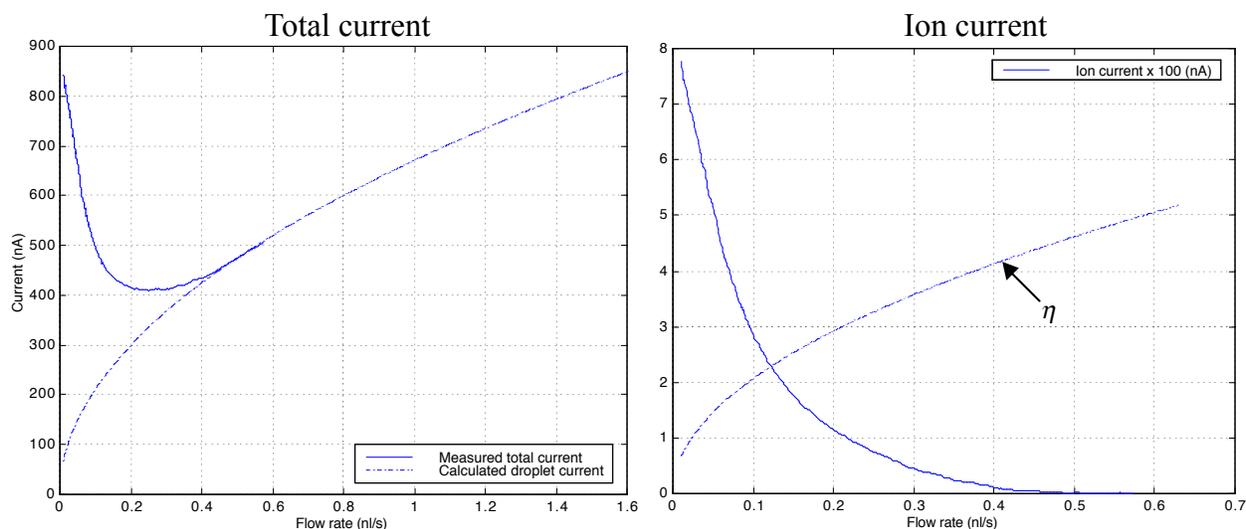


Session 24: Ion Emission and the Pure Ionic Regime

As discussed in the previous lecture, when the flow rate parameter $\eta = \sqrt{\frac{\rho K Q}{\gamma \epsilon \epsilon_0}}$ and the ratio Q/K are decreased, operation in the cone-jet mode will deliver smaller droplets with the possibility of producing fields strong enough to trigger ion evaporation from the cone-to-jet transition region, where the normal field is strongest. If η is reduced too much (typically less than 0.5), the cone-jet mode will become erratic and stable emission will not longer be possible. The interesting fact is that as η goes down, the ion emission (again, for sufficiently low Q/K) will increase in proportion to the total current in the beam. In fact, the total current will also increase because ions can transport charge much more effectively than droplets for a given mass flow. This behavior is shown in the figure below for a $K \sim 1$ Si/m Formamide + NaI solution (Lozano, 2002).

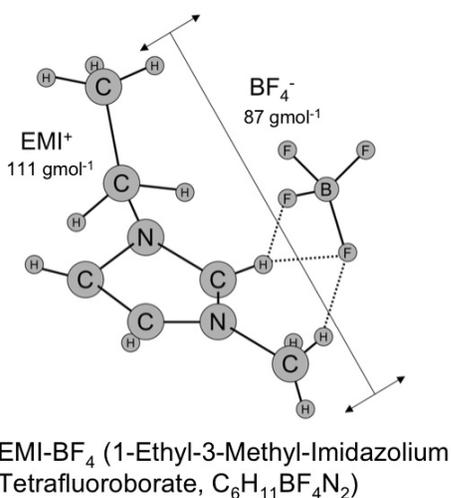


We could then conjecture that at some point, the whole current transport would be carried by ions alone with the droplet population simply disappearing. If this occurs, but the emission is stable within experimental resolution, then it is possible the liquid jet will be suppressed and ion emission will be produced from the stressed, closed-surface of the liquid. This situation is known as the pure ionic regime (PIR) and is obtained when the working fluid is an ionic liquid, or a room temperature molten salt. On the other hand, the PIR has not been observed with regular organic electrolytes, even with electrical conductivities several times higher than those of ionic liquids.

