

Coupled Molecular Dynamics – Three-Dimensional Poisson Simulations of Ionic Liquid Electrospray Thrusters

IEPC-2013-453

*Presented at the 33rd International Electric Propulsion Conference,
The George Washington University, Washington, D.C., USA
October 6–10, 2013*

Arnaud Borner* and Deborah A. Levin†
Pennsylvania State University, University Park, PA 16802

Molecular dynamics (MD) simulations are performed to model an electrospray thruster for the ionic liquid (IL) EMIM–BF₄ using an effective-force coarse-grained (CG) potential. The MD simulations provide insight into the atomistic modeling of a capillary-tip-extractor system, the basic elements of an electrospray thruster. A one-dimensional electric field showed an improvement in the model when compared to the use of a constant electric field. Then, the MD software was coupled to a Poisson solver derived from a Particle-In-Cell (PIC) code. A transient three-dimensional electric field was used at each timestep, taking into account the induced electric field due to space charge repulsion. It was found that the inhomogeneous electric field as well as that of the IL space-charge improved agreement between modeling and experiment. The influence of numerical parameters such as extraction potential and applied mass flow were studied. Particular emphasis was put on the importance of parameters relative to the grid used to solve Poisson's equation, such as the grid cell size and the boundary conditions in the vicinity of the capillary tip. The boundary conditions were found to have a substantial impact on the potential and electric field.

*Graduate Student, Department of Aerospace Engineering, apb170@psu.edu

†Professor, Department of Aerospace Engineering, dalevin@engr.psu.edu

Nomenclature

d	= capillary to extractor ring distance
$\delta x, \delta y, \delta z$	= celle lengths in x, y, z directions
$\vec{E}$	= electric field
E_{TIP}	= maximum electric field in the vicinity of the capillary tip
ϵ	= permittivity of medium
ϵ_0	= permittivity of free space
$f(t)$	= random force in Langevin thermostat
$\vec{F}$	= force
$F_{Potential}(t)$	= total force acting on capillary atoms
γ	= surface tension
i, j, k	= indexes
I	= current
k_B	= Boltzmann constant
k_{sp}	= spring constant
m	= mass
$\dot{m}$	= mass flow
ω_n	= natural frequency of spring mass system
ϕ	= potential
$\phi_{i,j,k}$	= potential on mesh node (i,j,k)
q	= charge
$r(t)$	= displacement
ρ_f	= density of charges
R_c	= capillary radius
V_{start}	= starting voltage
Δt	= timestep
T	= temperature
ξ	= damping constant
Z	= direction of extrusion

I. Introduction

Despite the existence for nearly twenty-years of electrosprays in fields such as biomedical engineering, microelectromechanical systems, pharmaceutical development, food sciences, and industrial and aerospace engineering applications,^{1,2} the physics of Taylor cone formation whereby a liquid surface is caused to deform under the presence of high electric fields³ is still not completely understood. One important application of electrosprays is colloid thrusters⁴⁻⁶ which can be used to provide small thrust levels with high specific impulse for satellite station keeping. Colloid thrusters (along with liquid metal ion sources⁷ and field emission thrusters (FEEPs)) are a particular kind of electrospray. Different electrospray operation modes are possible, depending on the characteristic of the propellant such as its electric conductivity, surface tension, and dielectric tension, as well as the mass flow. It has been shown that the main operation modes exhibit electrospray structures known as dripping, microdripping, cone-jet, spindle, simple jet, or ramified jet,⁸ although the focus of our studies are primarily of the cone-jet mode. The concept of generating propulsion from a liquid flow fed to the Taylor cone has been demonstrated by the presence of charged ions and droplets which are formed from the fragmentation of the jet downstream of the cone.⁹ The cone-jet mode^{9,10} can be further characterized by being in a pure ion mode, a pure droplet mode, or a mixed ion-droplet mode. The pure ion mode^{11,12} is very attractive since it provides a higher specific impulse than most other electrospray operation modes, offering greater mission planning flexibility. It was discovered^{13,14} that one propellant capable of operating in the pure ion mode at low temperature is the ionic liquid EMIM-BF₄ which will be discussed in this work. Ionic liquids (ILs) are characterized by a low temperature melting point (often under

100 ° C). The low viscosity, low volatility and reusability of ILs are more reason that make them attractable as propellants as opposed to more traditional organic solvents.

Although fluid models have provided important insights, however, the ultimate understanding of the physics of Taylor cone extraction is dominated by chemical interactions in the presence of strong electric fields at the atomistic level. Hence molecular dynamics (MD) is the only approach that will provide the level of understanding and predictive capability required for the use of ILs as electrospray thrusters. MD simulations using all-atom potentials have been used to study the properties of ILs such as EMIM–BF₄. de Andrade *et al.*¹⁵ studied computationally EMIM–BF₄ as well as other ILs by the means of molecular mechanical and quantum *ab initio* calculations with a force field based on the AMBER methodology.¹⁶ With respect to modeling of colloidal systems for propulsion applications, Takahashi and Lozano¹⁷ studied the evaporation of solvated and non-solvated ions of EMIM–BF₄ under high electric fields by using molecular dynamics (MD) simulations with the AMBER potential. However, these approaches are too computationally expensive to be extended to the scale of electrohydrodynamic approaches such as would be needed to characterize fundamental device performance. This work uses a coarse-grained (CG) potentials for MD simulations. The use of CG potentials to model EMIM–BF₄ was first demonstrated by Daily and Micci¹⁸ who estimated the ionic velocities and electrical conductivities of EMIM–BF₄ by using MD. They compared an all-atom model to two coarse-grained (CG) models, the simple coarse-grained and effective-force coarse-grained (EFCG)^{19,20} models. In our previous work,^{21,22} we demonstrated the use of a simple CG model to generate a complete electrospray by means of MD for EMIM–BF₄. Diffusion coefficients and electrical conductivities were calculated and showed good agreement with measured values and an electric field was applied to the system and the fraction, as well as the structures, of solvated and non-solvated ions were analyzed.

A number of laboratory measurements on EMIM–BF₄ IL electrosprays have been made,^{13,14,23,24} further making it a good candidate for fundamental MD studies. Romero *et al.*¹³ investigated the currents produced by EMIM–BF₄ at room temperature for various flow rates. Ionic, droplet, and total currents were measured and it was discovered that this IL behaved differently from more classic propellants such as NaI/formamide since it could reach the pure ionic regime at ambient temperature due its characteristics, mainly its conductivity and zero vapor pressure. The high volatility of the EMIM⁺ ion was identified as the main reason why the purely ionic regime was easier to attain when EMIM–BF₄ was used compared to any other IL with similar characteristics.

Despite the significant modeling and laboratory studies a number of fundamental challenges still exist towards a complete understanding of the EMIM–BF₄, as well as ILs, in general. Our previous work²² was the first to predict the conditions for the formation of a Taylor cone at the atomistic level by simulation. The Taylor cone can be both transient^{25,26} as well as steady⁹ in nature. To conduct an MD simulation of such a laboratory system a reasonable scaling of the capillary radius and length as well as the emitter-to-extractor distance dimensions must be proposed. Finally, the MD system must be sufficiently large that a jet can be created, reach a steady state, and produce a sufficient number of ion-types to characterize the emitted jet structure and current types. Figure 1 shows a summary of the different cone-jet structures that were obtained in our previous work²² for a constant electric field, e.g. here a Taylor cone, a cone-jet structure and a multi-jet structure at high field strengths.

With respect to the nature of EMIM–BF₄ specifically, a number of additional challenges are present. One of the reasons that EMIM–BF₄ is studied so extensively is that it is known to be an IL that easily reaches the pure ionic regime at ambient conditions, but, can also transition to a mixed ion/droplet regime at higher flow rates. Furthermore, a number of IL have been found to follow the famous $I \propto Q^{1/2}$ law when operating in the droplet mode, where I and Q are the emitted current and mass flow rates, respectively.^{9,27} EMIM–BF₄, however, does not follow this trend because of its rapid transition from pure ionic to mixed regimes at relatively low flow rates. In a purely ionic regime, Romero-Sanz¹³ hypothesized that for a fixed q/m , the ion current versus mass flow trend must be linear. If we assume that only monomers are emitted, doubling the mass flow will result in a doubling of the current due to the monomers. However, we will show that for the cases studied here with EMIM–BF₄ as the IL of choice we rarely see the emission of a single ion type. Instead we see a combination of monomers, dimers and trimers in the purely ionic regime, or in an even more complicated mixed regime case, droplets and ions, with ions often being the result of a droplet breakup. Therefore, finding an analytical trend for the current versus mass flow is almost impossible since varying the mass flow means alternating between different emission regimes.

