Numerical Simulation of Electrospray Droplets Dynamics

Jordi Grifoll\textsuperscript{1}, Ajith Kumar A.\textsuperscript{1} and Joan Rosell-Llompart\textsuperscript{1,2}

\textsuperscript{1} Universitat Rovira i Virgili, Departament d’Enginyeria Química, DEW Research Group, Avda. dels Països Catalans, 26, 43007, Tarragona, Spain

\textsuperscript{2} ICREA (Catalan Institution for Research and Advanced Studies), Barcelona, Spain

Abstract — We investigate the question of how to choose the appropriate time step in Lagrangian simulations of the droplet dynamics of electrosprays. While exploring which variables could be used to assess the time step used in the numerical integration, we found that numerical collisions between droplets is one of the most sensitive indicators. The results of these numerical collisions are also easily observable in snapshots of the droplets positions, where some droplets (outlier droplets) can be found outside of the plume envelope. A more detailed analysis of the results show that at very short time steps some collisions still take place, which are shown to be real collisions occurring inside the electrospray plume. The time step needed to simulate the droplets dynamics should be small enough to avoid collision events that are numerical artifacts and to allow the description of the real collision events.

Keywords— electrospray, numerical simulation, spray dynamics, droplets collisions.

I. INTRODUCTION

Electrospraying of liquids is a useful methodology to produce and control fine electrically-charged droplets. The methodology has been used with success in diverse applications, including the production of thin and uniform coatings [Roncallo et al., 2010], space thrusters [Krpoun and Shea, 2009] and mass spectrometry [Fenn et al., 1989].

A large and not always well understood variety of phenomena occurs during electrospraying, which explains why a general and detailed theoretical description of the processes in the different regimes and conditions is lacking, despite significant efforts in this direction [Gañán-Calvo, 2004].

Among the functioning modes, the so called cone-jet mode is usually preferred because it produces low dispersion of the droplet diameter in a stable configuration. In this mode, a liquid protrusion, called Taylor cone, is formed at the end of a capillary tube. A jet is ejected at the apex of the cone, which becomes unstable and breaks up into electrically-charged droplets. It is widely assumed that coulombic repulsion between the droplets precludes droplet collisions and aggregation. The droplets travel in the gas phase driven by the coulombic field and by the external electrical field created by the potential difference between the capillary tube and surrounding electrodes (typically a grounded plate positioned at some distance away from, and perpendicular to, the capillary).

In electrospray, several variables belonging to different parts of the system control its general characteristics. This includes, at least, liquid properties (electrical conductivity, dielectric constant, density, viscosity, surface tension), gas phase properties (viscosity, density), geometric parameters of the apparatus (capillary radius, capillary-to-plate distance), electrical tension between the capillary and the plate, and the liquid flow rate. The number of operational variables is so high that covering all the combinations experimentally is a demanding task. For a given system, even after knowing the main characteristics of the formed droplets, some important outcomes are not easily predictable, such as the area covered by the impinged droplets on the plate (collection plate), flux distribution over the plate, etc.

To help making such predictions and improve the understanding of electrospray droplet dynamics, Gañán-Calvo et al. (1994) developed a Lagrangian model of the droplets trajectories and simulated droplet plume dynamics for several systems. Based on this pioneering work, several researchers [Hartman et al., 1999; Wilhem et al., 2003; Rietveld et al., 2006; Jung et al., 2010] have used similar methodologies to predict the dynamics of electrospray droplets. In these works, however, no objective criterion is provided for choosing an appropriate time step for the simulation.

In this communication, we use this type of Lagrangian model, and develop a new methodology to select the appropriate numerical-integration time step. In addition, we focus on electrosprays populated with a much larger number of droplets than considered before, and report the spray plume transient for the first time.

II. METHODOLOGY

A. Governing equations

The motion of a droplet $i$ is described by its position vector $\mathbf{R}_i$ and velocity vector $\mathbf{V}_i$, which are functions of time $t$ that are obtained by solving its equations of motion:
\[
\frac{d^2 \mathbf{R}_i}{dt^2} = \mathbf{V}_i; \quad \frac{d \mathbf{V}_i}{dt} = \mathbf{A}_i \tag{1.a,b}
\]

where \( \mathbf{A}_i \) is the acceleration, i.e. the sum of forces acting on droplet \( i \) divided by its mass. The electrospray system is considered to be made of non-evaporating droplets that do not interact with each other aerodynamically, only electrostatically, and experience drag from the surrounding air, which is assumed to be still. Further, the droplet charge is assumed to be constant and to be located at a point (or droplet center). The droplets are emitted near the end of a conducting capillary tube, between it and a conducting flat plate of infinite extent. Under these constraints, equation (1b) becomes:

