ANALYSIS OF COLLISIONS THAT OCCUR BETWEEN EMITTED IONS IN ELECTROSPRAY GENERATED DROPLETS

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ABSTRACT
Electrosprays are used to generate particles for efficient propulsion in small satellites. Collisions result in energy and momentum transfer; it can have an effect on the efficiency of the satellites. At large electric field strengths which are about 1.5 V/nm or higher, several ions are emitted from a simulated droplet and collide with each other. In this paper, the collisions that occur between emitted ions in an electrospray simulation will be analyzed. The type of collisions, such as positive ion-positive ion, negative ion-negative ion, and neutral pair will be computed and it is seen that collisions between neutral pairs dominates. The simulation consists of a molecular dynamics package which simulates a droplet that is generated in an electrospray. The droplet contains 125 ion pairs of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TF2N), and ions are emitted from the droplet as an external field is applied on it. The droplet is inside a vacuum. The collisions will be analyzed by using the trajectory output files and computing intermolecular distances. It is seen that there is no change in energy in the molecules that experience a collision, but this has to be verified on a smaller timescale.

INTRODUCTION
Electrosprays have a variety of applications such as colloidal propulsion technology, ion beams and mass spectroscopy. The production of smaller spacecraft and satellites has increased the need for colloidal propulsion technology. Electrosprays are responsible for generating particles which increase the efficiency of the thruster. Electrosprays are generated by applying an electric field on a capillary tube. At the tip of the tube, a Taylor cone begins to form. When the strength of the electric field exceeds the surface tension of the Taylor cone, a steady jet is formed which breaks into droplets. The droplets in the presence of the electric field will begin to emit ions. The ion emission enhances the efficiency of the thruster. There are three modes in which the the ion thruster can be operated, ion mode, mixed ion-droplet mode, and only droplet mode. The mode of operation is determined by the flow rate in the capillary tube. The collisions that occur between the ions have an effect on this efficiency since energy and momentum will be transmitted between the ions. Increasing the flowrate will increase the thrust but reduce specific impulse. The leads the to the flowrate being chosen on basis of the size of the spacecraft or application that is desired. The droplet that is formed from the jet and the ion emission that takes place afterwards is modeled in this paper. The main focus is on the types of collisions that take place, cation to anion, cation to cation, or anion to anion.

SIMULATION METHODOLOGY
The collisions between the emitted ions from an electrospray droplet in a molecular dynamics simulation are computed. The molecular dynamics package used to generated the electrospray droplet is LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). An equilibrated droplet consisting of 125 ion pairs of EMIM-TF2N (1-ethyl-3-methylimidazolium...
bis(trifluoromethylsulfonylimide) will represent the electrospray droplet that will be placed in the electric field. A force-field is used to describe the potential energy between molecules and models bond stretching, angle bending, dihedral angles and torsion in aromatic rings which is modeled by the improper function. The functional form is

\[ U_{\text{total}} = U_{\text{bond}} + U_{\text{angle}} + U_{\text{dihedral}} + U_{\text{improper}} \]  

The actual potential form is

\[ U_{\text{total}} = k_0(r - r_o)^2 + k_\theta(\theta - \theta_o)^2 + k_\phi(1 + \cos(n\phi - \delta)) + k_\psi(\psi - \psi_o)^2 \]  

This consists of the intramolecular forces. The intermolecular forces which are the Van der Waals forces and the electrostatics are modeled by the Lennard-Jones potential and the Coulombic potential. The functional form for the intermolecular forces is

\[ 4\epsilon\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} + \frac{q_i q_j}{4\epsilon r_{ij}} \]  

This droplet was generated using a CHARMM forcefield, consisting of bond, angles, and improper to use a harmonic potential, and dihedrals to use a charmm potential. The force field parameters for EMIM are taken from Kelkar and Maginn who determined the accuracy of force field parameters for ionic liquids as well as their transport properties. The force field parameters for TF2N are taken from Lopez and Padua. The boundary conditions are shrinkwrapped, and the droplet is equilibrated for 3.8 ns before being placed in an electric field. The equilibration time is determined by the amount of time the droplet takes to attain maximum sphericity. The sphericity is computed by calculating the inertia tensor components and the resulting eigenvalues of the three principle axis. When the eigenvalues converge, the droplet attains maximum sphericity. Shrinkwrapped describes the non-periodic boundary conditions that contain all the atoms in the simulation box throughout the simulation. The droplet was placed into several electric fields ranging from 0.02 V/Nm to 2.5 V/Nm for 0.5 ns, and it is seen that ions are emitted from 1 V/Nm and above. Constant ion emission is occurring at electric field strengths of 1.5 V/Nm and greater, and the droplet shows complete dissociation at 2.0 V/Nm. For purposes of the collision analysis, the results of the droplet placed at the electric field 1.5 V/Nm will be considered. These results agree with previous work done by Takahashi and Lozano in their work on EMIM-BF4 droplets in electric fields. They observed ion emission in the range of 1.0 V/Nm and 2.5 V/Nm. A sampling of collisions that occur every 1000 timesteps is chosen to do the analysis on, although the average collision takes place on the timescale of 10-100 timesteps. A trajectory is generated consisting of the molecule ids, x,y, and z positions of the molecules at every 1000 timesteps. The molecule id contains information such as the type of molecule (EMIM or TF2N), mass, and charge of the molecule. The x,y, and z positions are taken at the center of mass of each molecule. The analysis code is written in python using the Numpy and SciPy package. The algorithm consists of iterating through each timestep, generating an array of molecule ids, x positions, y positions, and z positions. The emitted ion is computed by testing whether its radial position has a critical distance beyond the radius of the droplet. For each timestep, the center of mass of the droplet is recomputed consisting of only the ions that remain in the droplet without emitted ones. This is considered as the reference point for each timestep. A list of molecule ids consisting of emitted ions is generated. Another loop is performed testing the distance between each emitted ion and every other ion with a critical distance of 4 Angstroms to test whether a collision has taken place or not. This distance was chosen based on the distance between the center of masses of the cation and anion. Another list is then generated containing nested lists for each timestep with the pairs of molecule ids representing the collision. Using the pairs of molecule ids, the collisions can then be classified.