It was found^{21,22} that the constant electric field 0.5 V/nm provided the best fit for the experimental data of Romero-Sanz,¹³ although an over-estimation in the monomer current lead to an over-estimation in the

total current, as seen on Fig. 2. The higher monomer current was believed to be due to an over-estimate in the electric field away from the capillary, which led to excessive droplets and solvated ions breakups. Therefore, it was decided as a first step that the effects of a 1D variable electric field would be investigated (Sec. II). Then, a fully three-dimensional Poisson solver derived from Ref. 28 was coupled to the simulation. The influence of various parameters such as grid size, radius of the extraction ring, extraction potential and applied mass flow is presented in Sec III.

II. One-Dimensional Electric Field

II.A. Calculation and Fit

Using the field solver developed by Wang *et al.*,²⁸ Laplace's equation was solved for a domain of length 1 μm between the capillary tip and the circular extractor. A Dirichlet boundary condition (BC) was used on the surface of the capillary tip, and will be later designated as a "needle" BC. Due to the cylindrical geometry of the system around the axis from the center of the capillary to the center of the extraction ring, the electric field at any point in space is three dimensional. However, since the potential difference is applied one-dimensionally and no charged particles are involved in solving Laplace's equation, the electric field in the direction of extrusion, Z , is larger than in the two other perpendicular directions X and Y . Therefore an approximation that the electric field is only varying in one dimension and is negligible in the other two is reasonable. Figure 3(a) shows the $40 \times 40 \times 40$ mesh used and the voltage distribution obtained from the Laplace solver for the capillary at ground and the extractor ring at -10 V. Figure 3(b) shows the Z component of the electric field in the same case, as well as the axial symmetry of the field. Since most of the IL particles are present in a zone close to the tip of the capillary initially, the value of the electric field, E_z , was extracted along the line of symmetry of the system. The curved was then smoothed and fitted in 2 pieces with polynomial functions, as shown in Fig. 4. There is no fit for the data between the first two green squares because it represents a position inside the tip of the capillary, where the assumption that there is no electric field is made since the capillary is grounded. It can be seen that a maximum of 0.62 V/nm for the electric field is reached at the tip of the capillary when the extraction potential is -10V. Since Laplace's equation is linear, the one dimensional fitted electric field is directly proportional to the applied extraction potential. Therefore, the shape will be the same if the electric field is normalized by the extraction potential.

II.B. Influence of Potential and Mass Flow Rate

Initially, the applied voltage was varied between -10 and -100 V, in increments of -10 V. However, at an extraction voltage above -20 V, a very large majority of monomers, with a minority of solvated ions, and no droplets were observed. Therefore, voltages between -10 and -20 V were investigated, at a constant mass flow of 2.44×10^{-12} kg/s. Figures 5(a) and 5(b) show the currents obtained from the MD simulations, calculated at the ring 1000 Å from the capillary tip at these voltages. From comparisons of our previous work²² with the work of Romero-Sanz,¹³ we want to investigate ranges of mass flows and voltages where more dimers than monomers are observed and the droplet current is significant, but lower than ionic currents. In our previous MD modeling, in the presence of a constant electric field, we found that we were unable to predict the behavior of the electrospray at high mass flows when larger droplets are present. Therefore, since applied voltages of -13 and -15 V met the aforementioned characteristics, they were investigated in greater detail for different mass flow rates.

Figures 6(a) and 6(b) show a comparison of the experimental data from Romero-Sanz¹³ and the computed currents at extraction voltages of -13 and -15 V, respectively, when the mass flow was varied. As can be seen by comparison with Fig. 2, the obtained current values fit the experimental data much better than the computational data previously obtained when a constant electric field was used to extrude the IL.²² Figure 7 shows the monomer currents for applied voltages of -13 and -15 V, a constant electric field of 0.5 V/nm used in our previous work²² and Romero-Sanz' experimental data.¹³ An important decrease in the monomer current can be seen. Most notably, the dimer current always exceeds the monomer current, and every current seems to slightly over estimate measurements of Romero-Sanz, therefore contributing to the discrepancy in the total current.

III. Three-Dimensional Transient Electric Field

III.A. Poisson solver

A Poisson solver was developed²⁸ to simulate the plasma between the capillary tip and a planar electrode for the generic single emitter geometry shown in Fig. 8. A typical PIC solver has four modules: field solver, particle mover and two interpolation modules for weighting of particles to the field, and inverse weighting of the electric field back on to the particles. The particle mover used in this work is replaced by the MD software DL_POLY.²⁹ At each timestep, after the inter- and intra-molecular interactions are calculated by DL_POLY, the positions of all charged particles are passed to the Poisson solver. The field solver solves for the electrostatic field with space charges based on the gradient of the potential which is obtained by solving the Poisson equation,

$$\nabla \cdot \nabla \phi = -\frac{\rho_f}{\epsilon}. \quad (1)$$

The cartesian grid is single level and has uniform spacing. The solver is based on the finite difference approach in which the governing equation, Eq. 1, is discretized as follows:

$$\frac{\phi_{i+1,j,k} - 2\phi_{i,j,k} + \phi_{i-1,j,k}}{(\delta x)^2} + \frac{\phi_{i,j+1,k} - 2\phi_{i,j,k} + \phi_{i,j-1,k}}{(\delta y)^2} + \frac{\phi_{i,j,k+1} - 2\phi_{i,j,k} + \phi_{i,j,k-1}}{(\delta z)^2} = -\frac{\rho_f}{\epsilon}, \quad (2)$$

where i, j, k are indexes in x, y, z directions, and $\delta x, \delta y$ and δz are the cell lengths in x, y , and z directions respectively. The values of the coefficients of the left hand side (LHS) of Eq. 2 form a square matrix of dimension equal to the number of grid points. The unknown variables, ϕ , form the unknown vector. The linear matrix system is solved for the unknown vector in terms of the right hand side (RHS) of Eq. 2 using the generalized minimal residual method (GMRES).³⁰

Once converged values of the potential are obtained across the domain, the electrostatic field is computed for each grid point. The calculated electrostatic field is interpolated back from the grid points to the particle locations to compute the forces acting on the particles. Thus the interpolation routine is an important component of the PIC solver that significantly affects its accuracy.³¹ In this work, first order interpolation (linear weighting)³² is used to carry out charge and field interpolation. The electric field at each particle location is passed back to DL_POLY and the forces on the particles are calculated in the MD software as,

$$\vec{F} = q\vec{E}, \quad (3)$$

where q is the charge associated with a particle and $\vec{F}$, and $\vec{E}$ are the force and the field vectors, respectively. $\vec{E}$ is calculated from the potentials, ϕ , which are obtained by solving the Poisson equation (Eq. 2),

$$\vec{E} = -\vec{\nabla}\phi. \quad (4)$$

The IL particles are then moved across the domain using the forces calculated for each of the particles and the software advances to the next timestep.