\[
\frac{\pi d_i^3 \rho_d}{6} \frac{d \mathbf{V}_i}{dt} = -C_{Di} \frac{\pi}{8} d_i^2 \rho_f V_i |\mathbf{V}_i| + q_i E_{\text{ext}} + q_i \sum_{j \neq i} \frac{|\mathbf{R}_{ij}|^2}{4 \pi \varepsilon |\mathbf{R}_{ij}|^3} \tag{2}
\]

where \( d_i \) is the droplet diameter (m), \( \rho_d \) is the liquid density (kg/m\(^3\)), \( \rho_f \) is the air density (kg/m\(^3\)), \( C_{Di} \) is the drag coefficient [Abraham, 1970], \( q_i \) is the electrical charge carried by the droplet (C), \( E_{\text{ext}} \) is the external electrical field created by the potential difference between the capillary tube and the plate (V/m), \( R_{ij} = \mathbf{R}_i - \mathbf{R}_j \) is displacement between the position vectors of droplets \( j \) \([R_j = (x_j, y_j, z_j)]\) and \( i \) (m), and \( R_{ij} = \mathbf{R}_i - \mathbf{R}_j \) is the displacement between the position vectors from the image of droplet \( j \) in the plate \([R_j = (x_j, y_j, 2H - z_j)]\) to \( i \) (m) (where \( H \) is the separation between the capillary tip and the plate), \( \varepsilon \) is the air permittivity (taken as 8.854 \times 10^{-12} \text{ F/m} \), and \( N \) is the total number of droplets.

For each droplet, the initial condition for integration of equation (2) is taken as the velocity of the jet before it breaks up to form the droplets. The jet velocity has been estimated from the volumetric flow rate of the liquid to be sprayed and the assumed jet diameter. This jet diameter has been obtained from the average droplet diameter according to the classical Rayleigh equation, \( d_{\text{jet}} = \overline{d}/1.89 \), derived for uncharged jets. It has been observed experimentally that this relationship between jet diameter and droplet diameter is very similar in the case of charged and uncharged jets [Rosell-Llompart and Fernandez de la Mora, 1994 and references therein]. Rayleigh [Chandrasekhar, 1981] also stated that the jet becomes unstable to disturbances whose wavelengths are 4.5 times the droplet diameter. In this work we consider that the jet breaks after three wave lengths. The emission point of the droplets has been separated from the end of the capillary tube by one height of the Taylor cone plus 13.5 times the droplet diameter.

**B. numerical integration technique**

There is a large variety of integration schemes that can be used to solve equations (1a,b). Similar integration problems are encountered in the area of Molecular Simulation, for which it has been concluded that, although high order schemes can predict droplet positions more accurately, they tend to produce stronger drifts in the system energy over long simulation times, whereas some first order algorithms have little long-term energy drift [Frenkel and Smit, 2002].

We have implemented the Velocity Verlet first order algorithm, which has been extensively used in the Molecular Dynamics area [Allen and Tildesley, 1989], and was first proposed by Swope et al. (1982). It has been recommended over Euler algorithms because of its numerical stability and does not suffer from energy drift [Frenkel and Smit, 2002].

The algorithm advances the solution one time step from \( t \) to \( t + \Delta t \), according to

\[
\mathbf{R}_i(t + \Delta t) = \mathbf{R}_i(t) + \mathbf{V}_i(t) \Delta t + \frac{1}{2} \mathbf{A}_i(t) \Delta t^2 \tag{3.a}
\]

\[
\mathbf{V}_i(t + \Delta t) = \mathbf{V}_i(t) + \left[ \frac{\mathbf{A}_i(t) + \mathbf{A}_i(t + \Delta t)}{2} \right] \Delta t \tag{3.b}
\]

where the velocity needed to calculate the drag force at \( t + \Delta t \) is estimated as \( \mathbf{V}_d(t + \Delta t) = \mathbf{V}_d(t) + \mathbf{A}_d(t) \Delta t \).

**III. RESULTS AND DISCUSSION**

**A. System description**

To simulate an electrospray under realistic conditions, we consider the experimental system reported by Park et al. (2004) as their configuration Nozzle I (Table 1).

