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A new facility for electrospray propulsion studies with spatial resolution of the full beam and high-resolution mass analysis

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Final report: AFOSR grant FA9550-18-1-0165

ABSTRACT

This is the final progress report on Yale's AFOSR grant FA9550-18-1-0165, covering the full grant period from 6/1/2018 to 31/May/2022. Advances were made along four different lines: **(1)** Our main task, *A new facility for electrospray propulsion studies with spatial resolution of the full beam and high-resolution mass analysis*; **(2)** Studies on ionic liquid cluster fragmentation carried out in collaboration with Professor Paulo Lozano (MIT). This has included studies on a variety of instruments developed specifically for this task, using conventional and multiplexed mobility analyzers, and condensation particle counters; **(3)** The structure of magnetized conical tips; and **(4)** Propulsion based on heavy or multivalent ions, in collaboration with Dr. Kamran Ghiassi (Edwards Air Force Base). Along line **1**, an instrument capable of characterizing full electrospray plumes in vacuum in terms of energy, mass/charge and angular distribution has been developed and undergone continuous refinement in resolving power and sensitivity. The instrument determines key jet characteristics such as energy dissipated, jet potential, diameter and velocity at the breakup point. An initial characterization of the ionic liquid propellant EMI-FAP at a single flow rate and several temperatures has been published. A systematic study of EMI-FAP at many flow rates and temperatures was concluded in March 2022 and is still being analyzed. Along line **2** we contributed key kinetic information to the MIT group of Lozano. Our experimental technique has been further developed with three different new schemes to measure cluster ion fragmentation kinetics. One based on in flight fragmentation within a mobility analyzer has already been validated with ionic liquid trimer ion decomposition occurring at very high rates. Another based on slower reaction measurements inside a heated tube with uniform temperature was tested in the summer of 2021. This work remains unpublished because of a problem of turbulent transition for which a suitable theoretical interpretation turned out to be too difficult. A Laminar variant of this instrument has already completed fragmentation studies on 4 ionic liquids of widely varying masses. Along line **3**, several publications have resulted, aimed at understanding the largest tip curvature achievable in magnetized ferrofluids. Along line **4** we have obtained still unpublished data on the nature of electrospray ions produced by salts composed of small *divalent* anions or cations. We have also studied 3 singularly heavy ionic liquids developed at the Edwards Air Force Basis by Dr. Kamran Ghiassi, some of them also including divalent ions. Surprisingly, small doubly divalent salts produce mainly singly charged ions, apparently by attachment or loss of protons from the solvent. Ghiassi's heavy ionic liquids produced a very rich mix of singly and doubly charged cluster ions, some of which are highly unstable.

Level of attainment of Research Objectives

The original proposal objectives were summarized as follows: *The first few months will be devoted to tune the facility (maximize resolution and sensitivity) and improve protocols to acquire and analyze the large density of data obtained on spatially and mass resolved TOF spectra. Also to develop high-mass resolution ring collectors with conical faces. The rest of the first year (and possibly two extension years) will be devoted to investigate propellants capable of offering widely variable specific impulse (I_{sp}) at high efficiency. This includes mixtures of ionic liquids with neutral solvents of high boiling point (sulfolane, tetraglyme), as well as newly developed ionic liquids with singularly large molecular mass (500-5000 amu). A considerable effort will be devoted to identifying new promising propellants.*