III.B. Wall Modeling and Langevin Thermostat

The capillary is modeled as a one-zone wall model, in which the atoms are anchored to their lattice sites by springs.³³ The wall temperature is maintained by the Langevin equations,³⁴ allowing the wall to act like a thermal reservoir to dissipate energy transferred to the wall from the fluid³⁵ The one-zone wall model is a set of simple harmonic springs acting like a spring mass system.³⁵ The Langevin thermostat works by coupling every particle to a viscous background and a stochastic heat bath such that

$$m\ddot{r}(t) = -\xi m\dot{r}(t) + f(t) + F_{Potential}(t), \quad (5)$$

where ξ is the damping constant representing viscous damping due to fictitious thermostat particles, $F_{Potential}(t)$ is the total force acting on the capillary atoms (sum of spring force and Lennard-Jones interaction between the ionic liquid and the capillary atoms). The random force, $f(t)$, is a function of the damping force constant, ξ , is sampled from a Gaussian distribution, with zero mean value and a unit variance, **Gauss**(0,1), scaled by $\sqrt{\frac{2\xi m k_B T}{\Delta t}}$. Here, $\Delta t = 5$ fs is the timestep size, k_B is the Boltzmann constant and $T = 295$ K is the

desired temperature value. The damping constant is a function of the material properties of the system, and is obtained by

$$\xi = \frac{\pi\omega_n}{6} \quad (6)$$

$$\omega_n = \sqrt{k_{sp}/m}, \quad (7)$$

where ω_n is the natural frequency of the spring mass system and the k_{sp} is the spring constant, which is 46.8 N/m for Pt.³⁶ The Langevin thermostat ensures that the temperature of the ionic liquid in the capillary remains at 295 K even when a mass flow is applied. Figure 9 shows a comparison of the IL temperature when a mass flow of 4.88×10^{-12} kg/s was applied, with no effect from an applied potential. It can be seen that the temperature increases rapidly when no thermostat is used, while it remains relatively close to the starting value when the Langevin thermostat is used.

III.C. Influence of Grid Size

The influence of the grid size on the electric field and extrusion physics for an extraction potential of -40 V and a mass flow rate of 4.88×10^{-12} kg/s was subsequently studied. Three grids, a coarse, medium, and fine grid, each related by refinement factor of two, were compared. The coarse grid contained $10 \times 10 \times 20$ cells, while the fine grid contained $40 \times 40 \times 80$ cells. The dimension of the domain remained unchanged: $500 \times 500 \times 100$ Å. A snapshot in time of a system extruding from a Taylor cone was studied, and the values of the potential at the different mesh nodes were compared. Potentials were extracted at each mesh node location on the coarsest grid. The results are summarized in Table 1. The variations in the potential are measured in percentages: the absolute value of the potential change is normalized by the value of the potential on the coarsest grid, when Laplace's equation is solved, so that no effect of the space charge are present in the normalization. It can be seen that the difference in the potential between the medium and coarse grids is only 2.5 %. Since the computational time increase from a medium to a fine grid is tremendous, the medium grid was picked for further computations in this paper.

III.D. Influence of Boundary Conditions

Two sets of BCs for the computational domain were investigated. The first one, labeled as “plate” BC and shown on Fig. 10(a), consists of grounding ($V = 0$ V) the entire surface around the capillary (Dirichlet BC). The second one, labeled as “needle” BC and shown on Fig. 10(b), consists of grounding the surface of the capillary (a circle of radius 56 Å) with a Dirichlet BC, and using a Neumann BC ($E_Z = 0$) on the area around the capillary on that surface. In both cases, the other boundary conditions remain unchanged (Neumann BC on all other faces, except on the extraction ring that has a radius of 300 Å and a thickness of 90 Å, where a Dirichlet BC is applied with a potential of -40 V). Figures 11(a) and 11(b), and 12(a) and 12(b) show a comparison of the voltages and electric fields, respectively, in the direction of extrusion, for both BC types, when Laplace's and Poisson's equations are solved. It can be seen that the “plate” BC generates equipotential stripes when Laplace's equation is solved, whereas the “needle” BC generates a very high potential gradient in the vicinity of the capillary tip. In other parts of the domain, the potential is much more constant when the “needle” BC is used. Therefore, the electric field in the Z direction is very high in the vicinity of the capillary tip for the “needle” BC, compared to the field for the “plate” BC that is very constant over the domain except for a drop close to the extraction ring. The electric field obtained when Laplace's equation was solved with the “needle” BC is very similar to the one obtained in the case of the 1D model, since a “needle” BC was also used in that case. Figure 13 shows a plot of the electric field in the direction of extrusion for both BCs, when Laplace's and Poisson's equations are solved. Taking into account the space charge (*i.e.* between the Laplace and Poisson solutions) tends to decrease the electric field in the Taylor cone region when compared to the solution of Laplace's equation. That is because an accumulation of space charge reduces the field at the liquid surface. The maximum value reached by the normal electric field in the vicinity of the capillary tip is in much better agreement with the following equation derived by Martinez-Sanchez¹⁰

$$E_{TIP} = \frac{-2\phi/R_c}{\ln\left(\frac{4d}{R_c}\right)}, \quad (8)$$

where $d = 0.1 \mu\text{m}$ is the distance between the capillary and the extractor ring and $R_c = 56 \text{ \AA}$ is the capillary radius. For an applied potential of ϕ of -40 V, Eq. 8 predicts a maximum electric field of $1.67\text{E-}9 \text{ V/nm}$, which is very close to the value obtained when solving Poisson's equation for the "needle" BC, as seen on Fig. 13. Additionally, Carretero *et al.*³⁷⁻³⁹ computed, among other quantities, normal electric fields for a model of a colloidal jet, for various modified solutions of formamide. The shape of our normal electric field computed using the "needle" BC was observed to be much closer to the one obtained by Carretero *et al.*. Currents obtained for both types of BCs will be computed.

III.E. Influence of Mass Flow

The effect of the mass flow on the behavior of the cone-jet as well as the currents has been studied previously²² but it was hypothesized that the induced electric field should have an effect on the stability of the jet. In previous work, a good agreement with experiments was often observed at the lowest mass flows, but a sharp increase in the monomer current at high mass flow rates were observed during the transient part of the extrusion, leading to an overestimation of the total current.

An equation for the starting voltage, derived by Martinez-Sanchez,¹⁰ is

$$V_{start} = \sqrt{\frac{\gamma R_c}{\epsilon_0}} \ln \left(\frac{4d}{R_c} \right), \quad (9)$$

where $\gamma = 45.3 \text{ mN/m}$ is the surface tension of EMIM-BF₄ and ϵ_0 is the permittivity of free space.

Using this equation we obtain a value for our computational model of $V_{start} = 23 \text{ V}$. In Fig. 14(a), a comparison between the current computed at -40 V for the "plate" BC and the values measured by Romero-Sanz¹³ can be observed. It can be seen that the model agrees with the trends from Romero-Sanz, with the computational values underestimating the experimental values. The authors would like to point out that the starting voltage or distance between capillary and extractor ring are unknown for Romero-Sanz's experiments, making it hard to assess whether the ratio of applied voltage to starting voltage was the same for the experiments and our model. Therefore, in order to look at the trends at different currents, Fig. 14(b) represents the different currents normalized by the total current. It can be observed that the different ratios are very similar in the model and the experiments, the only small discrepancy arising from slightly different trends for the monomers and dimers when the mass flow increases. When comparing these results with the ones obtained in Ref. 22 for a constant electric field of 0.5 V/nm , it can be seen that all currents values were reduced, and that the ratio of monomer current to total current was strongly reduced, which seems to indicate our new model captures the local jet behavior better, and has reduced the overestimated droplet breakup that leads to the creation of too many monomers.

III.F. Influence of Extraction Potential

Figure 15 shows the trend of the calculated currents for the "plate" BC as a function of the applied extraction potential, for a fixed mass flow of $4.88 \times 10^{-12} \text{ kg/s}$. From experiments and previous calculations, we expected to see a progressive change from a mixed regime to a pure ion regime as the extraction potential increases, since a higher potential would generate higher electric fields that will tend to increase repulsive forces between ions and yield less stable solvated ions and droplets. As the potential increased from the starting value -25 to -40 V, the total current increased almost ten times. It is expected that a further increase in the extraction potential would lead to an almost complete breakup of the droplet current, first, then trimer current, and an additional increase in the monomer current. The currents for the "needle" BC are still being investigated, but are expected to be slightly higher than the ones for the "plate" BC.

