynamic viscosities of water, methanol, and 75%Methanol-25%Water volumetric mixture were measured with a Cannon-Fenske viscometer (Size #25). This viscometer gives the kinematic viscosity, \( \nu \), with the following relation at 22°C:

\[
\nu = C_0 t \left[ \text{mm}^2/\text{s} \right]
\]

where \( C_0 = 0.002010 \), and \( t \) is the recorded time that the liquid’s level varies from a certain marked line to the second mark. The results are listed in Table 7.1.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Time ( t ) [s]</th>
<th>Kinematic Viscosity ( \nu \times 10^6 ) [m²/s]</th>
<th>Density ( \rho ) [kg/m³]</th>
<th>Dynamic Viscosity ( \mu ) [Pa s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>538</td>
<td>1.0814</td>
<td>998.2</td>
<td>0.001079</td>
</tr>
<tr>
<td>Methanol</td>
<td>388</td>
<td>0.7799</td>
<td>792.1</td>
<td>0.000618</td>
</tr>
<tr>
<td>75%M-25%W</td>
<td>802</td>
<td>1.6120</td>
<td>843.6</td>
<td>0.001360</td>
</tr>
</tbody>
</table>

The viscosity of the mixture is higher than both of the pure liquids. Although this observation may seem extra ordinary, the reason behind it lays on the analysis of molecular interactions. The intermolecular forces in the mixture is stronger, which prevents the sliding of molecules past each other and results in a more viscous fluid [114], [128].
7.3.2 Surface Tension Calculation

The surface tension was calculated based on a proposed model for binary mixtures by Chunxi et al. [79], as following:

\[
\sigma_{\text{sol}} = (x_1 \sigma_1 + x_2 \sigma_2) - \frac{x_1 x_2 \mathcal{R} T}{x_2 + x_1 \Lambda_{21}} \left( \frac{\partial \Lambda_{21}}{\partial A} \right) \left[ 1 - \frac{1}{\Lambda_{21}} \right]
\]  
(C-2)

\[
\Lambda_{21} = \exp \left( - \frac{U_{21} - U_{22}}{\mathcal{R} T} \right)
\]  
(C-3)

\[
\frac{\partial \Lambda_{21}}{\partial A} = - \frac{\Lambda_{21}}{\mathcal{R} T} \left( \frac{\partial (U_{21} - U_{22})}{\partial A} \right)
\]  
(C-4)

\(x_1, x_2\) : molar fraction of first and second liquid

\(\sigma_1, \sigma_2\) : surface tension of first and second liquid

\(\Lambda_{21}, \frac{\partial \Lambda_{21}}{\partial A}\) : parameters calculated by Eqs. C-3 and C-4

\(A\) : surface area

\(U_{11} - U_{12}\) : the difference of interaction energy between the molecule pairs 11 and 12

The surface tension of methanol and water in 25°C as the first and second components are 0.02295 and 0.07225 N/m, respectively. For methanol and water the following was read from the table [79]:

\[
\frac{U_{21} - U_{22}}{\mathcal{R}} = -625.5
\]

\[
\frac{1}{\mathcal{R}} \left( \frac{\partial (U_{21} - U_{22})}{\partial A} \right) = -561.22 \times 10^{-5}
\]

Then the surface tension of solution is calculated as:

\[\Lambda_{21} = 8.157953\]
\[
\frac{\partial \Lambda_{21}}{\partial A} = 1.153638 \times 10^{-4}
\]

\[x_1 = 0.75\]

\[x_2 = 0.25\]

\[\sigma_{\text{sol}} = 0.025442 \text{ N/m}\]

This value shows a good agreement with the measurements for the methanol aqueous solutions performed by Vazquez et al. [129]. The temperature modifies the surface tension linearly [129]; however, due to small variation of temperature in our case, the changes are negligible. One should note that the molar volume of the components is considered equal in the calculations.

### 7.3.3 Density Correlation as a Function of Temperature

Measurements of Mikhail and Kimel [78] were adopted to estimate a correlation for density of 75\% Methanol-25\% Water volumetric mixture, based on temperature. Table 7.2 summarizes the density values in different temperatures:

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ([\text{kg/m}^3])</td>
<td>831</td>
<td>827</td>
<td>822</td>
<td>818</td>
<td>809</td>
</tr>
</tbody>
</table>

The following linear fit estimates the density of our solution, as its error from the experimental results is 5\%, at the worst case.

\[
\rho_{\text{sol}}(T_s) = 0.891 T_s + 1096.8 \quad \text{(C-5)}
\]
7.3.4 Thermal Conductivity as a Function of Temperature

The experimental data of thermal conductivity for vapor water and methanol at different temperatures was obtained from Toulukian et al. [130]. Then, the following equation was used to approximate the thermal conductivity of vapor mixture [131]:

\[ K_{\text{Mix}} = 0.5 \left( x_1 K_1 + x_2 K_2 \right) + \frac{x_1}{K_1} + \frac{x_2}{K_2} \]  \hspace{1cm} (C-6)

Sample thermal conductivities of the mixture is listed in table 7.3.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>550</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity [W/(mK)]</td>
<td>0.01517</td>
<td>0.02022</td>
<td>0.02527</td>
<td>0.03017</td>
<td>0.03525</td>
<td>0.04027</td>
</tr>
</tbody>
</table>

The following correlation was found with the temperature intervals of 10 Kelvins:

\[ K_v(T_{\text{ref}}) = -3.08 \times 10^{-9} T_{\text{ref}}^2 + 1.03 \times 10^{-4} T_{\text{ref}} - 0.0154 \]  \hspace{1cm} (C-7)

7.3.5 Latent Heat of Evaporation, Normal Boiling and Critical Temperatures

Similar to 5.2.3, we consider the evaporation ratio of the components is similar to their ratio in the mixture. In other words, the fraction of components in the mixture in gas phase is the same as their fractions in liquid phase. Although this assumption is erroneous, it is used to simplify the droplet evaporation solution. We also assume the transferred heat to the mixture is divided between the components, based on their mass ratio. Thus, the latent heat of the mixture in the boiling point can be estimated with:

\[ L_{\text{Mix @BT}} = y_1 L_{1@BT} + y_2 L_{2@BT} \]  \hspace{1cm} (C-8)

From the data of [132], the latent heat of water and methanol at their normal boiling points are 2253.64 and 1151.69 kJ/kg, respectively. Therefore:

\[ L_{\text{sol @BT}} = 1352.62 \text{ kJ/kg} \]
Latent heat of evaporation is a function of temperature. From [104], the latent heat in a certain temperature can be calculated based on a known value in a different temperature:

\[ L_2 = L_1 \left( \frac{1 - \frac{T_2}{T_c}}{1 - \frac{T_1}{T_c}} \right)^{0.38} \]  

(C-9)

The boiling temperature is usually selected as the reference point. The normal boiling and critical temperature of the solution are considered to be the weighted average by the mole fraction, between the values for pure components. These values are listed in table 7.4 [130].

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Methanol</th>
<th>75% Methanol-25% Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Boiling Point [K]</td>
<td>373</td>
<td>338</td>
<td>346.75</td>
</tr>
<tr>
<td>Critical Temperature [K]</td>
<td>513</td>
<td>647</td>
<td>546.5</td>
</tr>
</tbody>
</table>

Replacing these values into Eq. C-9 results in:

\[ L_{solv}(T_s) = 1943.2 \left( 1 - \frac{T_s}{546.5} \right)^{0.38} \]  

(C-10)

7.3.6 Specific Heat as a Function of Temperature

Correlations for the specific heat of methanol and water solution in liquid and gas phases are found here. The mixture values are calculated with the following equation:

\[ C_{pMix} = y_1 C_{p1} + y_2 C_{p2} \]  

(C-11)

The data for water and methanol in liquid and gaseous forms are read from [133]. Sample results of specific heat for mixtures are presented in table 7.5.
Table 7.5 Specific heat of 75\% methanol-25\% water volumetric mixture in gaseous and liquid forms

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>273</th>
<th>300</th>
<th>350</th>
<th>450</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{p_v} \quad [\text{J/kg K}]$</td>
<td>1419.2</td>
<td>1473.8</td>
<td>1577.2</td>
<td>1789.0</td>
<td>1894.7</td>
</tr>
<tr>
<td>$C_{p_{sol}} \quad [\text{J/kg K}]$</td>
<td>2676.3</td>
<td>2793.4</td>
<td>3132.1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The correlations, based on the data at intervals of 10 Kelvins, become:

$$C_{p_v} (T_{ref}) = 2.10 T_{ref} + 842$$ \hfill (C-12)

$$C_{p_{sol}} (T_s) = 3.28 \times 10^{-2} T_s^2 - 14.5 T_s + 4200$$ \hfill (C-13)
7.4 Appendix D: Additional Experimental Results

In this appendix, some of the performed experimental tests are presented and discussed.