RESULTS AND DISCUSSION

The collision list generated by the analysis code previously described contains a list of ion pairs that collide at every 1000 timesteps. The list of ion pairs are represented by the molecule ids which contain its identity information. There are 250 total ions and the ids are assigned from 0 to 249. The type of collision that occurs is determined by the anion or cation identity given by the pair of molecule IDs. The analysis is done for an electric field of 1.5 V/Nm. In the sampling of collisions that took place every 1000 timesteps, the majority of the collisions that took place were between a neutral pair (anion to cation). There were only three collisions that took place between a non-neutral pair. There were 3 cation-cation collisions, and no anion-anion collisions. A total number of 517 collisions were computed.

Table 1 shows an example of the data that was collected. At each timestep, a pair of molecule IDs are shown which represents a collision. The molecule ID represents the identity of the molecule by distinguishing the even numbers from the odd. An even number represents a cation, and an odd number represents an anion. The collision analysis was repeated for the droplet placed in an electric field 1.7 V/Nm and 2 V/Nm. It is found at 1.7 V/Nm, 229 collisions occur, with one cation-cation collision and the remaining neutral. At 2 V/Nm, 98 collision occur, with all neutral collisions. Since the droplet dissociates faster at higher electric fields, there is less time for collision to take place. This explains why at higher electric fields fewer collisions take place. The fact that a majority of collisions that occurred are between neutral pairs represent the fact that the intermolecular
potential had an impact on whether a collision is going to take place. Anion-anion and cation-cation pairs would have the tendency to naturally repel but the results of this simulation show that repulsion overcomes the momentum of the traveling ions in a strong electric field. The electric field on the emitted ions is not strong enough to overcome intermolecular repulsive forces. This means that in situations involving a system of ions where the number of collisions needs to be optimized, even numbers of anions and cations must be used in order to get the most effective result.

An attempt to calculate the collision cross section as a function of energy was made. This was first done by using the results of the previous simulation which outputs data every 1000 timesteps. Using the collision pair array described earlier, the molecule IDs of each pair were extracted and the x,y,z positions at their center of mass were used to calculate their collision diameters. The simulation outputs the components of the velocity vx, vy, vz and with the known masses of the molecule the kinetic energies can be computed. An array of collision diameters as well as an array of energies were generated. The array of energies contains the $\Delta KE$ of each molecule involved in the collision in order to determine how much energy was lost or transferred during the collision. The array generated contained only zeros, representing a $\Delta KE$ of zero for each molecule. The drawback to this analysis is that the simulation only produces the data every 1000 timesteps. Collisions in general take place on a timescale of 10-100 timesteps. The second simulation that is performed outputs data at every 50 timesteps. The trajectories were analyzed using the same data analysis as before. The collisions were successfully computed but for computing the diameters and energies, there had been a memory crash not allowing the calculation to finish. The calculation was performed on 2.6 GHz dual-core processor with 8 GB of memory. More optimized analysis code that handles smaller time scales needs to be developed in the future.

**CONCLUSION**

This paper examines the nature of collisions that occur among the ions emitted by an electrospray generated droplet. Collisions can impact the efficiency of thrusters. It is found that a majority of the collisions that occur among these ions are neutral collisions. Cation-cation collisions are rare and anion-anion collisions are not found at all. This results in a strong intermolecular repulsive force which the electric field does not overcome. It is also seen that there is no change in energy among the molecules involved in collision but the calculation was made on too large of a timescale. Future work in this area will involve computing the mean free path among colliding ions. This requires a higher resolution of data, since collisions occur on a timescale 10-100 timesteps rather than 1000 timesteps used in the current work. Currently, more efficient analysis code is being developed in order to produce that data.

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**CITING REFERENCES**