IV. Conclusion

A previously constant electric field was initially replaced by a one-dimensional electric field generated by a simulation of a multi-level PIC code solving Laplace's equation prior to performing MD simulations. Modifying the modeling of the electric field from a uniform to one dimensional led to a significant improvement in the agreement with experimental results by operating a reduction in the monomer and total currents, due to larger droplets breakup. When a full 3-D model for the electric field was used, with Poisson's equation solved at every time step and the induced field due to charged ions was taken into account, it was found

that the contribution of the induced field was important. Emphasis was put on the importance of numerical parameters relative to the grid used to solve Laplace's and Poisson's equations. The grid cell size was chosen as a compromise between convergence and acceptable computational time. The boundary conditions, especially on the tip of the capillary, were investigated in detail. The "plate" and "needle" BCs were defined and the values taken by the potential and electric fields, when both Laplace's and Poisson's equation were solved, were computed and compared. It was found that the "needle" BC generated very large potential gradients in the vicinity of the capillary tip, producing much higher electric fields. The shape and maximum value of the normal electric field varied accordingly to values computed by Martinez-Sanchez's equation¹⁰ and numerical values computed by Carretero *et al.*^{37–39} Currents were computed here for the "plate" BC, and the "needle" BC will be used in later work. When the mass flow increased, the ratio of ions and droplet currents normalized by the total current followed very closely the experimental trend from Romero-Sanz.¹³ Finally, the extraction potential was found to affect the extrusion regime, as an increase in the potential generated higher monomer and total currents, but lower trimer and droplet currents, since the electric field increases proportionally to the extraction potential.

V. Acknowledgement

The research being performed at the Pennsylvania State University is supported by the Air Force Office of Scientific Research through the MACEEP Grant No.FA9550-09-1-0695, whose support is gratefully acknowledged. The authors are grateful to John Daily for providing the DL_POLY²⁹ tabulated potential input file.

References

- ¹Chiarot, P., Sullivan, P., and Mrad, R. B., *J. Microelectromech. Sys.*, Vol. 20, 2011, pp. 12411249.
- ²Luedtke, W., Landman, U., Chiu, Y., Levandier, D., Dressler, R., Sok, S., and Gordon, M., "Nanojets, Electrospray, and Ion Field Evaporation: Molecular Dynamics Simulations and Laboratory Experiments," *Journal of Physical Chemistry A*, Vol. 112, 2008.
- ³Taylor, G. I., *Proc. R. Soc. London. Ser. A*, Vol. 280, No. 1382, 1964, pp. 383–397.
- ⁴Krohn, V., *Liquid Metal Droplets for Heavy Particle Propulsion*, Vol. 5, A. C. Press, New York and London, 1961.
- ⁵Krohn, V., "Glycerol Droplets for Electrostatic Propulsion," *ARS Electric Propulsion Conf., Berkeley, CA*, 1962.
- ⁶Mueller, J., "Thruster options for microspacecraft: a review and evaluation of state-of-the-art and emerging technologies," *Progress in Astronautics and Aeronautics*, Vol. 187, 2000, pp. 45–138.
- ⁷Prewett, P. D. and Mair, G. L. R., "Focused Ion Beams from Liquid Metal Ion Sources," *Surface and Interface Analysis*, Vol. 18, No. 5, 1992, pp. 377–377.
- ⁸Cloupeau, M. and Prunet-Foch, B., "Electrostatic spraying of liquids: Main functioning modes," *Journal of Electrostatics*, Vol. 25, No. 2, 1990, pp. 165 – 184.
- ⁹De La Mora, J. F. and Loscertales, I. G., "The current emitted by highly conducting Taylor cones," *Journal of Fluid Mechanics*, Vol. 260, No. -1, 1994, pp. 155–184.
- ¹⁰Martinez-Sanchez, M., "Lecture 23-25: Colloidal Engines. Appendix," 2004.
- ¹¹Gamero-Castano, M. and Hruby, V., "Electrospray as a Source of Nanoparticles for Efficient Colloid Thrusters," *Journal of Propulsion and Power*, Vol. 17, No. 5, 2001, pp. 977–987.
- ¹²Gamero-Castano, M., "Electric-Field-Induced Ion Evaporation from Dielectric Liquid," *Phys. Rev. Lett.*, Vol. 89, 2002.
- ¹³Romero-Sanz, I., Bocanegra, R., Fernandez de la Mora, J., and Gamero-Castano, M., "Source of heavy molecular ions based on Taylor cones of ionic liquids operating in the pure ion evaporation regime," *Journal of Applied Physics*, Vol. 94, No. 5, sep 2003, pp. 3599 –3605.
- ¹⁴Chiu, Y., Austin, B., Dressler, R., Levandier, D., Murray, P., Lozano, P., Katz, I., de la Mora, J., and Sanchez, M., "Mass Spectrometric Analysis of Colloid Thruster Ion Emission from Selected Propellants," *Journal of Propulsion and Power*, Vol. 21, No. 3, 2005, pp. 416–423.
- ¹⁵de Andrade, J., Bes, E. S., and Stassen, H., "Computational Study of Room Temperature Molten Salts Composed by 1-Alkyl-3-methylimidazolium Cations Force-Field Proposal and Validation," *The Journal of Physical Chemistry B*, Vol. 106, No. 51, 2002, pp. 13344–13351.
- ¹⁶Cornell, W. D., Cieplak, P., Bayly, C. I., Gould, I. R., Merz, K. M., Ferguson, D. M., Spellmeyer, D. C., Fox, T., Caldwell, J. W., and Kollman, P. A., "A Second Generation Force Field for the Simulation of Proteins, Nucleic Acids, and Organic Molecules," *Journal of the American Chemical Society*, Vol. 117, No. 19, 1995, pp. 5179–5197.
- ¹⁷Takahashi, N. and Lozano, P. C., "Computational Investigation of Molecular Ion Evaporation in Electrospray Thrusters," *44th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, Hartford, CT, July 21-23*, Vol. AIAA-2008-4533, 2008.
- ¹⁸Daily, J. W. and Micci, M. M., "Ionic velocities in an ionic liquid under high electric fields using all-atom and coarse-grained force field molecular dynamics," *The Journal of Chemical Physics*, Vol. 131, No. 9, 2009.