Ionic Liquids

These are a relatively new class of substances that, since the mid 1990's, have attracted significant attention due to their wide applicability in a variety of fields. An ionic liquid (IL) is a salt with a melting point near room temperature. Just like conventional inorganic salts, for example NaCl, IL's display appreciable electrical conductivity in the liquid phase (the melting point of NaCl is about 850°C). A very important difference between conventional electrolytes and IL's is that the latter do not have any solvent in their composition (i.e., all molecules are charged species - this is why we call them sometimes "plasma in a bottle"). As such, the interactions between particles in the liquid are *coulombic* in nature, as opposed to

Van der Waals, and therefore much stronger. In consequence, IL's exhibit practically zero vapor pressure at their melting points. This effectively means that they can be exposed to high vacuum conditions without evaporation, an advantageous feature for their use in space. Still, even with the strong interaction force between particles, the salt remains liquid at relatively low temperatures. This is because these particles are, for the most part (especially for the positive species), large, complex and very asymmetric molecular species for which it is hard to form solid, crystalline structures. The counter ion (the negative ion, in most cases) could be a complex organic molecule, and sometimes a much simpler inorganic or even a monoatomic species. The figure shows, for instance, a cartoon of the molecular structure of the liquid EMI-BF₄ (1-ethyl-3-methyl-imidazolium tetrafluoroborate).



This liquid has been thoroughly characterized with electrosprays and is relatively straightforward to achieve the PIR with it. The surface tension of most IL's tends to be similar to that of electrolytic solutions (typically 1/3 to 1/2 of water's). Their viscosities can vary widely depending on their composition, from relatively low (like water) to very high (like honey). A very important property is their large electrochemical window. This is the ability of molecules to accumulate charge over an electrode surface before electrochemically discharging to it and produce faradic currents. While most electrolytes have windows of about 1 V, ionic liquids can have 4-5 V. This is a reason why they are attractive substances for batteries and supercapacitors. Finally, these liquids have an outstanding range of thermal stability. They do not boil, but decompose at temperatures as large as 300-400°C. Some of them display supercooling tendencies

(like EMI-BF₄) and remain as liquids at temperatures below -50°C, significantly lower than their melting points. There are hundreds of different IL's described in the literature. In principle, there is a much larger number of possible compositions of IL's that could be synthesized. Some authors claim this number is in the millions.

When electrostatically stressed, and under sufficiently low flow rate, the PIR will be obtained with most IL's. Because of this, electrosprays working in the PIR are also known as ionic liquid ion sources (ILIS). The generic composition of the liquid is A⁺B⁻, where A⁺ is the positive ion and B⁻ is the negative ion (like in EMI⁺-BF₄⁻). Depending on the polarity of the extracting field, positive or negative ions will be obtained. These ions are of the form,

$$\begin{aligned} &A^+(A^+B^-)_n \text{ in the positive polarity} \\ &B^-(A^+B^-)_n \text{ in the negative polarity} \end{aligned}$$

where n is the degree of solvation. In most cases, only $n = 0, 1, 2$ are observed, with $n = 0, 1$ contributing with about half of the total emitted current each, and $n = 2$ taking just a small fraction, or none at all. It is then clear that more than one species, with an appreciable difference in mass, will be obtained from a single electrified meniscus. This *polydispersity* will have an effect on the performance of an electrospray thruster, as described next.

Propulsive Efficiency: Effect of Polydispersity

As in any propulsive device, an exhaust stream containing more than a single speed is a less than optimum arrangement, because the energy spent to accelerate the faster constituents is larger in proportion than the extra thrust derived from them.

Suppose our electrospray stream contains a mixture of ions of different mass (or a mixture of monodisperse droplets and ions). Let \dot{N}_j be the number of particles of type j emitted per second, and assume they are all accelerated through a voltage V , to a velocity,

$$c_j = \sqrt{\frac{2q_j V}{m_j}}$$

The total mass flow rate is,

$$\dot{m} = \sum_j \dot{N}_j m_j \quad (1)$$

and the total current is,

$$I = \sum_j \dot{N}_j q_j \quad (2)$$

The thrust is,

$$F = \sum_j \dot{N}_j m_j c_j = \sum_j \dot{N}_j \sqrt{2V m_j q_j} \quad (3)$$

The propulsive efficiency (the ratio of propulsive power to input power) is,

$$\eta_p = \frac{F^2}{2\dot{m}IV} = \frac{\left(\sum_j \dot{N}_j \sqrt{2V m_j q_j}\right)^2}{\left(2V \sum_j \dot{N}_j m_j\right) \left(\sum_j \dot{N}_j q_j\right)} \quad (4)$$