7.4.1 Effect of the Carrier Gas on a Water Jet

JICF images inside the vessel are shown in Fig. 7.1. Without any air, Fig. 7.1a, the jet is unaffected. Introducing the air crossflow bends and breaks the jet into droplets. The yellow lines in Fig. 7.1 show the inlet diameter of the vessel. Above the central zone, the jet is least affected. As the air flow increases, Fig. 7.1b-d, the added momentum from the air to the water jet increases, causing a larger bending angle for both the jet and the generated spray. Besides, the jet breakup location becomes closer to the tip with the crossflow. At some optimum range of airflow, Fig. 7.1e, the jet collapses close to the centerline; the produced droplets travel at the central zone, and are carried out of the vessel successfully. Above the optimum airflow range, Fig. 7.1f, the jet collapses above the centerline, and the droplets tend to move upwards and out of the central region. This behavior is attributed to the jet breakup location and the air pressure at the central region, which pushes the droplets into the upper recirculation zone. The low pressure behind the nozzle and high turbulence of the crossflow help this lift and dispersion.

![Figure 7.1 A liquid jet inside the test vessel, operating at different air crossflows](image)

Figure 7.1 shows the magnified spray jet and its dispersion at 12-48 Scfh crossflow, i.e. 22.7-91 m/s inlet velocity. At lower air flows, Fig. 7.2a-b, the generated droplets are segregated into two
regions: the main spray (between the yellow lines), and the dispersed droplets (between the yellow and the orange lines). Most of the droplets travel in the main spray; however, some of the droplets disperse, above the main spray. Ghosh and Hunt [70] showed that in a spray with different sizes, smaller droplets take a quicker bend in crossflow. In our case, the main crossflow, in the central zone of the vessel, is expected to have the same effect. At 49.2 m/s, Fig. 7.2c, the air flow is sufficient enough that it can bend the whole spray as one; therefore, no dispersion is observed. At higher crossflows, Fig 7.2d, the jet breakup point is above the centerline of vessel; therefore, the majority of generated droplets travel above the centerline. Similar to the low airflows, a portion of the spray disperses. At higher crossflows, the air pressure below the spray and the recirculation flow close to the wall cause this dispersion.

![Images showing different crossflows and their effects on droplet dispersion.](image)

**Figure 7.2** Magnified images of JICF inside the vessel, illustrating the dispersion of droplets

### 7.4.2 Effect of Crossflow on the Stability of Plume

Figures 7.3 and 7.4 illustrate the ES performance at 3-4 kV with 18 and 20 Scfh (34.1 and 37.9 m/s) air crossflows, respectively. In this set, the tip was located at the centerline and the solution flow rate was 2 µL/min. Three typical images for each voltage, captured at different instants, are shown. For better illustration, magnified images of the tip are illustrated at the top right corner of some of the images.
At 3 kV, Figs. 7.3a-c and 7.4a-c, no plume is produced; instead, a ligament or a jet pulsates out of the capillary sometimes. Emission of a liquid jet and its breakup into the droplets is observed in some of the images. The emitted liquid jet most likely undergoes the Rayleigh jet instability and
breaks into droplets. In cases such as Figs. 7.3b and 7.4d, the generated droplets look mono sized; however, for the cases at higher voltages, e.g. Fig. 7.4j and p, at least two droplet sizes are detectable. These observations are consistent with the study of Hartman et al. [28] on the generation of secondary droplets and the ES current. They captured a great percentage of secondary and satellite droplets at high currents and only a few at low currents.

Figure 7.4 The ES performance inside the vessel at 20 Scfh crossflow and 3-4 kV voltage
Increasing the voltage to 3.2-3.4kV, Fig. 7.3d-i, gives a better ES performance for 18 Scfh, where unstable plumes can be captured. Other forms of liquid emission still exist in these voltages, but instantaneous plumes are generated more frequently, with its peak at ~3.4 kV. Further increase of the applied voltage decreases the chance of plume generation, Fig. 7.3j-o, and no plumes are observed above a certain potential. At high voltages such as 3.8 kV, Fig. 7.3m-o plume and ligament pulsation occurs simultaneously. Figure 7.3j-l shows the ES operation at 4 kV. The images reveal the existence of corona discharge at this voltage (light purple), with simultaneous ejection of liquid at some instants.

For the crossflow rate of 20 Scfh at 3.2-3.6 kV, Fig. 7.4d-l, plumes are produced more rarely than the case of 18 Scfh. Besides, the combination of ligament and plume or liquid jets was captured at lower potentials. As shown in Fig. 7.4m-o, the plume generation becomes more frequent around 3.8 kV. In 20 Scfh, unlike the 18 Scfh, the corona discharge was not observed at 4 kV, Fig. 7.4p-r. In other words, the air flow suppresses the electric discharge. These observations also reveal a positive shift in the onset voltages for the ES operating in the unstable cone jet mode.

Upper and lower boundaries of voltages for a good unstable plume generation at different air crossflows are listed in Table 7.6. Due to the difficulties in capturing these instantaneous plumes, only approximate values are reported. Considering the 2% voltage reading error, a fairly linear variation of onset voltages with air crossflow was detected. In general, higher voltages are required to capture the stable, or instantaneous plumes, and the electric discharge, when the air crossflow is enhanced. Unfortunately, due to unpredictable and transient nature of the ESICF, deriving a quantitative graph for ES mode islands was very time consuming and impractical with our setup. Besides, the onset voltages for the operation of ESICF in different modes may vary, depending on the tip wetting and boundary conditions.

Table 7.6 Onset voltage range for unstable cone jet mode at medium air crossflows

<table>
<thead>
<tr>
<th>Air Crossflow [Scfh]</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
<th>18</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Velocity [m/s]</td>
<td>18.9</td>
<td>22.7</td>
<td>26.5</td>
<td>30.3</td>
<td>34.1</td>
<td>37.9</td>
</tr>
</tbody>
</table>
7.4.3 ES Performance at High Voltages and High Crossflows

Figure 7.5 ES performance at a high crossflow (~48 Scfh) and different operating voltages (4.4-5.2 kV)

Another set of images was captured to investigate the behavior of ES at ~48 Scfh (~91 m/s), and relatively high voltages, 4.4-5.2 kV. Each row of Fig. 7.5 has been assigned to one voltage and includes five images with the approximate time lapse of one-sixth of a second.

At 4.4 kV, Fig. 7.5a-e, one or more instantaneous jets were emitting at a time. The highest frequency and number of jets was captured at 4.6-4.8 kV, Fig. 7.5f-o, where ES operates in either the unstable cone jet, or the unstable multi-jet mode. We expect the highest spectrometer’s detection rate in this voltage range. This prediction is simply because the emission of jets is at its maximum level, which leads to the highest ion generation. According to Fig. 7.5p-y, at 5-5.2 kV,
the jet emission decreases and can be observed only in some instants. The ES operates in the unstable mode and the observed intermittent jets are most probably due to instantaneous balance of forces at the meniscus. At the high flow and voltage imaging, Taylor cone could not be observed clearly, however the jet emissions from various spots are the proof of instantaneous cone formation at different locations on the tip.

7.4.4 Effect of Voltage on Taylor cone, Jet, and Plume

The cone jet mode can be captured in a range of onset voltages. In this section, the effect of voltage change on the plume and the jet angles with and without air crossflow are presented. As mentioned before, the counter electrode has been located at the bottom of the vessel and other walls are nonconductive. In the ideal case, this orientation gives an axisymmetric equipotential field (plate and needle); however, if the walls become wet, they also will act as conductive ground electrodes. The nozzle was located close to the left wall; therefore, this wall can get wet easier than the others. As a result, the equipotential lines may become asymmetric and bend toward the left. This is not the case for the actual device, as the body is conductive and the ion source is located in the middle of the air inlet and outlet. The ES images at different voltages with and without the wetting of the left wall are presented in Figs. 7.6c-d and 7.6a-b, respectively. No airflow was introduced at these images. In both cases, the plume angle is decreased with increasing the voltage value. This effect is attributed to the increase of the external electric field between the nozzle and ground electrode(s). The equipotential lines become closer and, as a result, higher electric force is applied on the charged droplets; however, the drag force of stagnant air and columbic repulsions among droplets are not expected to change noticeably. The summation of these forces on droplets gives shorter traveling paths, i.e. closer to the nozzle axis, from the generated point to the counter electrode. This is equivalent to a smaller plume angle. The developed numerical model in chapter 5 also confirms these observations.

For the non-wetted wall, Fig. 7.6a-b, the electric field is symmetric; therefore, the deflection angle is, ideally, zero for all the onset voltages. In the case of wet wall, Fig. 7.6c-h, the jet is deflected to the left, due to the asymmetry of electric field. Determining the plume angle variation with voltage change at low air flows, and asymmetric electric field is not as simple as the no airflow case. In the mentioned condition, external electric and the air drag are two main forces affecting
the plume trajectory. These forces act in the opposite directions, when the droplets travel at the left side of the nozzle. With increasing the voltage, the jet deflects more to the left. Therefore, at least the direction of initial velocity of the generated droplets is different; i.e. the effect of air drag on them is not the same. Besides, the existing asymmetric electric field is not quantitatively known. Comparing various images showed that the variation of plume angle can be different from one case to the other. To understand and predict the plume trajectory, a numerical solution as in chapter 5 is required.

