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Molecular Dynamics Modeling of the Forces on [EMIM][BF_4] Ion Emissions and Emission Rates Due to Applied Electric Fields

Tanapat Bhakyapaibul[1], Deborah Levin[2], and Huck Beng Chew[3]
University of Illinois Urbana-Champaign, Urbana, IL, 61801, USA

Ionic liquids are stable propellants that are candidates for use with electrospray propulsion systems. Ionic liquids such as $[EMIM][BF_4]$ can be ionized by electric fields to produce emissions through various mechanisms including fragmentation. Processes like fragmentation can lead to reduced efficiency or erosion and need to be modeled at high-fidelity to develop a relationship between operating parameters such as the strength of the applied electric field and the resulting plume composition. By introducing a nanopore that allows us to maintain a curved liquid-vacuum interface, we are able to replicate the meniscus that forms at the tip of an electrospray emitter where ion emissions are produced when the applied electric field is able to overcome the surface tension of the liquid. Using ensembles of molecular dynamics simulations, it is possible to quantify the emissions produced by applying uniform electric fields of 1, 2, 4, or 6 V/nm for over 2 ns. These simulations reveal that the number of emissions and cumulative charge increase with the applied electric field. As the magnitude of the electric field increases from values of 1 or 2 V/nm to 4 or 6 V/nm, the predominant emission mechanism changes from heavier species such as dimers to lighter monomers. This atomistic model shows that as the electric field increases, it becomes easier to overcome the surface tension forces on the oscillating chains of ions that emerge at the liquid-vacuum interface to produce ion emissions. Lighter monomers can be cleaved from these chains more easily with stronger applied electric fields leading to fewer dimer and trimer emissions overall. The emissions counts and cumulative charge profiles computed from these simulations reveal that by controlling the applied electric field, it is possible to bias the ion emissions toward fewer dimer or trimer emissions. This is crucial to preventing the emission of heavier ion species that may fragment to create charged products that move at reduced velocities or neutral $[EMIM][BF_4]$ that cannot be accelerated further by the electric field.

I. Introduction

Electrosprays, a form of electric propulsion, utilize strong electric fields to produce thrust from propellants through ionization. These systems offer a method to precisely control small satellites and are also used in various manufacturing processes such as microchip fabrication. In electrospray devices, a propellant is fed through a capillary emitter. Ionic liquids like $[EMIM][BF_4]$ are easily-stored salt propellants comprised of cation-anion pairs with a net neutral charge that can be used to produce thrust when ionized. Due to the surface tension of the liquid, a meniscus forms at the emitter tip as the propellant is extruded through a capillary. In a typical electrospray setup, an extractor with an aperture is biased to a desired potential and placed downstream of the grounded capillary emitter [1]. The potential difference between the emitter and extractor produces an electric field that ionizes and accelerates the extruded propellant. When the electric field force overcomes the surface tension of the ionic liquid, the meniscus sharpens and may even transition to a Taylor Cone. At this point, various ion species are emitted. System parameters such as the applied electric field or mass flow rate are essential to controlling the thrust output of these devices and their efficiency.

A potential source of inefficiencies in electrospray devices is through fragmentation, a process where heavier ionic liquid species such as $[EMIM]_2[BF_4]$ dimers decompose to produce a secondary $[EMIM]$ cation and a neutral pair [1] [2]. These neutral pairs have no net charge and cannot be accelerated further by the applied electric field while the secondary cation may not be accelerated to its full potential. As a result these secondary emissions may drift off-axis or contribute to thrust at reduced speeds. The neutral pairs may collide with and erode the device itself, reducing

[1]Graduate Research Assistant, Department of Aerospace Engineering, tanapat2@illinois.edu
[2]Professor, Department of Aerospace Engineering, and AIAA Fellow, deblevin@illinois.edu
[3]Associate Professor, Department of Aerospace Engineering, hbchew@illinois.edu

the lifetime of these systems [2]. The secondary monomer emissions may proceed slower than primary ones thereby reducing the efficiency of the electrospray.