- ¹⁹Wang, Y., Izvekov, S., Yan, T., and Voth, G. A., “Multiscale Coarse-Graining of Ionic Liquids,” *The Journal of Physical Chemistry B*, Vol. 110, No. 8, 2006, pp. 3564–3575.
- ²⁰Wang, Y., Noid, W. G., Liu, P., and Voth, G. A., “Effective force coarse-graining,” *Phys. Chem. Chem. Phys.*, Vol. 11, 2009, pp. 2002–2015.
- ²¹Borner, A., Li, Z., and Levin, D., “Modeling of an ionic liquid electrospray using molecular dynamics with constraints,” *The Journal of Chemical Physics*, Vol. 136, 2012, pp. 124507.
- ²²Borner, A., Li, Z., and Levin, D., “Prediction of Fundamental Properties of Ionic Liquid Electrospray Thrusters using Molecular Dynamics,” *The Journal of Physical Chemistry B*, Vol. 117, No. 22, 2013, pp. 6768–6781.
- ²³Garoz, D., Bueno, C., Larriba, C., Castro, S., Romero-Sanz, I., Fernandez de La Mora, J., Yoshida, Y., and Saito, G., “Taylor cones of ionic liquids from capillary tubes as sources of pure ions: The role of surface tension and electrical conductivity,” *Journal of Applied Physics*, Vol. 102, No. 6, 2007, pp. 064913–064913.
- ²⁴Terhune, K. and King, L., “Ion and Droplet Mass Measurements of an Electrospray Emitter using an ExB Filter,” *32nd International Electric Propulsion Conference, 11-15 September 2011, Wiesbaden Germany*, Vol. IEPC-2011-299, 2011.
- ²⁵de la Mora, J. F., “On the Outcome of the Coulombic Fission of a Charged Isolated Drop,” *Journal of Colloid and Interface Science*, Vol. 178, No. 1, 1996, pp. 209 – 218.
- ²⁶Grimm, R. L. and Beauchamp, J. L., “Dynamics of Field-Induced Droplet Ionization: Time-Resolved Studies of Distortion, Jetting, and Progeny Formation from Charged and Neutral Methanol Droplets Exposed to Strong Electric Fields,” *The Journal of Physical Chemistry B*, Vol. 109, No. 16, 2005, pp. 8244–8250, PMID: 16851963.
- ²⁷Gamero-Castano, M. and de la Mora, J. F., “Direct measurement of ion evaporation kinetics from electrified liquid surfaces,” *The Journal of Chemical Physics*, Vol. 113, No. 2, 2000, pp. 815–832.
- ²⁸Wang, P., Borner, A., Korkut, B., Li, Z., and Levin, D., “Simulations of Electrospray in a Colloid Thruster with High Resolution Particle-in-Cell Method,” *submitted to the Journal of Propulsion and Power*, 2013.
- ²⁹Todorov, I., Smith, W., Trachenko, K., and Dove, M., Vol. 16, 2006, pp. 1911–1918.
- ³⁰Saad, Y. and Schultz, M. H., “GMRES: a generalized minimal residual algorithm for solving nonsymmetric linear systems,” *SIAM J. Sci. Stat. Comput.*, Vol. 7, No. 3, July 1986, pp. 856–869.
- ³¹Serikov, V. V., Kawamoto, S., and Nanbu, K., “Particle-in-cell plus direct simulation Monte Carlo (PIC-DSMC) approach for self-consistent plasma-gas simulations,” *Plasma Science, IEEE Transactions on*, Vol. 27, No. 5, 1999, pp. 1389–1398.
- ³²Birdsall, C. and Langdon, A., *Plasma Physics via Computer Simulations*, IOP Publishing Ltd., 1991.
- ³³Fan, X.-J., Phan-Thien, N., Yong, N. T., and Diao, X., “Molecular dynamics simulation of a liquid in a complex nano channel flow,” *Physics of Fluids*, Vol. 14, No. 3, 2002, pp. 1146–1153.
- ³⁴Adelman, S. and Doll, J., “Generalized Langevin equation approach for atom/solid-surface scattering: General formulation for classical scattering off harmonic solids,” *The Journal of Chemical Physics*, Vol. 64, 1976, pp. 2375.
- ³⁵Branam, R. D. and Micci, M. M., “Comparison of Wall Models for the Molecular Dynamics Simulation of Microflows,” *Nanoscale and Microscale Thermophysical Engineering*, Vol. 13, No. 1, 2009, pp. 1–12.
- ³⁶Kim, D. Y. and Micci, M. M., “Molecular Dynamics Simulations of a Liquid Gallium Electrospray Thruster,” *Journal of Propulsion and Power*, 2013, pp. 1–7.
- ³⁷Carretero, J., Higuera, F., and Martinez-Sanchez, M., “Modeling Developments on Colloid Thrusters,” *International Electric Propulsion Conference, Toulouse (Fr)*, 2003.
- ³⁸Carretero, J., Lozano, P., and Martinez-Sanchez, M., “Numerical Simulation of Taylor Cone-Jets and colloid thruster plumes,” *4th International Spacecraft Propulsion Conference*, Vol. 555, 2004, p. 106.
- ³⁹Carretero Benignos, J. A., *Numerical simulation of a single emitter colloid thruster in pure droplet cone-jet mode*, Ph.D. thesis, Massachusetts Institute of Technology, 2005.

Table 1. Percentage change in the potential at mesh nodes for three different grids. Coarse, medium and fine grids have respectively $10 \times 10 \times 20$, $20 \times 20 \times 40$ and $40 \times 40 \times 80$ cells. The potential difference was normalized by the value of the potential at that grid node in the case of the coarsest grid, when Laplace’s equation was solved.

Grid comparison	Potential change (%)	E_Z change (%)
Coarse/Medium	6.8	8.4
Medium/Fine	2.5	3.1

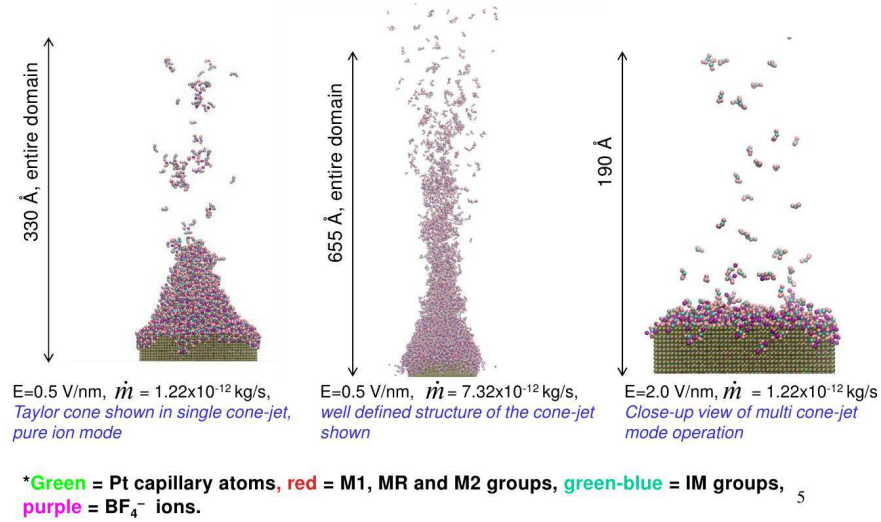


Figure 1. Summary of the different cone-jet structures obtained in our previous work²² for a constant electric field.

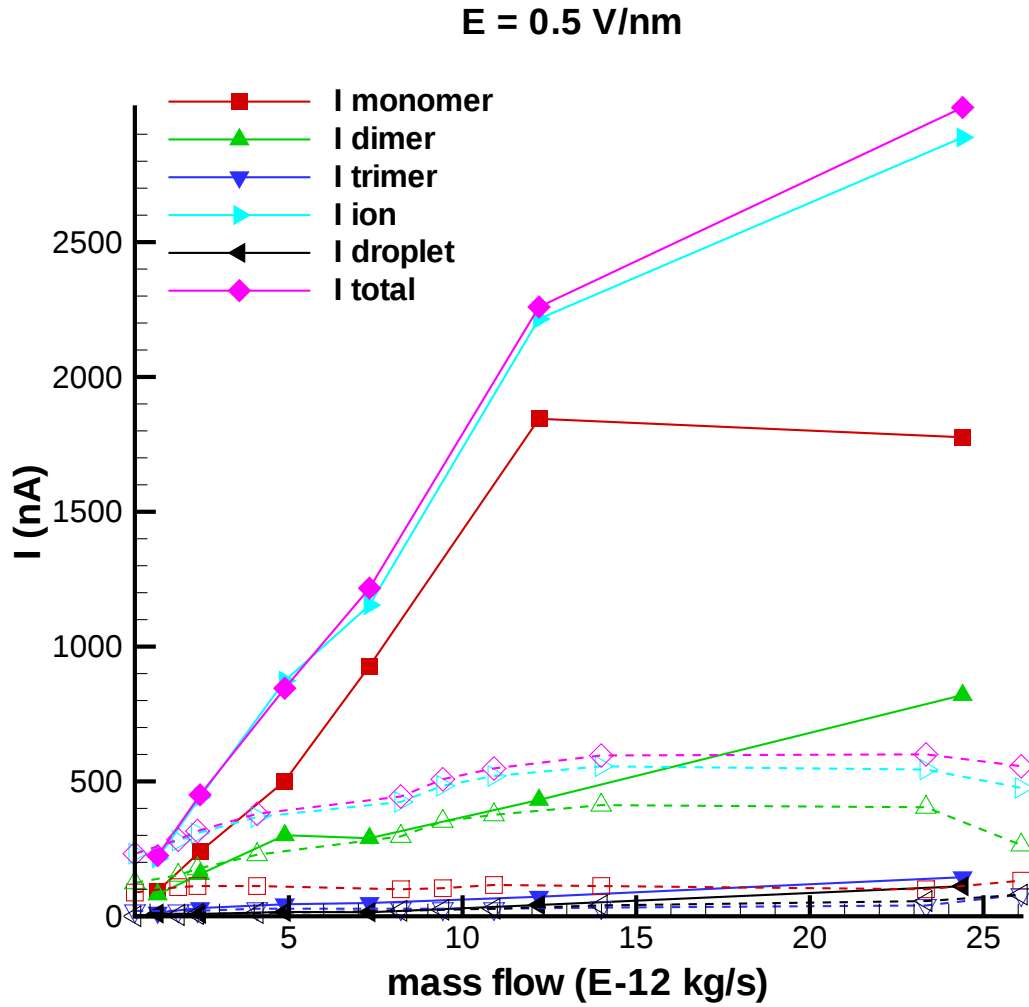


Figure 2. Currents as a function of the mass flow rate for the EFCG potential model and applied electric field of 0.5 V/nm. Solid lines represent the calculated currents while dashed lines represents the measured current values from Romero-Sanz *et al.*¹³