Figure 7.6g-h shows the close up images of the Taylor cone captured at 4 Scfh air crossflow; including the cone height and jet deflection angle measurements. Although the air flow was from left to right and the tip was located at the centerline, the jet initially bends to the left. This image demonstrates the deflection of the Taylor cone itself, as well as the increase of jet deflection angle. The cone is stable and stationary, but its size becomes smaller at the higher voltage.

Figure 7.6 Top: plume angles; Bottom: jet deflection at different applied voltages with 4 Scfh crossflow
7.4.5 Effect of Input Sequence on the ES Performance

In our experiments, we realized the sequence of applying voltage, solution flow, and air crossflow can significantly influence the ES operation and its characteristics, such as emitting jet angle. The discussion in this section is based on a case where the capillary tip is located at the centerline of the vessel, i.e. tip to counter electrode distance was set at 5 mm. Three different input orders are shown and discussed here, namely: (1) Solution-Voltage-Crossflow, (2) Voltage-Solution-Crossflow, and (3) Solution-Crossflow-Voltage.

In all of the previous cases, the solution flow was set initially, the voltage was modified to capture the cone jet mode (Sequence 1), and then, the behavior of ESICF was studied. The “Sequence 2” was performed with initially increasing the applied voltage to 2.81 kV. Before running the solution, all the liquid at the tip was ejected due to the applied voltage. The solution at 2 µL/min was introduced and, once the stable jet was formed, the air crossflow was added. As shown in Fig. 7.7a, even without the crossflow, the cone jet was formed initially at the right half of the tip and bended toward the right. This observation is purely attributed to the wetting of the tip. With the addition of crossflow, the ES undergoes the following stages: more bending to the right (Fig. 7.7b-c); dynamic behavior (Fig. 7.7d-f); unstable jet emission (Fig. 7.7g-l); and no emitting jet, (Fig. 7.7m-n). These steps are qualitatively similar to the first sequence. At low and medium crossflows, the cone jet mode is stable and dynamic/unstable, respectively. With increasing the airflow, the tip wetting extends. At high crossflows, when there is no jet emission, the liquid spreads on the whole tip. At crossflows as high as 50-80 Scfh, Fig. 7.7m-n, the air pressure pushes the liquid to the right end of the tip. The liquid floats upwards and rests at the wake region behind the nozzle.

When the airflow was closed, the ES acted similar to the Sequence 1, Fig. 7.7o. Here, the deflection of the cone jet to the left is due the asymmetry of the external electric field. Enhancing the crossflow from this point, gave a similar behavior to Sequence 1. Comparing Figs. 3.7 and 7.7, the Taylor cone size in the second sequence is smaller, even though the used voltage is lower.
Figure 7.7 ES and cone jet performance inside the vessel at 2.81 kV and different crossflows, using the input sequence 2 (Solution-Voltage-Crossflow)
In “Sequence 3”, 1 µL/min solution was introduced initially, then the air was set to the constant low flow of ~4.7 Scfh, and at last, the voltage was increased to 3 kV. Below this voltage the cone jet mode was not observed. Figures 7.8a-l and 7.8m-s depict the images of Sequence 3 at different voltages and their corresponding ES operation captured with Sequence 1, respectively. In Fig. 7.8a-b, the operation mode at 3 kV looks pulsating; where the meniscus elongates in the axial direction, a jet is ejected, and the meniscus returns to the cusp shape. In the pulsating mode, the emissions are more like ligaments and the jets are thicker than the one in the cone jet mode.

Increasing the voltage up to 3.5 kV, Fig. 7.8c-f, pushed the ES to the unstable or droplet ejection mode, where the liquid can eject in bulks or droplets. Due to short time of ejection, capturing the ejected liquid becomes exhausting at 6 fps; however, in some images the deformation of meniscus is obvious, Fig. 7.8e. Returning to 3.38 kV, Fig. 7.8g-l, resulted in the pulsating mode with more variation in ejection. No cone jet was achieved with this sequence and further efforts were not successful either. Above the 4.5 kV the corona discharge was observed with naked eye, but could not be captured in the images due to high light intensity of the used flash. At the end, when the crossflowing air was closed and the voltage was decreased to 3.25 kV, the ES operation mode became stable cone jet. All the corresponding ES images with the first sequence, operate in the stable cone jet mode, Fig. 7.8m-s.

Considering the meniscus as a control system, it works in the cone jet mode whenever the applied forces reach the balance, either steadily or instantaneously. We think the inability to form a stable cone jet with Sequence 3, was due to the perturbations that airflow causes on the surface of meniscus. In other words, the system operates in a highly transient and unstable way and the electric force cannot overcome the liquid instabilities on the surface. However, at Sequence 1, the liquid at the tip is initially stationary and ES initially operates in the cone jet mode. Therefore, when the crossflow is added, the system can stand the air force and still run in the stable, as the initial boundary conditions are met. In the latter, the ES operates in the cone jet mode up to some crossflow rate; but once the air force exceeds that level, strong fluctuations are introduced to the liquid surface and overcome the balance of the system.
Figure 7.8 Left: ES and cone jet performance inside the vessel at ~4.7 Scfh and different voltages, using the input sequence 3 (Crossflow-Solution-Voltage); Right: corresponding ES performance using sequence 1, at different voltages and with or without the crossflow.
7.4.6 Other Effects of Tip Wetting and Boundary Conditions on ESICF

So far we have discussed the influence of input sequence on our tip wetting and ES operation. Another way to alternate the wetting and ES performance is the temporary change of airflow or voltage. These effects are identified visually and presented in this section.

Figure 7.9a-b were both captured at 2.81 kV and 4 Scfh, with the solution flow rate of 2 µL/min and in an asymmetric equipotential field. However, Fig. 7.9b was taken after the air crossflow and voltage were increased up to 12 Scfh and 3.1 kV, respectively, and then returned to the same condition of Fig. 7.9a. The Fig. 7.9c-d are both taken at 2.85 kV and 8 Scfh. Similar to Fig. 7.9a-b, the difference between them is the temporary increase of crossflow and voltage. All of these cases behave stable and stationary. The temporarily addition of air crossflow has changed the shape of cone and has pushed it from the left side to approximately the center of the tip. Thus, in both cases, Fig. 7.9b and d, the jet emission takes place from the center and a smaller angle with respect to the crossflow direction. The emitting location and angle of jet are important parameters influencing the plume trajectory. This observation shows that the temporary variation of airflow can be used in favor of transporting generated ions inside the vessel to its outlet and the inlet of spectrometer.

Figure 7.9 Effect of temporary increase of air crossflow on the cone jet and tip wetting (a, c: before; b, d: after)
Figure 7.10 Effect of temporary increase of air crossflow on jet deflection and cone size at different applied voltages (a: before; b: after)

Figure 7.10a was captured at 3.38 kV and 2 µL/min, without air crossflow. Figure 7.10b was taken at 3.55 kV, after increasing the crossflow up to ~13 Scfh and then closing it. Comparing the applied potentials, without considering the procedure of achieving the cone jet, one should expect a larger jet deflection toward the left wall and a smaller Taylor cone at the higher voltage condition. However, Fig. 7.10 depicts exactly the opposite. At higher voltage, the Taylor cone height and the jet deflection angle have been increased and decreased, respectively (from 90 µm to 100 µm and 21° to 17°). In other words, the temporary airflow variation plays a crucial role in the cone size and jet deflection. The temporary air momentum toward the right, can change the boundary conditions of the meniscus and can overcome the effect of voltage increase.

Figure 7.11 demonstrates a possible negative effect of temporary voltage variation on ESI. These close up images of the tip were captured at 20 Scfh crossflow, and 2 µL/min solution rate. Stable but dynamic jet emission was captured at 3.75 kV, Fig. 7.11a-c. In these applied conditions, the existing cone at the tip is small and its exact boundary and size cannot be detected clearly; however, the consistency in jet emission can be appreciated. As shown, the medium to high crossflow disperses the droplets and prevents the formation of a bigger plume. At 3.8 kV, Fig. 7.11d-f, the cone jet becomes unstable. With reducing the voltage back to 3.75 kV, we were expecting a stable and dynamic cone jet, but the ES continued operating in unstable cone jet mode, Fig. 7.11g-l. In fact, the change in electrospraying mode modifies the tip wetting and meniscus boundary...
conditions. This change ruins the quasi-equilibrium balance among surface tension, electric field and air pressure, which is necessary to achieve the stable cone jet mode. The frequency of jet emission in the last conditions is more than the case of 3.8 kV. At the same time, a ligament or drop emission, Fig. 7.11h, can be observed for the latter.