Accurately modeling electrosprays at the atomic scale and beyond is important to understanding the optimal operating conditions for these devices and addressing the identified sources of inefficiency. The aim of the molecular dynamics modeling is to develop a correlation between the applied electric field with the generated emissions and plume composition. In previous studies involving atomistic, molecular dynamics simulations conducted with Sandia National Laboratories' Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), it was observed that over time, even under the influence of a strong electric field force, that the emissions at the molecular dynamics scale stopped [3] [4] [5]. In their study of surface tension in molecular dynamics simulations, Liu and Cao found that when an excess of liquid enters the meniscus, it may burst and result in an unstable geometry [6]. When this occurs, the surface tension is unable to maintain the conical meniscus from which emissions are drawn and emissions terminate.

In order to obtain the most accurate emission rates, it is important to identify the emission mechanisms that are present at the molecular scale to understand the effects of varied operating conditions on the emissions generated. The number of emissions and cumulative charge profiles produced directly and through processes such as fragmentation are obtained via molecular dynamics simulations with the aim of determining how the applied electric field strength affects the number and species of the resulting emissions. This will be crucial to improving the effectiveness of electrospray devices while also providing data for informing future models at larger time and length scales such as particle-in-cell simulations that seek to understand the influence of the operating conditions on the final plume properties and composition.

II. Methodology

The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) program is used to perform the molecular dynamics simulations. Molecular dynamics simulations typically involve representing all individual atoms or groups of atoms that comprise a system [3]. The interactions between an atom and its neighbors is computed using pre-calibrated potential fields. A modified version of the all-atom OPLS-2009 potential field is applied to model the inter- and intramolecular interactions among all the atoms that make up the system [7] [8].

The 127 x 127 x 320 Å simulation domain considered is shown in Fig. 1 and was chosen to accommodate a nanopore, a piston, and ample room for the emitted ions to travel. The lateral dimensions of the simulation domain are periodic while the Z-dimension is fixed to allow emissions to exit the system [5] [4]. Exactly 4,000 $[EMIM][BF_4]$ molecules are placed in the domain between a piston composed of non-interacting platinum and a 64-Å diameter nanopore [5]. This piston acts as a container for the liquid and is moved at a velocity of 2 m/s to replicate the mass flow rates seen in experiments such as those conducted by Romero-Sanz et al. in 2003 [10]. The liquid is extruded through the nanopore that was added based on the molecular dynamics work of Liu and Cao to induce the formation of an ionic liquid meniscus and study its surface tension [6]. This setup represents the very tip of an electrospray where liquid fed from a capillary exits through an opening and forms into a conical meniscus due to the surface tension of the ionic liquid. At the molecular dynamics scale, it is important to include this nanopore to replicate the tip region of the electrospray emitter where the electric field is essentially uniform.

The bulk ionic liquid is equilibrated to 425 K by applying a macrocanonical, NVT ensemble with a Nosé -Hoover thermostat for 50 ps. Equilibration at this elevated temperature is done to form an appropriate liquid-vacuum interface that is able to replicate the expected surface tension of $[EMIM][BF_4]$ in agreement with literature [11]. After this step is completed, the thermostat is applied exclusively to a 20 Å layer of the bulk ionic liquid to maintain the system temperature and prevent system collapse due to the liquid boiling. A microcanonical, NVE ensemble is then implemented over the rest of the ionic liquid and an electric field is applied to all atoms above the nanopore for 2 ns, reflecting the uniform field that develops around the capillary, which has a nominal potential of 0 V, due to an applied potential difference. This simulation setup is then run with 1, 2, 4, and 6 V/nm electric fields. Emissions and fragmentation are counted, and the cumulative charge is measured over time. By investigating the composition of the emissions, it is possible to identify the relationship between the applied electric field and the dominant emission mechanism.

III. Molecular Dynamics Modeling Results

In all of the molecular dynamics simulations, a meniscus forms as the ionic liquid is extruded through the nanopore. Three distinct phases are defined for further study: 1) Pre-Meniscus, 2) Post-Meniscus, and 3) Post-Emission. The

Pre-Meniscus phase is defined as the period from after the system is equilibrated until 1% of the atoms in the system are above the nanopore. The system then enters into the Post-Meniscus phase which lasts until the emissions stop in the Post-Emission phase. Fig. 2 shows the meniscus development in a 2 V/nm electric field where the 800 ps snapshot is close to when the meniscus has just formed. At 1200 ps, the system is in the Post-Meniscus phase while at 1600 ps it is at Post-Emission.