Restricting attention now to only two monodisperse species,

$$\eta_p = \frac{\left(\dot{N}_1 \sqrt{m_1 q_1} + \dot{N}_2 \sqrt{m_2 q_2}\right)^2}{\left(\dot{N}_1 q_1 + \dot{N}_2 q_2\right) \left(\dot{N}_1 m_1 + \dot{N}_2 m_2\right)} \quad (5)$$

The current carried by species 1 is $I_1 = \dot{N}_1 q_1$, and that carried by species 2 is $I_2 = \dot{N}_2 q_2$. If we let,

$$\beta_2 = \frac{I_2}{I} \quad \text{and} \quad \beta_1 = 1 - \beta_2 = \frac{I_1}{I} \quad (6)$$

then (5) can be written as,

$$\eta_p = \frac{\left(\beta_1 \sqrt{\frac{m_1}{q_1}} + \beta_2 \sqrt{\frac{m_2}{q_2}}\right)^2}{\beta_1 \frac{m_1}{q_1} + \beta_2 \frac{m_2}{q_2}} = \frac{[1 - (1 - \sqrt{\epsilon}) \beta_2]^2}{1 - (1 - \epsilon) \beta_2} \quad (7)$$

where,

$$\epsilon = \frac{(q/m)_1}{(q/m)_2} \quad (8)$$

Alternatively, if we work with the mass fractions $\alpha_j = \dot{m}_j/\dot{m}$, then,

$$\eta_p = \frac{\left(\alpha_1 \sqrt{\frac{q_1}{m_1}} + \alpha_2 \sqrt{\frac{q_2}{m_2}}\right)^2}{\alpha_1 \frac{q_1}{m_1} + \alpha_2 \frac{q_2}{m_2}} \quad (9)$$

It is easy to check that η_p is less than unity, unless $\beta_1 = 0$ or $\beta_1 = 1$ (or, alternatively $\alpha_1 = 0$ or $\alpha_1 = 1$). Minimum efficiency occurs with current and mass fractions,

$$\beta_2|_{\eta_p, \min} = \frac{1}{1 + \sqrt{\epsilon}} \quad \text{and} \quad \alpha_2|_{\eta_p, \min} = \frac{\sqrt{\epsilon}}{1 + \sqrt{\epsilon}} \quad (10)$$

and this minimum is,

$$\eta_{p, \min} = \frac{4\sqrt{\epsilon}}{(1 + \sqrt{\epsilon})^2} \quad (11)$$

Eq. (11) shows that it is important to keep ϵ from being too small. If operating in the ion-droplet mixed regime, this implies droplets being as small as possible (large $(q/m)_1$) and ions being as heavy as possible (not too large $(q/m)_2$).

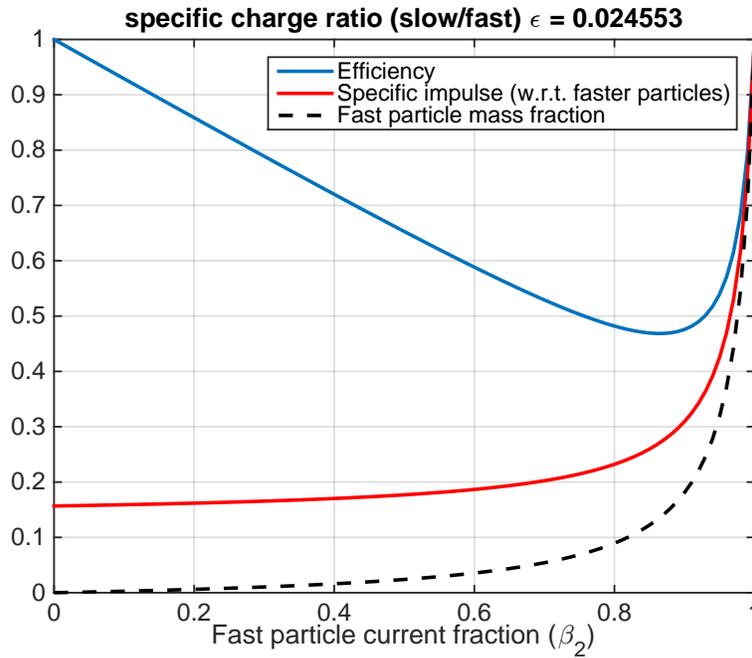
As an example of the mixed regime performance, assume a solution of Tetra-Heptyl Ammonium in Formamide, for which a specific charge of $(q/m)_1 = 5770$ C/kg has been observed (a maximum of about 10,000 C/kg has been achieved in saturated Formamide solutions). The corresponding solvated ions have a specific charge $(q/m)_2 = 2.35 \times 10^5$ C/kg. This means that $\epsilon = 0.0245$.