Figure 7.11 Effect of temporary increase of applied voltage on the ES performance and cone jet formation (air crossflow: 20 Scfh)
7.5 Appendix E: Derivations and Simplifications for Theoretical Analysis

This appendix includes a more detailed look to some of the parts mentioned in the analytical analysis (chapter 4).

7.5.1 Unsolved Electrified Jet Trajectory with Needle-Plate Configuration for Electric Field

The electric fields in a 2D Cartesian system, with considering the offset lengths, become:

\[
E_x = \frac{\sigma_c}{4\pi \varepsilon_0 (x + L_{off})} \left( \frac{2L_{Gr} - y - L_{Apex}}{\left\{ (x + L_{off})^2 + (2L_{Gr} - y - L_{Apex})^2 \right\}^{1/2}} \right) - \frac{y + L_{Apex}}{\left\{ (x + L_{off})^2 + (y + L_{Apex})^2 \right\}^{1/2}} \]  
(E-1)

\[
E_y = \frac{\sigma_c}{4\pi \varepsilon_0} \left( \frac{1}{\left\{ (x + L_{off})^2 + (2L_{Gr} - y - L_{Apex})^2 \right\}^{1/2}} + \frac{1}{\left\{ (x + L_{off})^2 + (y + L_{Apex})^2 \right\}^{1/2}} \right) \]  
(E-2)

Unfortunately, Eqs. E-1 and E-2 make the force balance equations too complicated for analytical solution. Therefore, we try to simplify these equations. The following assumptions are considered:

\[
L_{Gr} \gg x, y \quad \text{&} \quad L_{Apex}, L_{off} \approx 0
\]

Thus, Eqs. E-1 and E-2 become:

\[
E_x = \frac{\sigma_c}{4\pi \varepsilon_0 x} \left( 1 - \frac{y}{\left\{ x^2 + y^2 \right\}^{1/2}} \right) \]  
(E-3)

\[
E_y = \frac{\sigma_c}{4\pi \varepsilon_0} \left( \frac{1}{\left\{ x^2 + y^2 \right\}^{1/2}} \right) \]  
(E-4)
In an angled EJICF, we rotated the coordinates in a way that the jet emission direction falls on one of the axes (similar to §4.3.4). Figure 7.12 shows the aforementioned coordinates. If we want to solve the force balance in the rotated coordinates, we need to find the electric field expressions based on \(x'\) and \(y'\). \(x\) and \(y\) can be replaced with the following:

\[
\begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} x' \cos \beta_0 + y' \sin \beta_0 \\ -x' \sin \beta_0 + y' \cos \beta_0 \end{bmatrix}
\]  

(E-5)

Equations E-3 and E-4 based on \(x'\) and \(y'\) become:

\[
E_x = -\frac{\sigma_c}{4\pi \varepsilon_0 (x' \cos \beta_0 + y' \sin \beta_0)} \left( 1 + \frac{x' \sin \beta_0 - y' \cos \beta_0}{\left(x'^2 + y'^2\right)^{1/2}} \right)
\]

(E-6)

\[
E_y = \frac{\sigma_c}{4\pi \varepsilon_0} \left( \frac{1}{\left(x'^2 + y'^2\right)^{1/2}} \right)
\]

(E-7)

Considering the jet movement in the \(y'\) direction is small with respect to the \(x'\) direction:

\[
E_x = \frac{\sigma_c (1 + \sin \beta_0)}{4\pi \varepsilon_0 x' \cos \beta_0}
\]

(E-8)
Electric field in the $x'$ direction can be found by:

$$E_{x'} = E_x \cos \beta_0 - E_y \sin \beta_0 = \frac{\sigma c}{4\pi \epsilon_0 x'}$$  \hspace{1cm} (E-10)$$

Similar to §4.3.4, the force balance equations in the $x'$ direction were written resulting to the following ODEs:

$$\frac{d^2 x'}{dt^2} = \begin{cases} a \left( b - \frac{dx'}{dt} \right)^2 + \frac{c}{x'} & \left[ u_g \cos \beta_0 \geq \frac{dx'}{dt} \right] \\ -a \left( b - \frac{dx'}{dt} \right)^2 + \frac{c}{x'} & \left[ u_g \cos \beta_0 \leq \frac{dx'}{dt} \right] \end{cases}$$ \hspace{1cm} (E-11)$$

$$\frac{d^2 x'}{dt^2} = \begin{cases} a \left( b - \frac{dx'}{dt} \right)^2 + \frac{c}{x'} & \left[ u_g \cos \beta_0 \geq \frac{dx'}{dt} \right] \\ -a \left( b - \frac{dx'}{dt} \right)^2 + \frac{c}{x'} & \left[ u_g \cos \beta_0 \leq \frac{dx'}{dt} \right] \end{cases}$$ \hspace{1cm} (E-12)$$

where constants are:

$$a = \frac{2C_{D,x'} \rho_g}{\pi \rho_d \delta_j}, \hspace{0.5cm} b = u_g \cos \beta_0, \hspace{0.5cm} c = \frac{\sigma c \sigma_j}{\pi \epsilon_0 \rho_j \delta_j}$$ \hspace{1cm} (E-13)$$

Equations E-11 and E-12 are autonomous ODEs. Here, only the effort to solve the first ODE is shown. First we reduce the order of ODE as following:

$$\frac{dx'}{dt} = v, \hspace{0.5cm} \frac{d^2 x'}{dt^2} = \frac{dv}{dt} = v \frac{dv}{dx}$$ \hspace{1cm} (E-14)$$

$$v \frac{dv}{dx'} = a(b - v)^2 + \frac{c}{x'}$$ \hspace{1cm} (E-15)$$

$$\left[ a(b - v)^2 + \frac{c}{x'} \right] dx' - vdv = 0$$ \hspace{1cm} (E-16)$$

Equation E-16 is nonlinear. Then we need to see whether this equation is exact or not. A first order ODE in the form of, $p(x,y)dx + q(x,y)dy = 0$ is called exact if $\frac{\partial p}{\partial y} = \frac{\partial q}{\partial x}$. Based on this definition, Eq. E-16 is not an exact equation. For inexact ODEs, solution may be found with defining an integrating factor, $\gamma(x,y)$, and to make the ODE exact with multiplying by this factor:
\[
\frac{\partial (\gamma p)}{\partial y} = \frac{\partial (\gamma q)}{\partial x}
\] (E-17)

If we can find a \( \gamma \), the ODE becomes solvable. From Eq. E-17:

\[
\gamma \frac{\partial p}{\partial y} + p \frac{\partial \gamma}{\partial y} = \gamma \frac{\partial q}{\partial x} + q \frac{\partial \gamma}{\partial x}
\] (E-18)

\[
\gamma(x,y) = \frac{\frac{\partial \gamma}{\partial x} - p \frac{\partial \gamma}{\partial y}}{\frac{\partial p}{\partial y} - \frac{\partial q}{\partial x}}
\] (E-19)

In order to be able to calculate \( \gamma \), its answer needs to be independent of either \( x \) or \( y \). For the case of \( x \), a \( \gamma \) should be found as:

\[
\gamma(x) = -p \frac{\partial \gamma(x)}{\partial x}
\] \quad (E-20)

Therefore, \( \frac{\partial p}{\partial y} \frac{\partial q}{\partial x} \) must be a function of \( x \). Then, \( \gamma \) can be found as following and the exact solution of the autonomous ODE can be derived:

\[
\frac{d\gamma}{\gamma} = \left( \frac{\partial p}{\partial y} - p \frac{\partial q}{\partial x} \right) dx
\] \quad (E-21)

\[
\gamma(x) = e \left( \int \frac{\partial p}{\partial y} - p \frac{\partial q}{\partial x} \right) dx
\] \quad (E-22)

Similarly, if \( \gamma \) is a function of \( y \), we have:

\[
\gamma(y) = e \left( \int \frac{\partial q}{\partial x} \frac{\partial p}{\partial y} - \frac{\partial p}{\partial y} \right) dy
\] \quad (E-23)
The corresponding $\gamma$s for Eq. E-16, become:

\[
\gamma(x') = e \left( \int \frac{\partial}{\partial v} \left[ a(b-v)^2 + \frac{c}{x'} \right] \frac{\partial}{\partial x'} \right) dx' = e^{\left( \frac{-2ab}{v} + 2a \right)x'} = \gamma(x', v)
\]

(E-24)

\[
\gamma(v) = e \left( \int \frac{\partial}{\partial x'} \left[ a(b-v)^2 + \frac{c}{x'} \right] \frac{\partial}{\partial v} \right) dv = e \left( \int \frac{2a(b-v)}{a(b-v)^2 + \frac{c}{x'}} dv \right) = \gamma(x', v)
\]

(E-25)