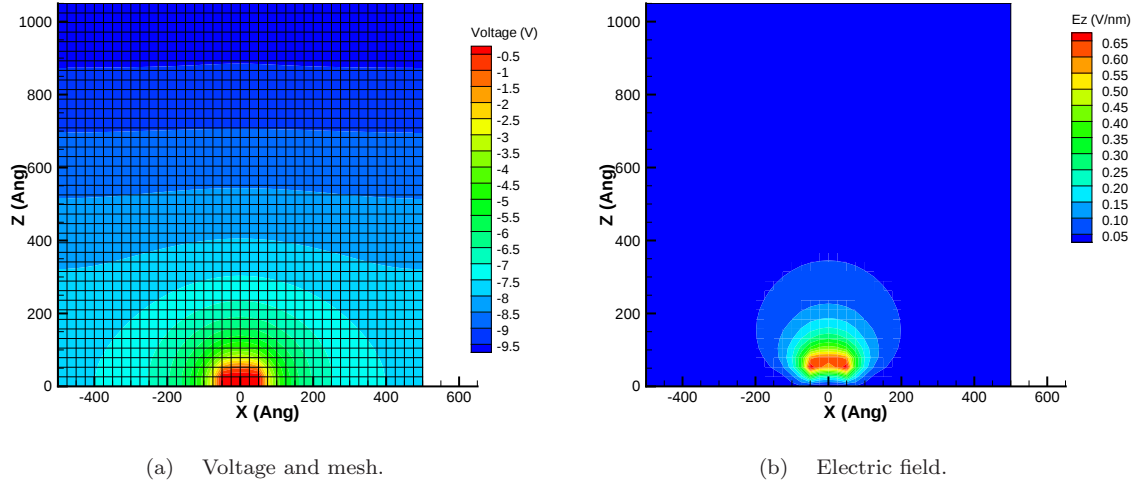


Figure 3. Mesh, voltage and electric field in the direction of extrusion, obtained from the multi-level PIC solver,²⁸ for an extraction voltage of -10 V.

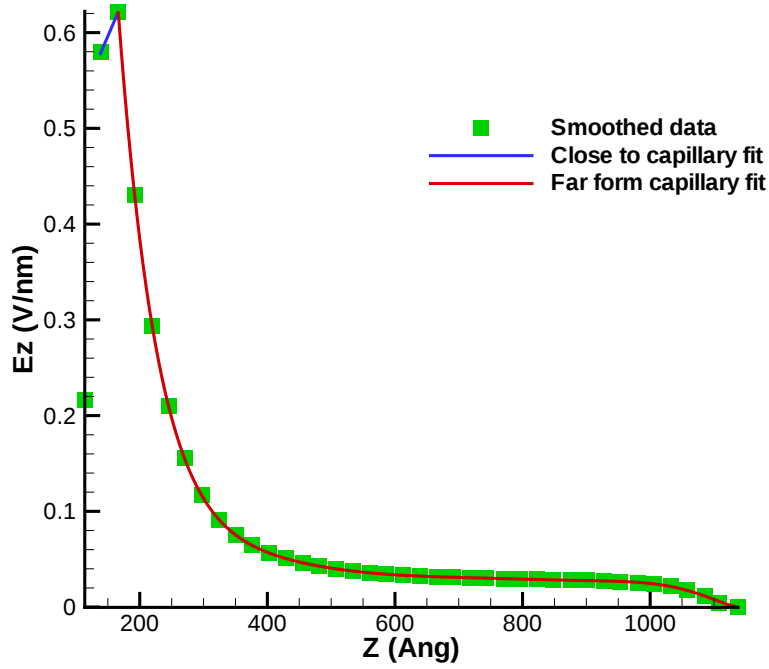
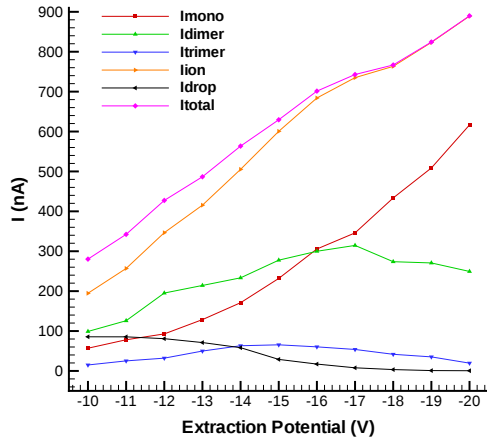
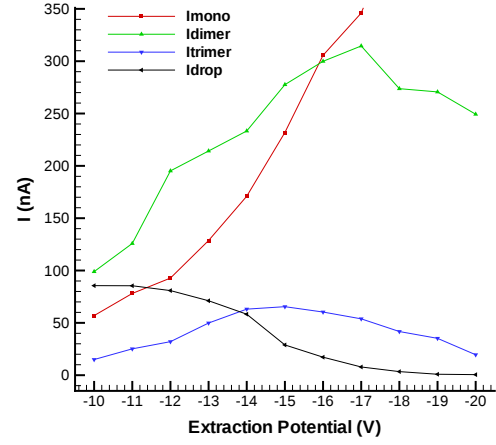


Figure 4. 1D smoothed and fitted electric field in the direction of extrusion.

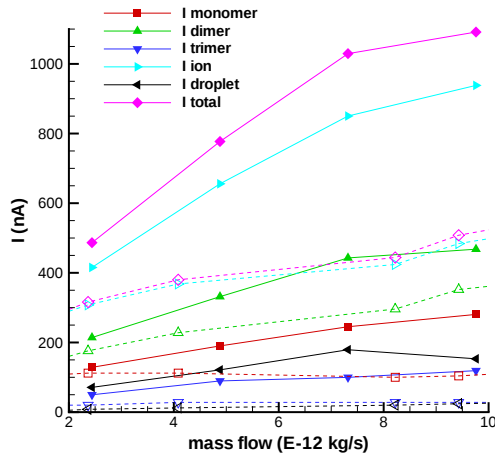


(a) All currents.

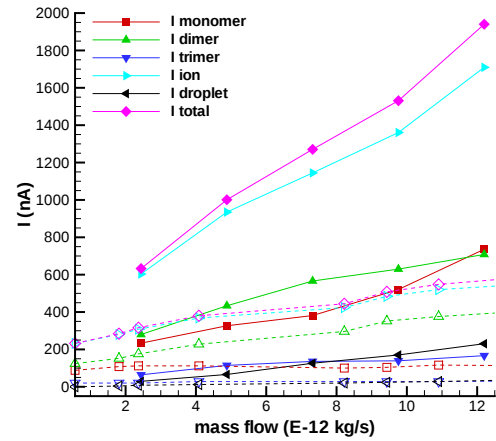


(b) Monomer, dimer, trimer and droplet current.

Figure 5. Currents as a function of the extraction potential at a mass flow of 2.44×10^{-12} kg/s.



(a) -13 V extraction potential.



(b) -15 V extraction potential.