The specific impulse can be expressed as,

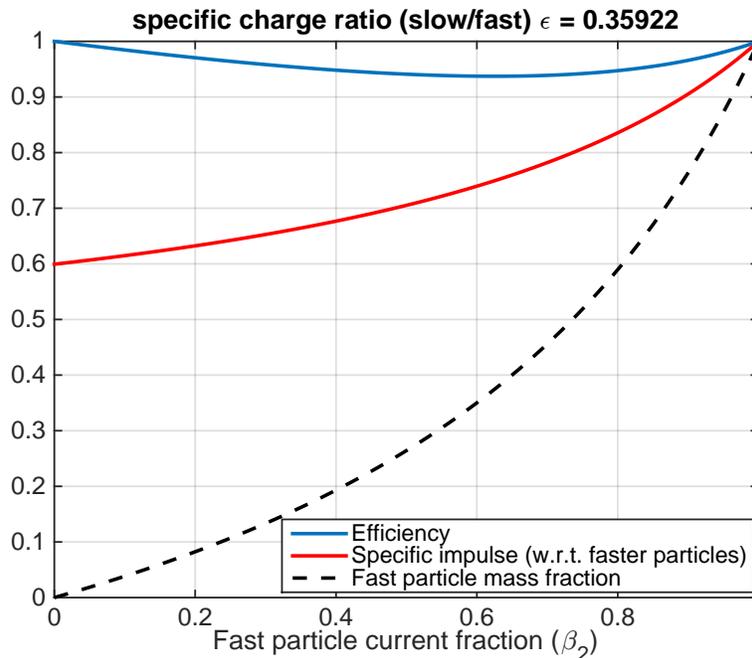
$$gI_{sp} = \sqrt{2V \left(\frac{q}{m}\right)_1 \frac{1 - (1 - \sqrt{\epsilon}) \beta_2}{1 - (1 - \epsilon) \beta_2}} = \sqrt{2V \left(\frac{q}{m}\right)_2 \frac{\sqrt{\epsilon} - (\sqrt{\epsilon} - \epsilon) \beta_2}{1 - (1 - \epsilon) \beta_2}} \quad (12)$$

and the efficiency is as given by (7). Under these conditions, the figure shows η_p , I_{sp} normalized to the fast species, and the mass fractions as functions of β_2 (the ion content).

The figure clearly illustrates the two efficient regimes at low and very high ion fraction, with poor performance in between. If $\eta_p = 0.6$ is arbitrarily chosen as the minimum acceptable efficiency, the ion current fraction should be below 58% or above 97%. From here, we could



calculate that the low β_2 regime ($\beta_2 < 0.58$) requires voltages greater than 1.5 kV, 6 kV or 13.2 kV for I_{sp} of 500, 1000, 1500 s, respectively, and is therefore probably acceptable for I_{sp} less than about 700s. The high β_2 regime, on the other hand, requires very low voltages (under 2 kV even for $I_{sp} = 1500$ s), which is very desirable, provided a stable Taylor cone can still be maintained.



In the case of the PIR, we can expect an impact in efficiency too, but since the difference in ion mass is not as dramatic as that between droplets and ions, we expect this impact to be less severe. For example, the figure shows a case for EMI-BF₄ in the PIR. The mass of EMI is 111 g/mol and BF₄ is 87 g/mol. Assume that we only have ions with $n = 0$ and $n = 1$ (the monomer and the dimer). In this case, the ratio of specific charge (for singly charged

species) of dimer to monomer will be $\epsilon = 0.359$, much closer to unity than in the previous example. In this case, the efficiency never drops below about 93% and the specific impulse is always $> 60\%$ of its maximum value (in this case, β_2 refers to the faster, monomer species).

Other efficiency losses arise from:

- (a) Energy efficiency. In the previous analysis we assumed all particles traveled at a velocity corresponding to the full accelerating potential. While in the cone-jet mode there is a strong ohmic loss (as high as 100's of volts), in the PIR it is observed that ions are emitted with an energy very close to the emitted potential. A drop of a few eV's has been observed (~ 7 eV in EMI-BF₄), which out of 1 kV applied voltage represents a drop of less than 1% in efficiency.
- (b) Beam spreading. Most electrosprays will produce emission away from the centerline as the beam spreads. This angle varies with operating conditions, but it has been found that in most cases it is about 20°, thus decreasing the efficiency by a few percent more.
- (c) Ion fragmentation. Since ions with $n > 0$ are emitted, it is possible for some of these to break-up in flight, thus producing neutral species. If this fragmentation occurs before full ion acceleration, then there will be an impact on efficiency.