None of the calculated $\gamma$s are independent from $x'$ or $v$. Thus we conclude that this method does not give us a solution. We could not find an analytical method to solve Eqs. E-11 and E-12. An analytical solution can be derived when the external electric force is considered to be constant during the integration (as described in §4.3.4).
7.5.2 Velocity and Acceleration Equations in the x Direction for an EJICF

In this part, the non-dimensional form of jet velocity and acceleration are provided:

\[
\frac{dx^*}{dt^*} = \frac{u_g}{u_j} + \sqrt{\frac{\rho_j}{\rho_g}} \frac{2\pi \xi \varepsilon_{i,x}}{C_{Dx}} \tan \left( \frac{L_j}{d_j} \sqrt{\frac{\rho_g}{\rho_j}} \frac{8C_{Dx} \xi \varepsilon_{i,x}}{\pi} t^* \right)
\]

\[
+ \tan^{-1} \left[ -\left( \frac{u_g}{u_j} \sqrt{\frac{\rho_g}{\rho_j}} \frac{C_{Dx}}{2\pi \xi \varepsilon_{i,x}} \right) \right]
\]

(E-26)

For \( \frac{u_g}{u_j} \geq \frac{dx^*}{dt^*} \) & \( \xi \varepsilon_{i,x} > 0 \)

\[
\frac{dx^*}{dt^*} = \frac{u_g}{u_j} + \sqrt{\frac{\rho_j}{\rho_g}} \frac{2\pi \xi \varepsilon_{i,x}}{C_{Dx}} \tanh \left( \frac{L_j}{d_j} \sqrt{\frac{\rho_g}{\rho_j}} \frac{8C_{Dx} \xi \varepsilon_{i,x}}{\pi} t^* \right)
\]

\[
+ \tanh^{-1} \left[ -\left( \frac{u_g}{u_j} \sqrt{\frac{\rho_g}{\rho_j}} \frac{C_{Dx}}{2\pi \xi \varepsilon_{i,x}} \right) \right] \]

(E-27)

For \( \frac{u_g}{u_j} \leq \frac{dx^*}{dt^*} \) & \( \xi \varepsilon_{i,x} > 0 \)

\[
\frac{d^2x^*}{dt^*^2} = \frac{4 \left( \frac{L_j}{d_j} \right) \xi \varepsilon_{i,x}}{\cos^2 \left( \frac{L_j}{d_j} \sqrt{\frac{\rho_g}{\rho_j}} \frac{8C_{Dx} \xi \varepsilon_{i,x}}{\pi} t^* + \tan^{-1} \left[ -\left( \frac{u_g}{u_j} \sqrt{\frac{\rho_g}{\rho_j}} \frac{C_{Dx}}{2\pi \xi \varepsilon_{i,x}} \right) \right] \right)}
\]

(E-28)

For \( \frac{u_g}{u_j} \geq \frac{dx^*}{dt^*} \) & \( \xi \varepsilon_{i,x} > 0 \)

\[
\frac{d^2x^*}{dt^*^2} = \frac{4 \left( \frac{L_j}{d_j} \right) \xi \varepsilon_{i,x}}{\cosh^2 \left( \frac{L_j}{d_j} \sqrt{\frac{\rho_g}{\rho_j}} \frac{8C_{Dx} \xi \varepsilon_{i,x}}{\pi} t^* + \tanh^{-1} \left[ -\left( \frac{u_g}{u_j} \sqrt{\frac{\rho_g}{\rho_j}} \frac{C_{Dx}}{2\pi \xi \varepsilon_{i,x}} \right) \right] \right)}
\]

(E-29)

For \( \frac{u_g}{u_j} \leq \frac{dx^*}{dt^*} \) & \( \xi \varepsilon_{i,x} > 0 \)
7.5.3 Angled EJICF – High Electric Fields – Model 2

![Diagram of velocities and forces at a cylindrical element in crossflow and uniform electric field](image)

Figure 7.13 Velocities and applying forces at a cylindrical element in crossflow and uniform electric field (for high electric fields - model 2)

In this model, similar to the first model at §4.3.4, a cylindrical element is considered. We also assume the jet diameter remains constant, and the jet can experience acceleration in its emission direction. However, instead of axis rotation to the jet direction, the force balance is solved for the x and y directions in parallel. An additional simplifying assumption is added and discussed below.

The relative velocity of jet and gas, as shown in Fig. 7.13, is:

\[ |U_{rel}| = \sqrt{\left( u_g - \frac{dx}{dt} \right)^2 + \left( \frac{dy}{dt} \right)^2} \] (E-30)

This relative velocity causes shear and drag forces on the element. In order to avoid coupling problem, we assume the angle of relative velocity is constant and equals to its initial angle:

\[ \varphi_0 = \tan^{-1} \left( \frac{u_j \cos \beta_0}{u_g - u_j \sin \beta_0} \right) \] (E-31)

In other words, the relative velocity components are related with:

\[ \left( u_g - \frac{dx}{dt} \right) = \left( \frac{dy}{dt} \right) \tan \varphi_0 \] (E-32)
This is the main assumption that differentiates this model from the first one. As the total drag force is applied normal to the jet, the relative velocity that causes the drag is the projection of total relative velocity. Based on the projected relative velocity, $U_{rel} \cos(\varphi_0 - \beta_0)$, the total drag force is expressed as:

$$|F_{D_{total}}| = \frac{1}{2} C_D \rho g (U_{rel} \cos(\varphi_0 - \beta_0))^2 A_{Fr}$$  \hspace{1cm} (E-33)

This velocity is the same as the relative velocity in the $x'$ direction, mentioned in the first model. Substituting Eq. E-30 into E-33, and finding its projection in the x and y directions, gives the drag force in each direction:

$$|F_{D_x}| = \frac{1}{2} C_D \rho g \left( \left( u_g - \frac{dx}{dt} \right)^2 + \left( \frac{dy}{dt} \right)^2 \right) A_{Fr} \cos^2(\varphi_0 - \beta_0) \cos \beta_0$$  \hspace{1cm} (E-34)

$$|F_{D_y}| = \frac{1}{2} C_D \rho g \left( \left( u_g - \frac{dx}{dt} \right)^2 + \left( \frac{dy}{dt} \right)^2 \right) A_{Fr} \cos^2(\varphi_0 - \beta_0) \sin \beta_0$$  \hspace{1cm} (E-35)

Implementing Eq. E-32 into E-34 and E-35, results in:

$$F_{D_x} = \frac{1}{2} C_D \rho g \left( u_g - \frac{dx}{dt} \right) \left( u_g - \frac{dx}{dt} \right) A_{Fr} \cos^2(\varphi_0 - \beta_0) \cos \beta_0$$  \hspace{1cm} (E-36)

$$F_{D_y} = \frac{1}{2} C_D \rho g \left( \frac{dy}{dt} \right) \left( \frac{dy}{dt} \right) A_{Fr} \cos^2(\varphi_0 - \beta_0) \sin \beta_0$$  \hspace{1cm} (E-37)

Therefore, the force balance equations, after neglecting the shear and gravity, become:

$$\Sigma F_x = \rho_j \frac{\pi d_j^2 h d^2 x}{4} \frac{d^2 x}{dt^2}$$  \hspace{1cm} (E-38)

$$\frac{1}{2} C_D \rho g \left( u_g - \frac{dx}{dt} \right) \left( u_g - \frac{dx}{dt} \right) A_{Fr} \cos^2(\varphi_0 - \beta_0) \cos \beta_0 + \sigma_j A_{surf} E_x = \rho_j \frac{\pi d_j^2 h d^2 x}{4} \frac{d^2 x}{dt^2}$$  \hspace{1cm} (E-39)

$$\frac{d^2 x}{dt^2} = \frac{2 C_D \rho g \cos^2(\varphi_0 - \beta_0) \cos \beta_0}{\pi d_j \rho_j} \left( u_g - \frac{dx}{dt} \right) \left( u_g - \frac{dx}{dt} \right) + \frac{4 \sigma_j E_x}{\rho_j d_j}$$  \hspace{1cm} (E-40)
\[
\frac{d^2 x}{dt^2} = a' \left( b' - \frac{dx}{dt} \right)^2 + c' \quad \text{(E-41)}
\]

\[
\Sigma F_y = \rho_1 \frac{\pi d_j^2 h d^2 y}{4} \quad \text{(E-42)}
\]

\[
\frac{1}{2} C_D \rho g \frac{(-\frac{dy}{dt})}{\sin^2 \varphi_0} \left| \frac{dy}{dt} \right| A_{Fr} \cos^2 (\varphi_0 - \beta_0) \sin \beta_0 + \sigma_j A_{surf} E_y = \rho_1 \frac{\pi d_j^2 h d^2 z}{4} \quad \text{(E-43)}
\]

\[
\frac{d^2 y}{dt^2} = -\frac{2C_D \rho g \cos^2 (\varphi_0 - \beta_0) \sin \beta_0}{\pi d_j \rho_j} \frac{dy}{dt} \frac{dy}{dt} + \frac{4\sigma_j E_y}{\rho_j d_j} \quad \text{(E-44)}
\]

\[
\frac{d^2 y}{dt^2} = \left( \frac{dy}{dt} \right)^2 + e' \quad \text{(E-45)}
\]