The main original technical goal was accordingly to improve and exploit our new experimental facility to investigate the composition and spatial distribution of nanodrops and ions in an electrospray plume in vacuum, such as are often used in space micropropulsion. An instrument previously developed in collaboration with Dr. Steve Gildea of the Air Force Lab was already available at Yale. However, early in our studies, graduate student Luis Perez-Lorenzo explored the possibility of extending the measurement routine to determine not just the initially proposed velocity and angular distribution of particles, but to include also energy measurements. This was readily implemented in the existing facility. Unexpectedly, the new tests revealed that the common assumption that the energy of most particles would be close to the emitter voltage was substantially incorrect. Consequently, it became necessary to include energy analysis in all our measurements. This required much longer experiments to systematically scan over many rather than just one energy. It also resulted in considerably more complex and difficult to analyze data sets. On the other hand, the mechanism leading to wide energy distributions was seen to be due to the conversion of electrical energy into jet energy prior to jet breakup into drops. The detached drops were then accelerated from a common initial velocity and electrical potential at the jet breakup point. This naturally resulted in different final velocities and energies for particles having different mass/charge. This peculiar behavior was strikingly manifested in the fact that particles with a narrow energy range had a narrow range of velocities. And the resulting relation between mean energy and mean velocity was completely coherent with the mechanism of a two-step acceleration process, first as a single jet for all particles, and then as a purely electrostatic acceleration of isolated drops and ions. A most interesting consequence of this behavior was that one could infer from our measurements on drops several key characteristics of the jet, even though the jet itself cannot be directly probed. These jet properties were its electrical potential, velocity and diameter at the breakup point. These parameters had been previously inferred in several earlier brilliant studies by Dr. Manuel Gamero. However, this had been possible in relatively simple sprays of low viscosity electrolytes, that tended to break up into only two classes of droplets: main drops and satellites. In that case, a separate measurement of energy distributions and velocity distribution of these two droplet classes revealed the three jet properties mentioned. Interestingly, Gamero's remarkable feat could now be extended to the complex sprays produced by Taylor cones of ionic liquids. This was enabled by Perez-Lorenzo's novel strategy to determine energy and velocity distributions, not separately in parallel, as previously done, but jointly in series. Namely, we were for the first time determining joint probability distributions $P(\xi,u)$ of energy and velocity, rather than the corresponding separate distributions $P(\xi)$ and $P(u)$. Another considerable improvement of our measurements over previous art was that, as stated in our original proposal, we were determining angular distributions, which in turn enabled much improved resolving power in the determination of both the energy and the velocity of particles moving far from the axis of the collector.

Naturally, the novel possibilities opened up by our new technique of measuring the three-dimensional distribution of the spray in polar angle, energy and velocity, $I(\theta, \xi,u)$, came at a cost. In addition to the drastically increased data acquisition time, and the complexity of the data set and its analysis, the measured current was now dispersed in these three variables, greatly decreasing signal/noise at each particular value of θ, ξ and u. Dealing with these difficulties was a real tour de force for Mr. Perez Lorenzo.

Consequently, although new jet characterization goals not originally proposed were achieved, not all original objectives were reached. First, the *high-mass resolution ring collectors with conical faces* were not developed at all. The reason was that these geometries were theoretically advantageous only for particles having fixed energy. This turned out not to be the case for our sprays, whose energy was widely spread. Even for particles of a given class, resolution in energy turned out to be limited by the inherent randomness of the drop breakup process. Therefore, this geometrical refinement would have had no practical benefit. The second main goal was *to investigate propellants capable of offering widely variable specific impulse (I_{sp}) at high efficiency. This included mixtures of ionic liquids with neutral solvents of high boiling point (sulfolane, tetraglyme), as well as newly developed ionic liquids with singularly large molecular mass (500-5000 amu).* This goal was completed with one ionic liquid, EMI-FAP, but not with *neutral solvents such as sulfolane and tetraglyme*. In compensation, EMI-FAP was studied at a fairly wide range of temperatures, while the proposal did not include this commitment. The EMI-FAP propellant thoroughly investigated is within the proposed 500-5000 amu mass range. The molecular weight of the neutral EMI-FAP salt is 556 amu. In the investigated negative emission mode, the thoroughly dominant ion is the dimer, with a molecular weight of 1001 amu. EMI-FAP is in fact the heaviest ionic liquid commercially available, and has demonstrated the expected singular advantage of its relatively high mass in increasing propulsive efficiency. We did receive from our colleague Dr. Ghiassi several considerably heavier ionic liquids, which were studied by other methods. However, the extremely high viscosity of these heavier materials precluded their direct investigation in our vacuum electrospray facility. The proposed study of electrolytes of either *sulfolane* or *tetraglyme* was precluded due to a number of complications. First, the effort involved in the new measurement routine left little time for this task. Second, the finite volatility of these solvents requires the use of very small emitting tips, which can be produced only in pulled glass. However, the extended measurement routine developed permitted the very useful measurement of the electrical energy dissipated, which in turn required the use of conducting tips. We were then confined to commercial metallic tips, which are not available with tip diameters below 50 μm. Finally, our development of a heated emitter offered great advantages in the investigation of ionic liquids, but was of limited use in the study of electrolytes whose volatility was already hard to manage at room temperature. In spite of these practical considerations, we still believe that the future study of *sulfolane* or *tetraglyme* electrolytes should be of considerable interest once the required effort is invested in resolving the practical difficulties noted.