Figure 6. Currents as a function of the mass flow rate. Solid lines represent the calculated currents while dashed lines represents the measured current values from Romero-Sanz *et al.*¹³

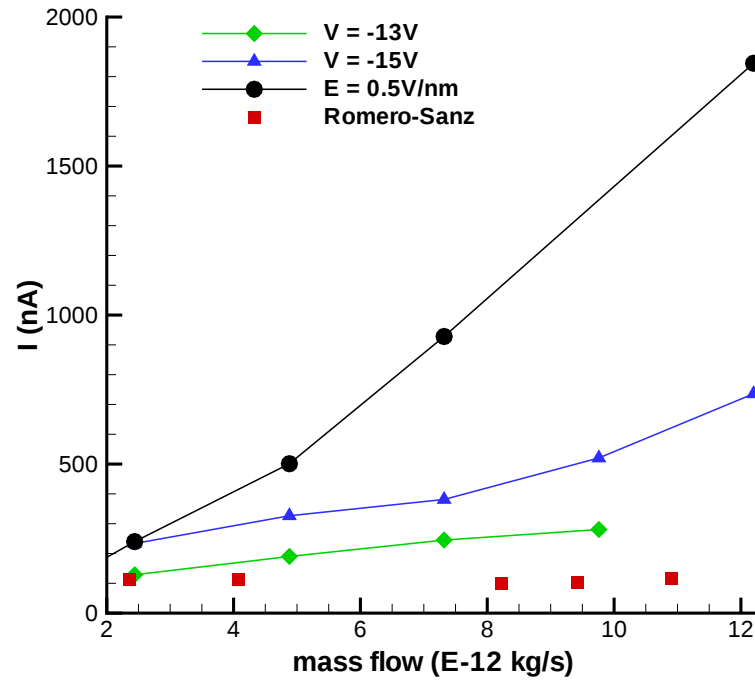


Figure 7. Comparison of the monomer currents for extraction potentials of -13 and -15 V, a constant electric field of 0.5 V/nm^{22} and the experimental data from Romero-Sanz.¹³

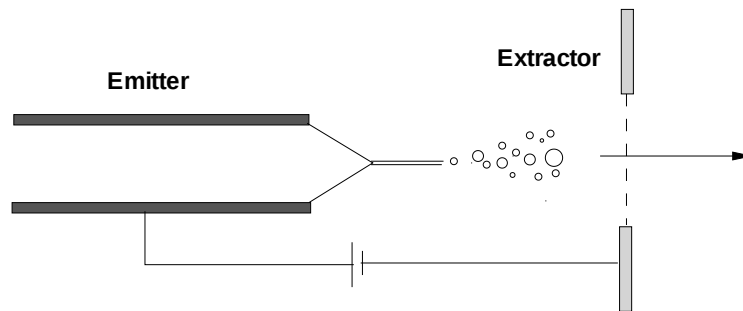


Figure 8. Single emitter colloid thruster.

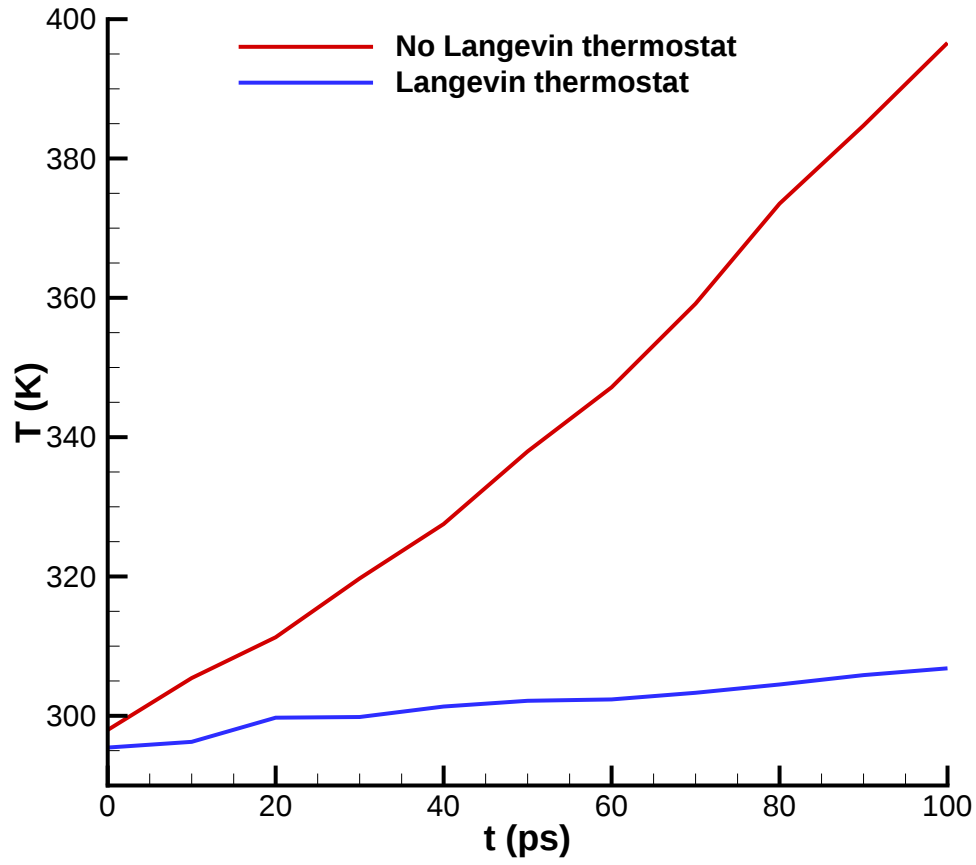


Figure 9. Comparison of the temperature of the ionic liquid with and without the application of a Langevin thermostat on a the capillary atoms. The applied mass flow is 4.88×10^{-12} kg/s.

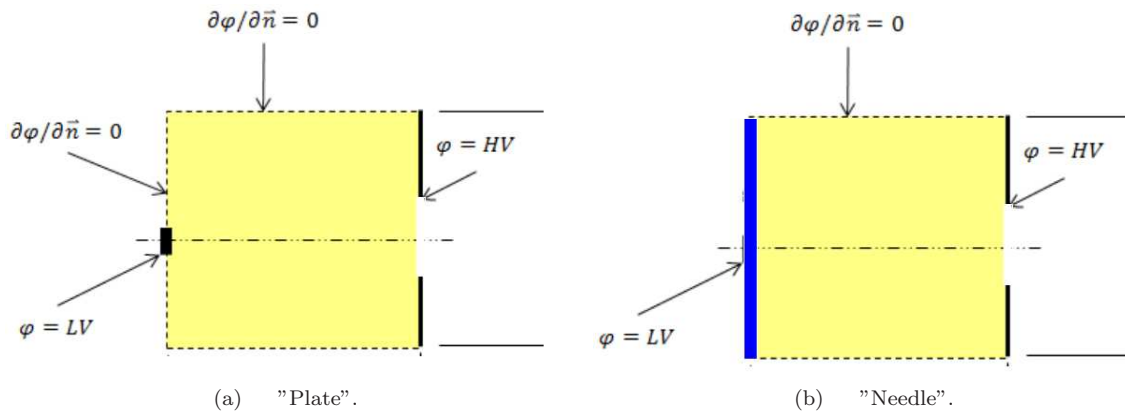


Figure 10. Boundary conditions for the computational domain.

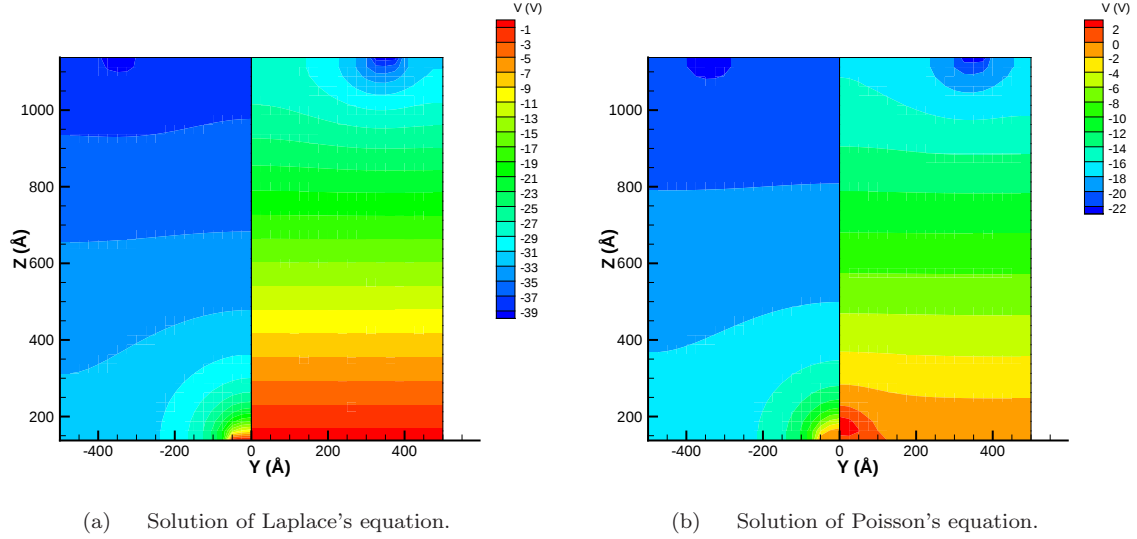


Figure 11. Voltages in a cross-section of the computational domain ($X=0$ Å) for an applied potential of -40 V at the extraction ring, for the “needle” (left) and “plate” (right) BCs.