For the drag force toward the right in the x direction and upwards in the y direction, the constants of Eqs. E-38 and E-42 are:

\[
a' = \frac{2C_D \rho g \cos^2 (\varphi_0 - \beta_0) \cos \beta_0}{\pi d_j \rho_j} \quad b' = u_g \quad c' = \frac{4\sigma_j E_x}{\rho_j d_j} \quad \text{(E-46)}
\]

\[
d' = -\frac{2C_D \rho g \cos^2 (\varphi_0 - \beta_0) \sin \beta_0}{\pi d_j \rho_j} \quad e' = \frac{4\sigma_j E_y}{\rho_j d_j} \quad \text{(E-47)}
\]

Equations E-41 and E-45 can be solved separately:

<table>
<thead>
<tr>
<th>( \frac{d^2 x}{dt^2} )</th>
<th>( \frac{d^2 y}{dt^2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{dx}{dt} = v )</td>
<td>( \frac{dy}{dt} = w )</td>
</tr>
<tr>
<td>( \frac{d^2 x}{dt^2} = \frac{dv}{dt} )</td>
<td>( \frac{d^2 y}{dt^2} = \frac{dw}{dt} )</td>
</tr>
<tr>
<td>( \frac{dv}{dt} = a' \left( b' - v \right)^2 + c' )</td>
<td>( \frac{dw}{dt} = \frac{d w^2 + e'}{dt} )</td>
</tr>
<tr>
<td>( \frac{dv}{a' \left( b' - v \right)^2 + c'} = dt )</td>
<td>( \frac{dw}{d' w^2 + e'} = dt )</td>
</tr>
</tbody>
</table>
\[
v = \sqrt{\frac{c'}{a'}} \tan \left( \sqrt{a'c't + k_1} \right) + b'
\]

\[
w = \sqrt{-\frac{e'}{d'}} \tanh \left( \sqrt{-d'e't + k_3} \right)
\]

\[
dx = \left( \sqrt{\frac{c'}{a'}} \tan \left( \sqrt{a'c't + k_1} \right) + b' \right) \, dt
\]

\[
dy = \left( \sqrt{-\frac{e'}{d'}} \tanh \left( \sqrt{-d'e't + k_3} \right) \right) \, dt
\]

\[
x(t) = b't - \frac{1}{a'} \ln \left( \cos \left( \sqrt{a'c't + k_1} \right) \right) + k_2
\]

\[
y(t) = -\frac{1}{d'} \ln \left( \cosh \left( \sqrt{-d'e't + k_3} \right) \right) + k_4
\]

The hyperbolic solution for \( y \) is conditional and have answer when the drag force is smaller than the external electric force, i.e. \( \left| \frac{dy}{dt} \right| \sqrt{-d'/e'} < 1 \). If \( \left| \frac{dy}{dt} \right| \sqrt{-d'/e'} > 1 \), the solution of \( x \) becomes in the form of \( \ln|\sinh| \). In the same manner, the integral constants take the form of \( \coth^{-1} \) and \( \ln|\sinh| \), respectively.

To derive the trajectory equation between \( x \) and \( y \), \( t \) is calculated from \( y(t) \) and replaced in \( x(t) \):

\[
t = \frac{\cosh^{-1}(e^{(k_4-y)d'}) - k_3}{\sqrt{-d'e'}}
\]

\[
x = b' \left( \frac{\cosh^{-1}(e^{(k_4-y)d'}) - k_3}{\sqrt{-d'e'}} \right)
\]

\[-\frac{1}{a'} \ln \left( \cos \left( \sqrt{-d'e'} \left( \cosh^{-1}[e^{(k_4-y)d'}] - k_3 \right) + k_1 \right) \right) + k_2
\]

Or in a more simplified form:

\[
x = A \cosh^{-1}(e^{By+C}) - D \ln(\cos[E \cosh^{-1}(e^{By+C}) + F]) + G
\]
The coefficients are computed with the input values. $k_1$, $k_2$, $k_3$, and $k_4$ are integration constants, which are found based on the following initial conditions:

$$x(0) = 0, \quad y(0) = 0, \quad \dot{x}(0) = u_j \sin \beta_0, \quad \dot{y}(0) = u_j \cos \beta_0$$  \quad (E-53)

These conditions give the following integration constants:

$$k_1 = \tan^{-1} \left[ \frac{\sqrt{a'}}{c'} \left( u_j \sin \beta_0 - b' \right) \right], \quad k_2 = \frac{1}{a} \ln(\cos[k_1])$$  \quad (E-54)

$$k_3 = \tanh^{-1} \left[ u_j \cos \beta_0 \sqrt{\frac{d}{e'}} \right], \quad k_4 = \frac{1}{d} \ln(\cosh[k_3])$$  \quad (E-55)

The non-dimensional format of trajectory equation after replacing the integration constants and coefficients into Eq. E-48 becomes:

$$x^*(t^*) = \frac{u_g}{u_j} t^* + \left( \frac{d}{l_j} \right) \left( \frac{\rho_j}{\rho_g} \right) \frac{\pi \cos^2 \phi_0}{2 C_D \cos^2(\phi_0 - \beta_0) \cos \beta_0}$$

$$\times \ln \left( \cos \left( \tan^{-1} \left( \frac{\sin \beta_0 - \frac{u_g}{u_j} \cos(\phi_0 - \beta_0)}{\cos \phi_0} \sqrt{\left( \frac{\rho_g}{\rho_j} \right) C_D \cos \beta_0 \frac{1}{2 \pi \epsilon_i_{x_{t^*}}}} \right) \right) \right)$$  \quad (E-56)

where,
\[ t^* = \left( \frac{d_j}{L_j} \right) \frac{\sin \varphi_0}{\cos(\varphi_0 - \beta_0)} \sqrt{\left( \frac{\rho_1}{\rho_g} \right) \frac{\pi}{8C_D E_{i,j} \sin \beta_0}} \left( \begin{array}{c} \cosh \left[ \tanh^{-1} \left( \frac{\cos \beta_0 \cos (\varphi_0 - \beta_0)}{\sin \varphi_0} \right) \sqrt{\left( \frac{\rho_g}{\rho_1} \right) C_D \sin \beta_0 \frac{2 \pi E_{i,j}}{2 \pi E_{i,j}}} \right] \\ \cosh^{-1} \left[ \frac{\cosh \left( \tanh^{-1} \left( \frac{\cos \beta_0 \cos (\varphi_0 - \beta_0)}{\sin \varphi_0} \right) \sqrt{\left( \frac{\rho_g}{\rho_1} \right) C_D \sin \beta_0 \frac{2 \pi E_{i,j}}{2 \pi E_{i,j}}} \right) }{\cosh \left( \tanh^{-1} \left( \frac{\cos \beta_0 \cos (\varphi_0 - \beta_0)}{\sin \varphi_0} \right) \sqrt{\left( \frac{\rho_g}{\rho_1} \right) C_D \sin \beta_0 \frac{2 \pi E_{i,j}}{2 \pi E_{i,j}}} \right)} \right] \right) \]

\[ E - \frac{5}{7} \]

7.5.4 Angled EJICF – High Electric Fields – Model 3

Figure 7.14 Left: applied forces on a skewed cylindrical element under the effect of gas crossflow and uniform electric field; Right: the frontal area in the y direction
(for high electric fields - model 3)
Similar to model 2, this model is written in the x and y directions and the jet diameter is considered to remain constant. However, as shown in Fig. 7.14, the infinitesimal element is a tilted cylinder. The drag force is calculated in both directions, separately, based on the relative velocities of each component:

\[
F_{D,x} = \frac{1}{2} C_{D,x} \rho g \left( u_g - \frac{dx}{dt} \right) \left| u_g - \frac{dx}{dt} \right| A_{Fr,x}
\]

(E-58)

\[
F_{D,y} = \frac{1}{2} C_{D,y} \rho g \left( -\frac{dy}{dt} \right) \left| \frac{dy}{dt} \right| A_{Fr,y}
\]

(E-59)

As shown in these equations, two separate drag coefficients are defined in two directions. They are calculated with the correlation of flow past cylinder, Eq. 4-4, using the Reynolds numbers based on the relative velocities in each direction. Besides, two separate frontal areas are defined in the x and y directions and are considered constant. The area is a rectangle for the x direction but in the y direction it is the portion of circular cross section, shown at Fig. 7.14:

\[
A_{Fr,x} = h \times d_j
\]