When ions enter the region above the nanopore in the applied electric field, they are accelerated due to the force of the field. In order to ensure that the spurious emissions caused by the sudden application of strong electric field forces on atoms near rest are not considered, only emissions produced in the Post-Meniscus phase are counted. In the absence of an applied electric field, no emissions are produced, however, the meniscus continues growing over time. This is in alignment with previous studies that show that a minimum electric field of about 1-1.5 V/nm is required to overcome surface tension and produce emissions [4] [12]. In order to obtain a large enough sample of emissions, five runs are completed for each applied electric field. An average is taken across the ensemble of simulations to obtain the number of emissions of each species for the various applied electric field strengths. The emissions are categorized as monomers, fragmented monomers, dimers, trimers, neutrals, or clusters / droplets. Positively-charged $[EMIM]$ monomers may be produced via the fragmentation of heavier species like $[EMIM]_2[BF_4]$ dimers or $[EMIM]_3[BF_4]_2$ trimers. These fragmented monomers are accompanied by neutral $[EMIM][BF_4]$ molecules that are unable to be accelerated further by the applied electric field. Clusters or droplets are any positive species with more than three cations and may also fragment into lighter species.

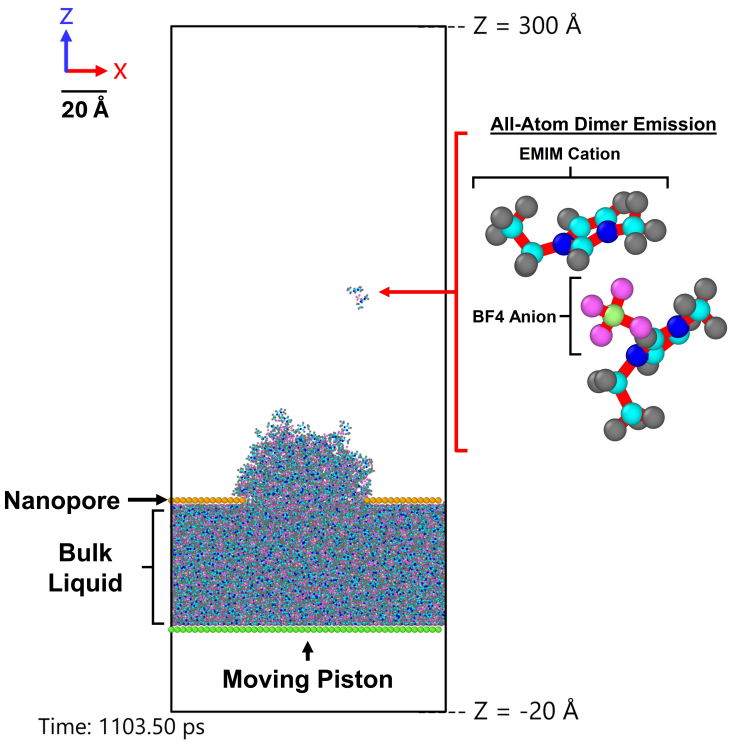

Fig. 1 The piston-nanopore setup for 4,000 ionic liquid molecules with periodic boundaries in the X- and Y-directions and a fixed condition in the Z-direction with an example of an all-atom representation of an $[EMIM]_2[BF_4]$ dimer emission. Hydrogen atoms are shown in grey while carbon and nitrogen are teal and blue, respectively. Boron is shown in magenta while the pale lime at the core of the anion is the fluorine. Both the nanopore and piston are composed of platinum atoms [9] [5].