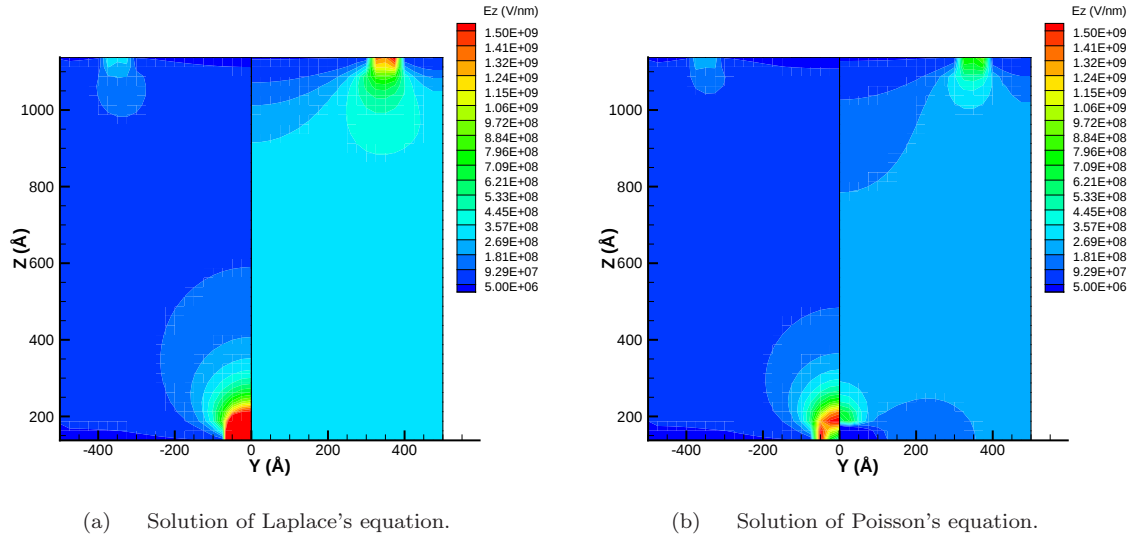


Figure 12. Electric fields in the direction of extrusion, in a cross-section of the computational domain ($X=0$ Å) for an applied potential of -40 V at the extraction ring, for the “needle” (left) and “plate” (right) BCs.

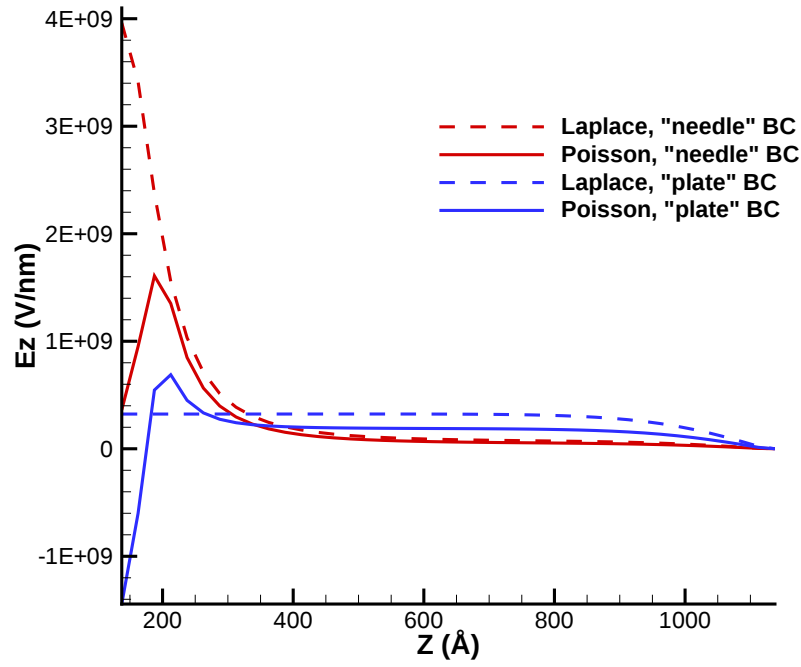


Figure 13. Electric field in the direction of extrusion for $X=Y=0$ Å, when Laplace's and Poisson's equations are solved, for both types of BCs.

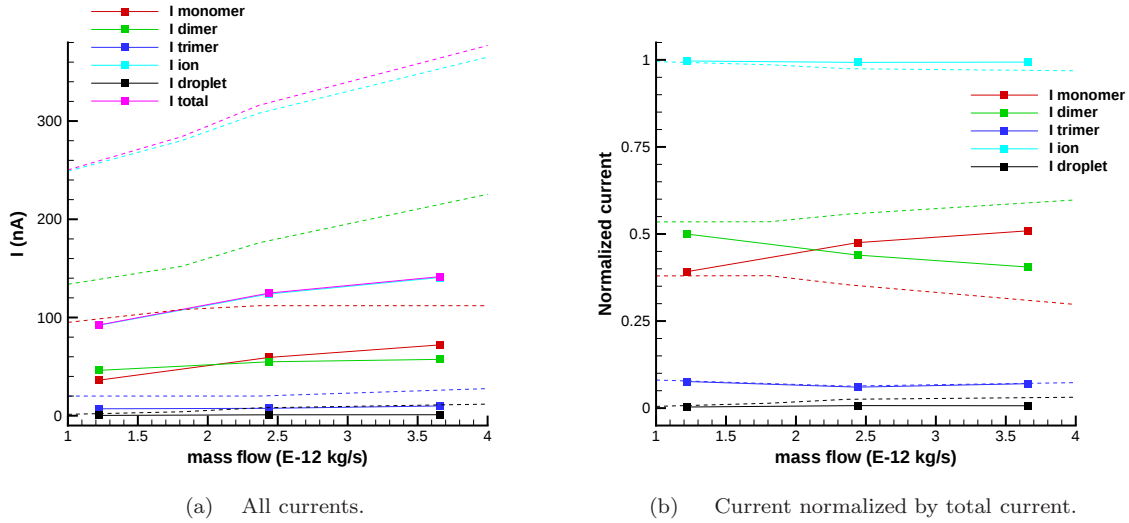


Figure 14. Currents as a function of the mass flow rate for an applied voltage of -40 V and the "plate" BC. Solid lines represent the calculated currents while dashed lines represents the measured current values from Romero-Sanz *et al.*¹³

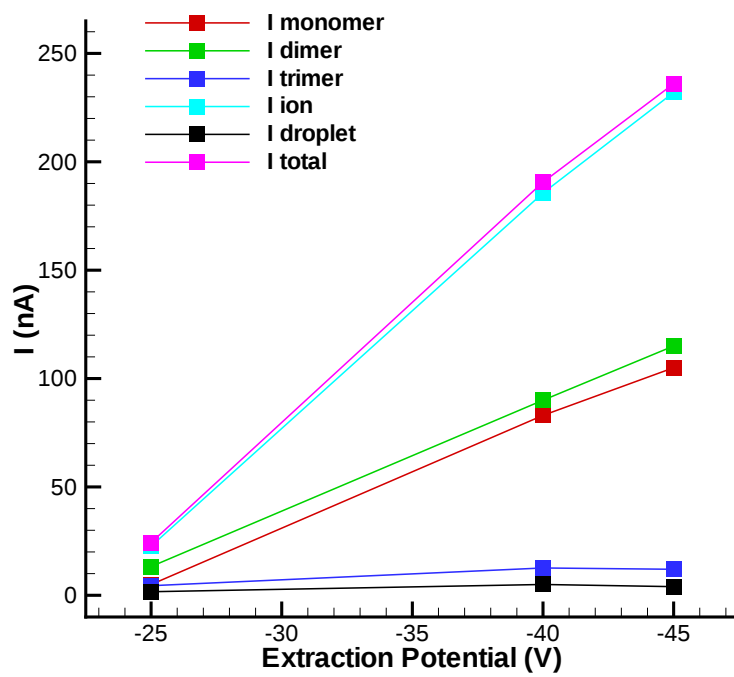


Figure 15. Currents as a function of the extraction potential for a mass flow rate of 4.88×10^{-12} kg/s for the “plate” BC.