(E-60)

\[
A_{Fr,y} = \frac{d_j^2}{4} \cos^{-1} \left( 1 - \frac{2h \tan \beta_0}{d_j} \right) - \left( \frac{d_j}{2} - h \tan \beta_0 \right) \sqrt{d_j h \tan \beta_0 - h^2 \tan^2 \beta_0}
\]

(E-61)

One should note that \( h \tan \beta_0 \) must be smaller than the jet radius, and the answer of \( \cos^{-1} \) is in radian. For simplicity a triangle area, shown with dashed lines in Fig. 7.14, is adopted to approximate this frontal area:

\[
A_{Triangle} = h \tan \beta_0 \sqrt{d_j h \tan \beta_0 - h^2 \tan^2 \beta_0}
\]

(E-62)

where, \( \beta_0 = \tan^{-1} \left( \frac{u_{jr}}{u_{jz}} \right) \). The exact frontal area, Eq. E-61, is \( \sim 1.4 \) times bigger than the triangle’s area. The frontal area in the y direction with maximum error of 10% is estimated with:

\[
A_{Fr,y} \approx 1.4 h \tan \beta_0 \sqrt{d_j h \tan \beta_0 - h^2 \tan^2 \beta_0}
\]

(E-63)

Similar to model 2, the general form of force balance equations become:
\[
\begin{align*}
\frac{d^2x}{dt^2} &= a' \left( b' - \frac{dx}{dt} \right)^2 + c' \\
\frac{d^2y}{dt^2} &= d' \left( \frac{dy}{dt} \right)^2 + e'
\end{align*}
\]
(E-64) (E-65)

where coefficients are:

\[
\begin{align*}
a' &= \frac{2C_{D,x} \rho_g}{\pi d_i \rho_j}, \\
b' &= u_g, \\
c' &= \frac{4\sigma_j E_x}{\rho_j d_j}
\end{align*}
\]
(E-66)

\[
d' = \frac{-2.8 \ C_{D,y} \rho_g \tan \beta_0 \sqrt{d_i h \tan \beta_0 - h^2 \tan^2 \beta_0}}{\pi d_i^2 \rho_j}, \\
e' = \frac{4\sigma_j E_y}{\rho_j d_j}
\]
(E-67)

The solution of Eqs. E-64 and E-65 results into Eqs. E-48 and E-49, respectively. The integral coefficients are found with Eqs. E-54 and E-55 and similar initial conditions. The non-dimensional form of trajectory equation, after replacing the coefficients, becomes:

\[
x^*(t^*) = \frac{u_g}{u_j} t^* + \left( \frac{d_i}{L_j} \right) \left( \frac{\rho_j}{\rho_g} \right) \frac{\pi}{2C_{D,x}} \times \ln \left( \frac{\cos \left( \tan^{-1} \left[ \left( \sin \beta_0 - \frac{u_g}{u_j} \right) \sqrt{\left( \frac{\rho_g}{\rho_j} \right) \frac{C_{D,x}}{2\pi E_{i,j,x}}} \right] \right)}{\cos \left( \frac{\rho_g}{\rho_j} \frac{8C_{D,x} E_{i,j,x}}{\pi} \left( \frac{L_j}{d_i} \right) \right) t^* + \tan^{-1} \left[ \left( \sin \beta_0 - \frac{u_g}{u_j} \right) \sqrt{\left( \frac{\rho_g}{\rho_j} \right) \frac{C_{D,x}}{2\pi E_{i,j,x}}} \right] \right)}
\]
(E-68)

where,
The maximum value that $h \tan \beta_0$ can take is the radius of jet, $d_j/2$; therefore, $R_{El}$ is always smaller than 0.5. The maximum height of element that one can select is:

$$h_{\text{max}} = \frac{d_j}{2 \tan \beta_0}$$

The trajectory prediction by the third model of high electric fields depends on the height of elements. In this model, the jet trajectory is predicted with two element heights; once with the highest value, $d_j$, and the other time with a very small value, $10^{-10}$ m, i.e. close to the molecular size of the operating fluid.

7.5.5 Predictions of Angled EJICF at High Electric Fields - Models 2 and 3

In this section the results of trajectory equations, derived at §7.4.3 and §7.4.4, is presented. Table 7.7 lists the input and initial conditions of the tested cases. These cases are similar to the ones discussed at §4.4.
Table 7.7 Trajectory prediction cases and inputs of the derived equations for an EJICF

<table>
<thead>
<tr>
<th>Case #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crossflow [Scfh]</td>
<td>4</td>
<td>4</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>q/m [C/kg]</td>
<td>J and T</td>
<td>V and N</td>
<td>J and T</td>
<td>V and N</td>
</tr>
<tr>
<td>β₀ [Rad]</td>
<td>π/10</td>
<td>π/10</td>
<td>π/8</td>
<td>π/8</td>
</tr>
<tr>
<td>φ₀ [Rad]</td>
<td>1.128</td>
<td>1.128</td>
<td>0.599</td>
<td>0.599</td>
</tr>
<tr>
<td>( \frac{d_j}{L_j} )</td>
<td>0.0233</td>
<td>0.0233</td>
<td>0.0233</td>
<td>0.0233</td>
</tr>
<tr>
<td>( \frac{u_g}{u_j} )</td>
<td>0.76</td>
<td>0.76</td>
<td>1.73</td>
<td>1.73</td>
</tr>
<tr>
<td>( \frac{\rho_g}{\rho_j} )</td>
<td>(1.39 \times 10^{-3})</td>
<td>(1.39 \times 10^{-3})</td>
<td>(1.39 \times 10^{-3})</td>
<td>(1.39 \times 10^{-3})</td>
</tr>
<tr>
<td>( \varepsilon_{i,j,x'} )</td>
<td>(-6.95 \times 10^{-4})</td>
<td>(-1.26 \times 10^{-3})</td>
<td>(-2.13 \times 10^{-3})</td>
<td>(-3.86 \times 10^{-3})</td>
</tr>
<tr>
<td>( \varepsilon_{i,g,x'} )</td>
<td>(-8.65 \times 10^{-1})</td>
<td>(-1.57)</td>
<td>(-5.10 \times 10^{-1})</td>
<td>(-9.24 \times 10^{-1})</td>
</tr>
<tr>
<td>( \varepsilon_{i,j,y'} )</td>
<td>(-1.93 \times 10^{-2})</td>
<td>(-3.49 \times 10^{-2})</td>
<td>(-1.85 \times 10^{-2})</td>
<td>(-3.35 \times 10^{-2})</td>
</tr>
<tr>
<td>( \varepsilon_{i,j,x} )</td>
<td>(5.85 \times 10^{-3})</td>
<td>(1.06 \times 10^{-2})</td>
<td>(5.99 \times 10^{-3})</td>
<td>(-1.09 \times 10^{-2})</td>
</tr>
<tr>
<td>( \varepsilon_{i,j,y} )</td>
<td>7.29</td>
<td>13.2</td>
<td>1.43</td>
<td>2.6</td>
</tr>
<tr>
<td>Re(_{x'})</td>
<td>0.7</td>
<td>0.7</td>
<td>1.55</td>
<td>1.55</td>
</tr>
<tr>
<td>C(_{D,x'})</td>
<td>12.0</td>
<td>12.0</td>
<td>8.03</td>
<td>8.03</td>
</tr>
<tr>
<td>Re(_{x})</td>
<td>0.44</td>
<td>0.44</td>
<td>1.31</td>
<td>1.31</td>
</tr>
<tr>
<td>Re(_{y})</td>
<td>0.92</td>
<td>0.92</td>
<td>0.89</td>
<td>0.89</td>
</tr>
</tbody>
</table>
Figures 7.15 to 7.18 show the trajectories of the listed cases, predicted by different theoretical models. In model 2, a simplifying assumption was added to model 1, indicating, the angle of relative velocity between the gas and jet remains constant. This assumption is exact if the jet travels on a straight line. In all four cases, these two models are very close to each other. In other words, this assumption is fairly justified, as long as the jet trajectory is fairly linear.