In conclusion, the main proposed goal of discovering new propellants has been achieved. EMI-FAP has been shown to greatly surpass in propulsive efficiency all previously investigated ionic liquids in the relevant high thrust regime associated with drop emissions. Similarly, the other main goal to *maximize resolution and sensitivity of the new facility, and improve protocols to acquire and analyze the large density of data obtained on spatially and mass resolved TOF spectra* has been attained well beyond what was originally proposed. These successes, however, took place at dates substantially behind those originally planned. They were in fact significantly completed only thanks to the one year extension granted in consideration of the covid lockdown.

Accomplishments in electrospray emission studies

The main activity was the improvement and systematic use of our vacuum facility to investigate the emissions of the propellant EMI-FAP over a broad range of emitted currents and source temperatures. After submitting for publication our initial results with EMI-FAP at 3 temperatures and under a single spray condition (L. J. Perez-Lorenzo, J. Fernandez de la Mora, Probing electrically driven nanojets by energy and mass analysis in vacuo, J. Fluid Mech. (2022), vol. 931, A4, doi:10.1017/jfm.2021.771), a strenuous effort by Mr. Perez-Lorenzo was devoted to improve the quality of the data. The plan for this effort was described in our request for a no cost extension, and has now been completely successful. The noise level was notably reduced. The response time and sensitivity of the charge detector were also greatly improved. The purchase of two additional oscilloscopes has accelerated substantially the speed of data acquisition. These instrument developments, and the parallel improvements in the routine for data acquisition and analysis were completed by March 2022. These developments then enabled relatively fast progress in the systematic study of EMI-FAP under many emission currents and temperatures. This experimental campaign was essentially completed by May/2022. Mr. Perez Lorenzo then devoted most of his time to an initial analysis of his new data, and to its writing as the core of his PhD. Thesis. The Thesis was successfully defended on July 2022, shortly after termination of this grant. A thorough description of the many findings made there will be reported as part of the continuation of this grant, as the effort of analyzing the vast body of data obtained will take perhaps up to one year. Nevertheless, a number of important preliminary conclusions became available before the termination of this grant, and may be summarized here in preliminary fashion.

A first important conclusion is that the quality of the data from the improved system is vastly superior to that of their predecessors. The resolution in the time of flight data is splendid, and the noise is drastically decreased. Monomer, dimer and trimer ions now produce clearly distinguishable sharp steps. The thorough expansion of the range of flow rates and currents studied provides a far more complete picture of the evolution of the spray. A considerable increase in specific impulse (I_{sp}) is obtained both at decreasing flow rate and at increasing temperature. However, the full potential of these two control parameters could not be exhaustively covered due to our present inability to reach the minimum flow rate of stable sprays available at the highest temperatures. The difficulty is strictly practical. It is due to the large response times of the meniscus at very low propellant flow rates. Its solution would require the use of emitting tip diameters considerably below the approximate ~50 μm of the metallic capillaries presently employed. We know how to do that by making smaller pulled glass tips and making them conductive by deposition of tin oxide.