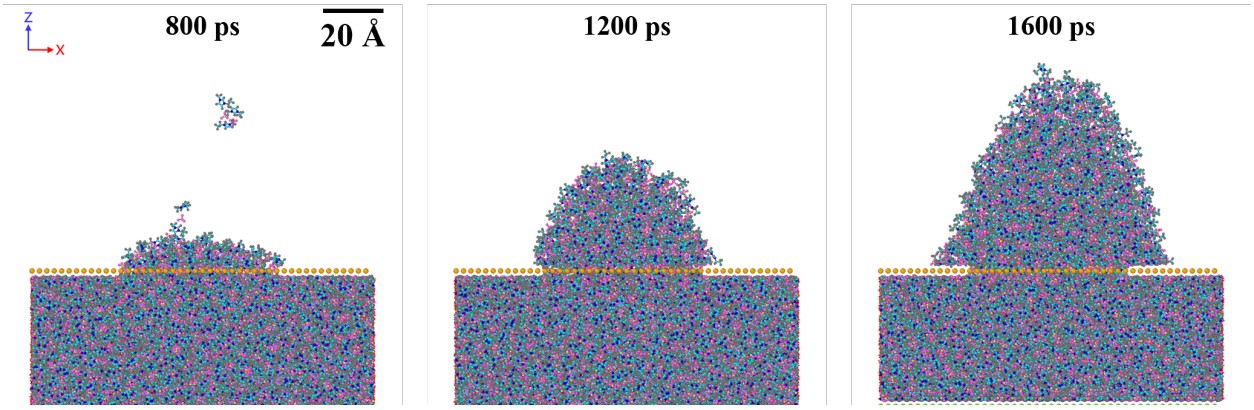

Fig. 2 All-atom (AA) snapshots of piston-nanopore system in a 2 V/nm electric field with spheres representing atoms that comprise the ionic liquid. The orange spheres make up the nanopore. The snapshots show the development of the meniscus over time and the emission of a dimer at 800 ps. All snapshots are at the scale indicated in the 800 ps snapshot.

In Fig. 3, the total number of emissions increases with the strength of the applied electric field. At lower applied electric fields of 1 or 2 V/nm, the majority of the ion emissions generated are dimers or heavier species. On average, 0.4 monomers are emitted across the five runs conducted at 1 V/nm. For the 2 V/nm electric field, the number of monomer emissions increases from 0.4 to 7 monomers on average. This is a significant increase over the 1 V/nm case and can be attributed to the applied electric field exceeding the critical field strength required to overcome surface tension and produce ion emissions. However, as with the 1 V/nm case, heavier species such as dimers and trimers still dominate over monomers. When combined, the dimers and trimers make up about 82 and 62% of all emissions on average for the 1 and 2 V/nm electric fields, respectively. No more than one fragmentation was observed across the ensemble runs for the 1 and 2 V/nm cases that each ran for 2 ns. Since these electric fields show a strong preference for species like dimers and trimers that can fragment, more fragmentations could result over time. This would lead to the production of neutrals and charged species that are not accelerated to the maximum velocity possible under the specified electric field.

When the electric field increases to 4 V/nm, the average number of monomer and dimer emissions fall within one standard deviation of each other. Comprising 50% of all emissions on average, the number of monomer emissions exceeds the dimer population for the first time in the conducted molecular dynamics simulations. The trend is made clearer when the electric field increases to 6 V/nm. In this case, the average number of monomer emissions and its associated standard deviation fall outside of one standard deviation of the dimer population signifying that across the five ensemble runs at 6 V/nm, the monomers are the primary ion emission mechanism. While dimers are still present, these simulations demonstrate that by tuning the applied electric field strength, it is possible to control the types of emissions produced by an electrospray device.