The external electrical field was calculated solving Laplace’s Equation for the electrostatic potential \( \phi \) in the region between the capillary and the plate, in cylindrical coordinates, using a very fine non-homogeneous grid. The

**Table 1 System description**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capillary-to-plate separation (m)</td>
<td>( H )</td>
<td>0.03</td>
</tr>
<tr>
<td>Count mean diameter (( \mu \text{m} ))</td>
<td>( \overline{d} )</td>
<td>8.84</td>
</tr>
<tr>
<td>Coefficient of variation (-)</td>
<td>( \sigma_d/\overline{d} )</td>
<td>0.209</td>
</tr>
<tr>
<td>Capillary potential (V)</td>
<td>( \Phi_0 )</td>
<td>4000</td>
</tr>
<tr>
<td>Liquid flow rate (( \mu \text{L/min} ))</td>
<td>( Q )</td>
<td>20</td>
</tr>
<tr>
<td>Electrical current (nA)</td>
<td>( I )</td>
<td>37.4</td>
</tr>
</tbody>
</table>

*From Park et al. (2004)*
boundary conditions were $\phi = \Phi_0$ at the capillary and Taylor cone surfaces; $\phi = 0$ V at the plate ($z = H$), $\partial \phi / \partial z = 0$ at $z = -10H$, and $\partial \phi / \partial r = 0$ at $r = 10H$. These two last boundary conditions were located far away of the droplets plume location, to avoid their influence of the external field computed values in the zone of forces calculation. The external field values in the zone $0 < z < H, 0 < r < 2H$ were stored in an array so they were ready available when needed during the droplets dynamics computations. The droplet size distribution is log-normal.

Another important property of the system is the time needed to reach the steady state from an initial no-droplet condition, at the beginning of the simulation. In the previous literature, the formation of the electrospay plume is not highlighted, probably because it consumed relatively few computer resources, thus representing a small fraction of the total simulated time. In our electrospay system, however, with a greater number of droplets, the transient takes more computational effort (becoming a non-negligible fraction of the total simulated time) and must thus be identified before interrogating the steady state for spray variables. Figure 1 shows the number of droplets in the plume for $0 < t < 0.2$ s, growing from zero initially, to approximately 26000 at $t \sim 0.1$ s, beyond which the number of droplets remains almost constant, implying a steady state plume.

### B. Numerical results

To make an efficient use of the computational resources available, it is important to select the longest time step $\Delta t$ that results in accurate droplets dynamics calculations. In
order to identify an output variable that is sensitive to the time step, we have simulated the system for different time steps, within the relative large range $5 \times 10^{-7} < \Delta t < 2 \times 10^{-5}$ s. We have found that several output variables describing droplet distribution (radial flux distribution on the plate, droplets velocity distribution within the plume, and location of the plume envelope) have low sensitivity to $\Delta t$. Meanwhile, snapshots of the droplets’ position in the steady plume showed that in some simulations there were droplets outside of the plume envelope, here referred to as “outlier droplets”. Figure 2 shows three snapshots at $t = 0.2$ s obtained using the time steps of $1 \times 10^{-6}$, $2 \times 10^{-6}$ and $5 \times 10^{-6}$ s. While there are no outlier droplets for $\Delta t = 1 \times 10^{-6}$ s, the number of outlier droplets increase as $\Delta t$ increases, showing that the number of outlier droplets is sensitive to the time step.

To understand better the connection between outlier droplets and increased time step, we have investigated the cause for the outlier droplets, which we have found to be numerical collisions that occur within the plume. Figure 3 depicts the trajectories of two droplets involved in one typical collision, when $\Delta t = 5 \times 10^{-6}$ s. The sequential dots on each trajectory show the droplets’ positions at the end of successive time steps, while the trajectories’ projection on the xy plane are included for clarity. During this collision, a relatively large and fast droplet ($12 \mu m$ diameter, trajectory 1$\rightarrow$1’) approaches from behind a smaller and slower droplet ($9 \mu m$, trajectory 2$\rightarrow$2’). At some point, the droplets’ center-to-center distance became less than the sum of their radii, meaning that if they had been real droplets they would have physically touched (assuming spherical shape).

As the result of this numerical collision, the smaller droplet accelerates dramatically, changing the initial trajectory direction as it shoots out of the plume envelope.

Next we have studied whether these numerical collisions are distributed in the plume or appear concentrated in any regions. From here on, we simplified the definition of a collision as happening when the separation between any pair of droplet centers was found to be less than one droplet count mean diameter (Table 1), instead of the sum of radii. Figure 4 shows a histogram of the $z$-positions of the collisions recorded during a simulation between $0 < t < 0.25$ s using $\Delta t = 1 \times 10^{-5}$ s. Almost all collisions occur in a zone close to the emission point ($l_0 = 0.5$ mm). The farthest collision recorded was at 5.6 mm from the emission point ($z = 6.1$ mm), and the maximum number of collisions takes place at 0.5 mm. At this axial location, the mean axial droplet velocity has a maximum, which indicates a cause-effect relationship between collisions and droplet speed.