The most novel finding in the new measurement series is the ability to determine with sufficient precision the electrical power dissipated in the formation of the Taylor cone. This power naturally leads to heating of the propellant in the final region where the Taylor cone evolves into a nanometer jet. Therefore, the temperature in this key region where the jet diameter and emitting current are fixed may differ considerably from the temperature assigned to the meniscus. This important consideration has been previously discussed in pioneering work by Manuel Gamero, who has also noted the key role played by dissipation in the formation of Taylor cone-jets. A striking finding in our work is that the observed relation between emitted current and propellant flow rate does not obey established scaling laws when the dissipative temperature rise is ignored. But if one assumes that all the dissipated power is turned into heating of the jet, then the conventional scaling laws based on liquid properties at this higher temperature are satisfied. This circumstance provides high confidence on the correctness of the measured dissipation. We believe these dissipation measurements are the first obtained so far for an ionic liquid. Gamero has previously studied this effect in electrolytes of neutral solvents and inferred from them the corresponding scaling laws. However, our 2022 article has shown that these laws do not apply to ionic liquids, probably due to their much higher viscosity relative to Gamero's electrolytes. Therefore, we expect to be able to use the new data to extend Gamero's results to the realm of ionic liquids.

With the exception of the PhD Thesis of Luis Perez-Lorenzo, these very recent results have been disseminated only at several AFOSR presentations at Dr. Mitat Birkan contract meetings, and our 2022 Journal of Fluid Mechanics article.

Accomplishments in the characterization of the singularly heavy and multivalent ionic liquids synthesized at the Air Force Laboratory by Dr. Ghiassi and colleagues. There has been no progress along this line beyond the developments reported in our previous report. The main finding was the high tendency of the charged species emitted from Ghiassi's divalent salts to adopt singly charged combinations of anions and cations, such that the mass/charge would be considerably larger than originally expected. This result is theoretically most favorable to increase propulsion efficiency, although this remains to be demonstrated in real propulsive scenarios. This finding has widened the synthetic possibilities open to Dr. Ghiassis's group, from which a number of new salts have resulted. Dr. Ghiassi has kindly offered sending these new materials to Yale, but their analysis will have to wait until other more urgent tasks make suitable progress.

Accomplishments in the study of the fragmentation kinetics of ionic liquid clusters. Our earlier findings were summarized in our previous report. We described the development of a new facility where the selection of cluster ions took place at the same temperature as the reaction chamber, whence there was no ambiguity in the thermodynamic state. This work remains unpublished as we discovered that the reactive flow changed from laminar to turbulent in certain parts of the heated tube. This work has recently been extended with a new reaction tube of wider diameter, where the flow remains laminar under all conditions. 4 ionic liquids have been characterized by Mr. Maxime Jalabert visiting from SupAero (Toulouse, France). His Yale stage extended from mid March to late August 2022. His main experimental results were completed in August, after the end of this grant. The data are not yet fully analyzed, but several preliminary conclusions can be reported. The ionic liquids tested were EMI-BF_4, EMI-FAP, EMI-trifluromethilsulfonate, and trihexiltetradecylphosphonium-FAP. They cover a wide range of molecular weights, from less than 200 to about 700 amu. The main finding is that the clusters from the heavier ions are considerably more thermally unstable than those of the lighter ions. There is absolutely no doubt about this result, which, however, appears to go counter the published findings from Miller and Lozano at MIT. It is too early to provide a firm explanation for this paradoxical situation. One possibility raised in recent work by Gamero is that a potential source of fragmentation is the collision of the cluster ions with neutrals in the chamber due to an insufficient vacuum. Whether this was a problem in the MIT study remains to be clarified.

Several publications on condensation detectors have resulted from studies related to these fragmentation experiments. The condensation detector is a very sensitive device able to detect nanodrops and clusters with 100% efficiency by growing them into visible drops. Accordingly, they increase greatly the sensitivity with which we can study the decomposition of clusters. Related work has typically been carried out at only symbolic cost to the AFOSR, thanks to young visitors that have spent several months in our lab supported by their own institutions.

Accomplishments in the study of magnetized conical tips. Progress along this front was described in our previous report. No further developments have arisen since then. In fact, an article submitted to J. Fluid Mechanics with Mr Kartikey Misra as the first author has since been withdrawn. The reason was that Mr. Misra indicated that he had lost confidence in his calculations on the shape of the meniscus shape, and declared himself incapable of repairing this problem. We trust completely the experimental results reported, as well as all other theoretical considerations adduced. Nevertheless, the article must be kept on hold until the dubious meniscus calculations are correctly executed.