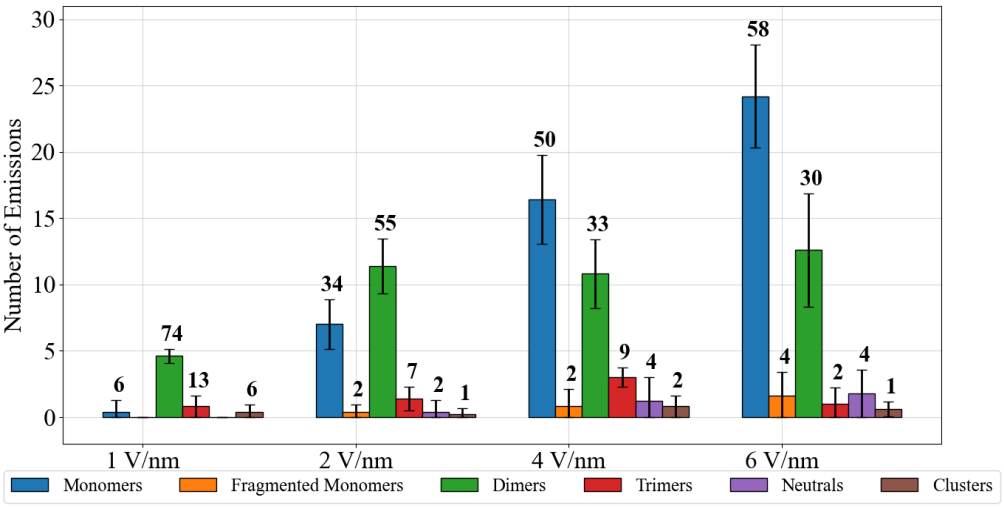

Fig. 3 Average number of ion species emissions with associated standard deviations and percent of total emissions (bold number above each bar) for each applied electric field strength.

Measuring the charge due to ion emissions that accumulate over time allows for the quantification of the relationship between the applied electric field and the total number of emissions. A plot of the cumulative charge as a function of time is shown in Fig. 4. The cumulative charge curves in Fig. 4 have been shifted in time to when 1% of the total number of ions in the system are above the nanopore so that only the steady emissions that occur after the meniscus has formed are included. By plotting the cumulative charge as a function of time, it is possible to see at what time the emissions stop (i.e., the time at which the cumulative charge plateaus). In all four cases, the emissions stop well before the end of the simulation at 2050 ps.

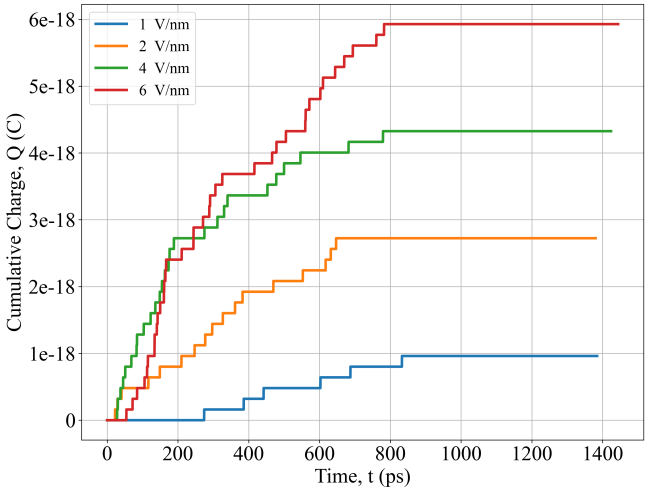

Fig. 4 All-atom (AA) cumulative charge for all ion emissions over time in a 1, 2, 4, and 6 V/nm applied electric field for the first of five ensemble runs.

In the first run of five ensemble simulations shown in Fig. 4, all emissions cease by 1000 ps after the formation of the meniscus. Moreover, the final cumulative charge increases as a function of the applied electric field strength, confirming that the stronger fields produce more emissions over the same time period after the formation of the meniscus. Both the 4 and 6 V/nm cases show a steep increase in the cumulative charge between 0 and 400 ps, indicating a high current at

these times. In the 1 and 2 V/nm cases, the final cumulative charge is approached gradually with both curves showing shallower slopes. Throughout these simulations, as long as the meniscus is maintained and has not become unstable, emissions are produced at a steady rate in the Post-Meniscus regime. In previous studies conducted without a nanopore, the electric field acts on a flat liquid-vacuum interface that can more effectively resist the field force due to the larger surface area, leading to fewer emissions once spurious emissions are discounted [4]. Instead of a burst of emissions, these simulations show a period of steady emissions after the formation of the meniscus prior to the termination of emissions once the meniscus bursts and the propellant overflows.

IV. Discussion

As the bulk ionic liquid is extruded into the region above the nanopore, the meniscus builds and eventually bursts as its surface tension is unable to hold the liquid together and the intermolecular forces governed by the all-atom potential model are overcome and the liquid expands [6]. When this occurs, the meniscus is no longer stable and liquid spreads across the nanopore. As a result, it becomes more difficult for emissions to occur as the liquid-vacuum interface loses its curvature which previously provided emission sites under the influence of fewer neighboring ions. In Fig. 4, this instability of the meniscus is likely the cause for the plateauing of the cumulative charge curves and the cessation of emissions by about 1000 ps after 1% of all ions are above the nanopore.