For the third model, instead of the previous assumption, the drag force was calculated separately in 2D. The chosen elements were 4 orders of magnitude different in height; however, the results showed that the trajectories are very close to each other. This model has the minimum bending predictions toward the right side and does not show agreement with the experimental data. The reason lays in the calculated drag force and drag coefficients. One may propose a better calibration of the model and the drag coefficients based on the experiments. However, at this time, we do not consider this model an accurate one.
Case #1

Figure 7.15 The non-dimensional trajectory of the angled EJICF - Case #1
Figure 7.16 The non-dimensional trajectory of the angled EJICF - Case #2
Figure 7.17 The non-dimensional trajectory of the angled EJICF - Case #3
Figure 7.18 The non-dimensional trajectory of the angled EJICF - Case #4
7.5.6 Gravity and Shear Forces vs. Electric Force on an EJICF

For an orthogonal ESICF, §4.3.1, gravity, shear, and electric forces are applied in the y direction. In this section we compare the significance of these forces are compared. The electric force on a cylindrical element is applied downwards and is calculated with:

\[ F_{E,y} = \sigma_j A_{surf} E_y = \sigma_j E_y \pi d_j h \]  \hspace{1cm} (E-72)

The jet moves downwards and the air is stagnant in this direction. This condition is equivalent to the case when the air flows upwards with velocity \( u_j \) on a stationary cylinder. Considering the velocity condition and boundary layer over this cylinder is similar to a laminar flow past a plate, the shear stress at the surface is approximated by Eq. E-73:

\[ \tau_{surf} = 0.332 \sqrt{\frac{\rho_g \mu_g u_j^{3/2}}{y}} \]  \hspace{1cm} (E-73)

Equation E-72 shows the shear depends on \( y \) and its maximum value is at the beginning of cylinder, i.e. next to the breakup location in our jet. The maximum shear force on a cylindrical element can be found by:

\[ (F_{\text{Shear}})_{\text{MAX}} = A_{surf} \times (\tau_{surf})_{\text{MAX}} = A_{surf} \times 0.332 \sqrt{\frac{\rho_g \mu_g u_j^{3/2}}{h/2}} \]  \hspace{1cm} (E-74)

The gravity force is calculated by:

\[ F_g = \rho_j A_c h g = \frac{\pi d_j^2 g \rho_j}{4} h \]  \hspace{1cm} (E-75)

The ratio of maximum shear and gravity forces over the electric force are estimated with:

\[ \frac{(F_{\text{Shear}})_{\text{MAX}}}{F_{E,y}} = \frac{0.332 \sqrt{\frac{\rho_g \mu_g u_j^{3/2}}{h/2}}}{\sigma_j E_y} \]  \hspace{1cm} (E-76)

\[ \frac{F_g}{F_{E,y}} = \frac{\rho_j d_j g}{4\sigma_j E_y} \]  \hspace{1cm} (E-77)
Equation E-76 shows that the ratio between shear and electric forces depends on the height of the element and its maximum occurs when the assumed element has the lowest height. The thinnest element can be one molecule in height. The molecular size of the components of the working solution is approximately 1 Å (10^{-10} m). Equations E-76 and E-77 are calculated based on the following inputs:

\[
E_y = 10^6 \text{ V/m} , \quad \sigma_j = 10^{-4} \text{ C/m}^2 , \quad u_j = 10 \text{ m/s} , \quad d_j = 5 \mu\text{m}
\]

\[
\rho_g = 1.173 \text{ kg/m}^3 , \quad \mu_g = 1.81 \times 10^{-5} \text{ kg/(m s)} , \quad \rho_j = 843.6 \text{ kg/m}^3
\]

Based on Eqs. E-76 and E-77, the ratios of shear and gravity forces on the electric force become 12.17 and 1.03 \times 10^{-4}.

The shear and electric forces are comparable for the jet location very close to the breakup point. However, if we move only 1 \mu m away from this point on the jet, the value of shear force drops by two orders. Thus, as the jet length is ~120 \mu m, we can fairly neglect the effect of shear force on the general force balance. The effect of gravity is negligible in our models as it is four orders of magnitude smaller.
7.6 Appendix F: Velocity Profile Approximations Inside the Vessel

The derivation of laminar, turbulent and Gaussian velocity profiles inside a circular pipe is illustrated in this appendix. Laminar and turbulent profiles are adopted from [73]. The Gaussian profile is derived from its general form, where the standard deviation is considered to be one-third of pipe radius. This assumption is consistent with Albertson et al. [102].

The maximum velocity in each profile, \( U_{\text{Max}} \), is found based on the average velocity, \( U_{\text{Avg}} \), using the continuity equation:

\[
U_{\text{Avg}} \pi r_p^2 = \int_0^{r_p} u_g(r) \ 2\pi r \ dr \quad (F-1)
\]

The calculated value is replaced in the profile’s equation afterwards. In the code, the pipe radius, \( r_p \), is substituted with the expansion radius of expanding air, \( r_{\text{ex}} \). In sudden expansion, the average velocity in each cross section is a function of \( x \) (see §4.2.1).

### 7.6.1 Laminar

\[
u_g(r) = U_{\text{Max}} \left( 1 - \frac{r^2}{r_p^2} \right) \quad (F-2)
\]

\[
\int_0^{r_p} 2\pi U_{\text{Max}} r \left( 1 - \frac{r^2}{r_p^2} \right) \ dr = 2\pi U_{\text{Max}} \left[ \frac{r^2}{2} - \frac{r^4}{4r_p^2} \right]_0^{r_p} = \frac{U_{\text{Max}}}{2} \pi r_p^2
\]

\[
U_{\text{Max}} = 2U_{\text{Avg}} \quad (F-3)
\]

\[
u_g(x, r) = 2U_{\text{Avg}}(x) \times \left( 1 - \frac{r^2}{r_{\text{ex}}^2} \right) \quad (F-4)
\]
7.6.2 Turbulent

\[ u_g(r) = U_{\text{Max}} \left( 1 - \frac{r}{r_p} \right)^{1/7} \]  

(F-5)

\[
\int_0^{r_p} 2\pi U_{\text{Max}} r \left( 1 - \frac{r}{r_p} \right)^{1/7} \, dr = 2\pi U_{\text{Max}} \left[ \frac{-7}{120} (r_p - r)(7r_p - 8r) \left( 1 - \frac{r}{r_p} \right)^{1/7} \right]_0^{r_p} \\
= \frac{49U_{\text{Max}}}{60} \pi r_p^2 
\]

\[ U_{\text{Max}} \approx 1.225U_{\text{Avg}} \]  

(F-6)

\[ u_g(x, r) = 1.225U_{\text{Avg}}(x) \times \left( 1 - \frac{r}{r_{\text{Ex}}} \right)^{1/7} \]  

(F-7)

7.6.3 Gaussian

\[ u_g(r) = U_{\text{Max}} e^{-4.5 \left( \frac{r}{r_p} \right)^2} \]  

(F-8)

\[
\int_0^{r_p} 2\pi U_{\text{Max}} r e^{-4.5 \left( \frac{r}{r_p} \right)^2} \, dr = 2\pi U_{\text{Max}} \left[ e^{-4.5 \left( \frac{r}{r_p} \right)^2} \right]_0^{r_p} \\
= \frac{(1 - e^{-4.5})U_{\text{Max}}}{4.5} \pi r_p^2 
\]

\[ U_{\text{Max}} \approx 4.55U_{\text{Avg}} \]  

(F-9)

\[ u_g(x, r) = 4.55U_{\text{Avg}}(x) \times e^{-4.5 \left( \frac{r}{r_{\text{Ex}}} \right)^2} \]  

(F-10)
7.7 Appendix G: Simulation Results for the ES Plume Inside the Vessel at 8 Scfh Crossflow

Figure 7.19 Plume trajectory prediction in 8 Scfh crossflow inside the vessel; adopted models in the run: laminar/turbulent velocity profile - Vonnegut and Neubauer’s charge correlation - non-evaporative droplets
Figure 7.20 Plume trajectory prediction in 8 Scfh crossflow inside the vessel; adopted models in the run: laminar/turbulent velocity profile - Vonnegut and Neubauer’s charge correlation - evaporative droplets.
Figure 7.21 Plume trajectory prediction in 8 Scfh crossflow inside the vessel; adopted models in the run: laminar/turbulent velocity profile - Jones and Thong’s charge correlation - non-evaporative droplets
Figure 7.22 Plume trajectory prediction in 8 Scfh crossflow inside the vessel; adopted models in the run: laminar/turbulent velocity profile - Jones and Thong’s charge correlation - evaporative droplets
Figure 7.23 Plume trajectory prediction in 8 Scfh crossflow inside the vessel; adopted models in the run: Gaussian velocity profile - Vonnegut and Neubauer’s charge correlation - non-evaporative droplets
Figure 7.24 Plume trajectory prediction in 8 Scfh crossflow inside the vessel; adopted models in the run: Gaussian velocity profile - Vonnegut and Neubauer’s charge correlation - evaporative droplets
Figure 7.25 Plume trajectory prediction in 8 Scfh crossflow inside the vessel; adopted models in the run: Gaussian velocity profile - Jones and Thong’s charge correlation - non-evaporative droplets
Figure 7.26 Plume trajectory prediction in 8 Scfh crossflow inside the vessel; adopted models in the run: Gaussian velocity profile - Jones and Thong’s charge correlation - evaporative droplets. 
Figure 7.27 Predicted flight times at 8 Scfh crossflow with Jones and Thong’s correlation

Figure 7.28 Predicted flight times at 8 Scfh crossflow with Vonnegut and Neubauer’s correlation
Figure 7.29 Average velocities at 8 Scfh crossflow with Jones and Thong’s correlation

Figure 7.30 Average velocities at 8 Scfh crossflow with Vonnegut and Neubauer’s correlation