Incidentally, we note that while droplets become outliers close to the emission point (Figure 4), they can be found at any $z$ position downstream (Figure 2c). Therefore, after they collide and leave the spray envelope near the emission region, they travel toward the plate outside of the plume envelope, closely following the electric field lines.

These observations have shown that the number of outlier droplets is correlated with increased time step, and that the outliers are the result of numerical collisions occurring near the droplet emission point. They also suggest that a criterion based on the frequency of numerical collisions
might perhaps be used for assessing the appropriateness of a time step. To explore this possibility, Figure 5 shows the collision count per 1000 time steps as function of the time step for $5 \times 10^{-7} \leq \Delta t \leq 2 \times 10^{-5}$ s. For these simulations we have taken as initial condition the system state (droplets’ positions and velocities) at $t = 0.2$ s which was previously simulated using $\Delta t = 1 \times 10^{-6}$ s (the state shown in Fig. 2a). The simulation code then ran for the period $0.20 < t < 0.25$ s using the different time steps shown. Figure 5 shows that the collision count per 1000 time steps decreases as the time step decreases, as expected, but levels out to a non-zero value for small $\Delta t$’s, of approximately 6 counts/1000 steps. The fact that the collision count does not tend to zero as $\Delta t \to 0$ indicates that such “residual” collisions are not numerical artifacts but, rather, real collision events that take place inside the electrospray plume. In fact, as $\Delta t$ decreases, a real collision will eventually be sampled multiply, and the sampling frequency will grow in inverse proportion to the decrease in $\Delta t$, thus leading to a constant collision count, and a $\Delta t$-independent asymptote, as is found in Figure 5. Therefore, an approximate criterion for choosing an appropriate $\Delta t$ could be based on proximity to the asymptote of the collision count, so that real collisions can be properly described (which involve the most rapid changes in electrostatic field experienced by any droplets in the spray). By applying this criterion to figure 5, one would expect an appropriate $\Delta t$ for this system to not exceed $2 \times 10^{-6}$ s.

To further build upon this rationale, in Figure 6 we have graphed the average number of time steps needed to describe each collision event for the same simulations of Figure 5. When $\Delta t > 2 \times 10^{-6}$ s this number is nearly unity, indicating that $\Delta t$ is not short enough to describe the details of a collision event (be sampled multiply). Notice that the Verlet integration scheme (as with any first order scheme) considers that during a time step the forces remain constant and equal to their value at the beginning of the time step. Therefore, when a large time step is used, two colliding droplets that are very close at time $t + \Delta t$ may have barely noticed their mutual repulsion force at time $t$. In this situation, the numerical scheme does not conserve energy and the majority of collisions are therefore numerical artifacts (not real). For $\Delta t < 2 \times 10^{-6}$, on the other hand, the average number of time steps needed to describe a collision increases above 1, becoming almost 4 for $\Delta t = 5 \times 10^{-7}$ s (Fig. 6). In this case, the numerical collision events correspond to real collisions. While the number of droplets involved in real collisions is not zero, as typically assumed for electrospray systems, it is small in the system simulated here, with 3200 collisions/s, and 0.4 % of the droplets involved.

In sum, we have learned that when the time step of integration $\Delta t$ is small enough to preclude outlier droplets, it is also capable of sampling (describing) real collisions. In other words, the absence of outlier droplets in a simulation (an easy check requiring no data post-processing) is a sufficient criterion to choose the time step.

IV. CONCLUSIONS

Detailed simulations of the droplets dynamics of an electrospray plume have been performed. In the simulations some droplets are present outside of the plume envelope (outlier droplets) when the time step used in the numerical integration is too large for describing properly the droplet
interactions. These outlier droplets are the result of collisions that occur near the emission point. When the time step is reduced, the number of outliers is also reduced and they disappear at low enough time steps.

Analysis of the numerical description of the collision events allows distinguishing between collisions that are numerical artifacts and real collisions described by several time steps. Such real collisions are infrequent, but not nonexistent, as usually assumed for electrosprays. In the simulated system, these collisions have been useful in providing an objective basis for choosing an appropriate time step of the simulation at under $2 \times 10^{-6}$ s, which is also when the outlier droplets disappear.

ACKNOWLEDGMENTS

The research was financially supported by the Ministerio de Educación y Ciencia (Spain), project CTQ2008-05758/PPQ and by the Generalitat de Catalunya (ref. 2009SGR-01529). Ajith Kumar A. also acknowledges a scholarship granted by the Universitat Rovira i Virgili.

REFERENCES