Aside from the increase in the cumulative charge over time, the electric field also affects the composition of the ion emissions produced. This is evidenced by the ensemble simulation results shown in Fig. 3 which indicate that at lower applied electric fields such as 1 or 2 V/nm, there is a preference for the emission of heavier species such as dimers over lighter species like monomers. When the field approaches 4 V/nm, the composition of the emissions shifts to a more even mixture of monomers and dimers. Finally, at 6 V/nm, the ion emissions are dominated by monomers. Overall, this trend indicates that lower fields produce more dimers while higher fields produce monomers. When an emission is about to occur, a chain of ions emerges at the tip of the meniscus. An example would consist of a cation-anion-cation chain that is attached to the meniscus. In the same negative electric field and assuming these ion chains remain static, the net force on this chain or an even longer one would be the +1 charge of a cation. In a weaker electric field, it would be difficult for the force of the field to overcome the bond between the ions in the chain. However, these ion chains oscillate prior to emission. As the chain oscillates, the net force changes and may even double if the two cations are aligned with the electric field. In a weaker electric field like 1 or 2 V/nm, the alignment of the forces on the ion chain would likely be required to produce an emission. Since all of the ions above the nanopore feel the same electric field force, a greater mass is required to produce emissions. As a result, weaker electric fields lead to a preference for heavier ion emissions like dimers or trimers. As the electric field strength increases, it becomes easier for the field to break the bonds of an ion chain. As a result, monomers can more easily be cleaved from these ion chains resulting in more monomer emissions at higher applied electric fields. While monomers created by fragmentation are present in these molecular dynamics simulations, they make up less than 5% of the total number of ion emissions regardless of the applied electric field strength. These results suggest that a greater number of simulations or longer runtimes would need to be implemented to get a significant number of fragmentation events to quantify their rates.

These molecular dynamics simulation results demonstrate the important relationship between the applied electric field with the current produced, but also reveal their effect on the types of ion emissions that are generated. Since dimers and other heavy species are capable of fragmenting and producing neutrals and slower monomers, the ability to control the types of emissions may be crucial to preventing inefficiencies in electrospray systems. These results show that by increasing the electric field, it is possible to create a preference for monomer emissions which would tend to decrease fragmentations overall.

In their review of experiments and simulations, Prince et al. observed that experiments typically found dimers to be the dominant species in terms of ion emissions while simulations found monomers to be the majority of emissions [13]. The molecular dynamics results here show that there is a clear dependence on the electric field strength once steady emissions are achieved, after the formation of the meniscus. While monomers make up the majority of emissions between 4 and 6 V/nm applied electric field strengths, the results of the 1 and 2 V/nm ensemble simulations demonstrate that dimers comprise the majority of ion emissions in agreement with the experiments described by Prince et al. [13]. These results show that for an all-atom potential model, the electric field is a primary driver for the dominant emission mechanism.

V. Conclusion

The molecular dynamics simulations show a correlation between the strength of the applied electric field and the resulting emission rates. Moreover, these results demonstrate that the primary emission mechanism is also dependent on the applied electric field. Eventually, all emissions stop with the specific time influenced by the balance between the electric field strength and the surface tension or other forces that may oppose emissions. In the cumulative charge curves shown for varied electric fields in Fig. 4, the charge and related current are an approximately linear function of the applied electric field, increasing with the magnitude of the field.

Increasing the strength of the electric field not only increased the number of emissions, but also changed the species emitted over time with weaker fields dominated by dimer emissions and stronger fields able to cleave significantly more cation emissions from the meniscus. With the results of this molecular dynamics electrsopray tip model, it is possible to predict the composition of a plume and potentially control the emitted species produced by an electrospray device. Since dimers and trimers can fragment to produce neutrals that cannot be accelerated further and off-axis ions, it may be necessary to control the emitted species and create a bias toward monomers to reduce inefficiencies and the production of species that could collide and erode the surfaces of the electrospray.

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