The beam polydispersity is the largest contributor of efficiency losses in electro spray thrusters operating in the PIR. Interestingly, this inefficiency in the use of energy displays as heating of the beam, not heating of the thruster. Only the energy efficiency drop contributes to ohmic heating. This means that electro spray thrusters in the PIR regime will run “cold” as practically no dissipation occurs.

Field Evaporation

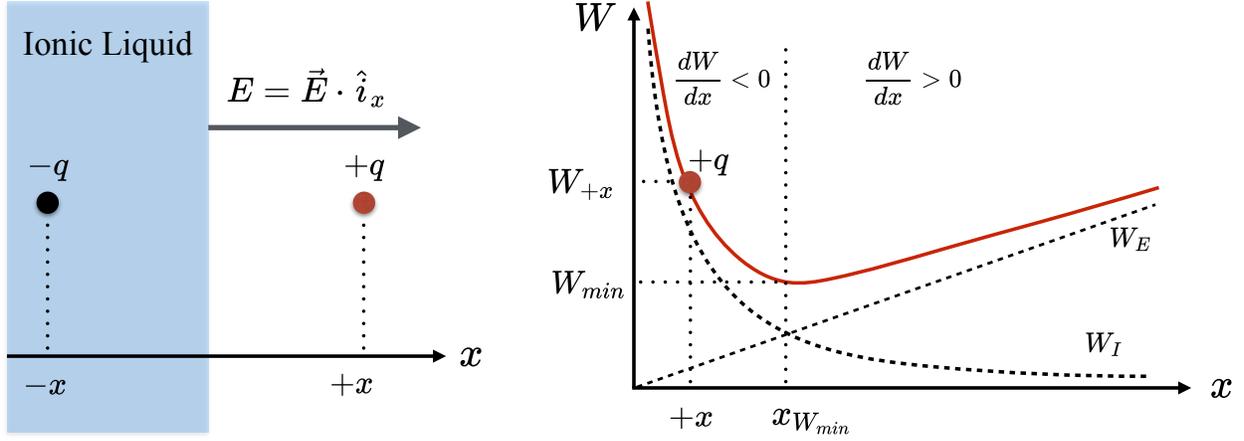
The emission of charge from an ionic liquid surface can be modeled as an activated process, in a similar way to conventional evaporation, or thermionic emission. In this case, the equilibrium analysis yields the following expression for current density,

$$j = \sigma \frac{kT}{h} \exp \left[-\frac{\Delta G}{kT} \right] \quad (13)$$

where σ is the surface charge density, k is Boltzmann's constant, h is Planck's constant, ΔG is the free energy of solvation for the extraction of a specific type of ion (of the order of 2 eV for many solvated ions, known separately). This means that ion evaporation would only produce significant fluxes when kT becomes of the order of ΔG , which means 1000's of degrees! Since the IL cannot withstand that thermal environment, an electric field is applied to facilitate the emission process.

A simple 1D model for this situation is shown in the drawing. In here we can see an ion of charge q located just outside of the liquid-vacuum interface at a distance x . There are two forces acting on this ion with respect to the interface. A repelling force from the applied field $F_E = qE$, and a force due to the “image” charge $-q$ located at $-x$, given by $F_I = \frac{-q^2}{4\pi\epsilon_0(2x)^2}$.

The work required to bring this charged particle from $+\infty$ to its location from the surface is given by,



$$W = \int_{\infty}^x (F_E + F_I) dx = \int_{\infty}^x qE dx - \int_{\infty}^x \frac{q^2}{4\pi\epsilon_0(2x)^2} dx \quad (14)$$

Assuming that the field E vanishes at ∞ , this integral evaluates to,

$$W = W_E + W_I = qEx + \frac{q^2}{16\pi\epsilon_0 x} \quad (15)$$

The work is minimum W_{min} at some distance $x_{W_{min}}$ from the interface. We can clearly see that the force acting on the charged particle will be negative (attractive to the interface) as long as $dW/dx < 0$ (to the left of the minimum), which is the case in all space when the applied electric field $E = 0$, and this is the reason why very high (unattainable) thermal energy would be required to bring the particle from $+x$ to ∞ . The distance $+x$ should be comparable to the size of the molecular ion. Assuming that is the case, then $W_{+x} \approx \Delta G$.

When the electric field is non-zero, the particle does not need to be moved all the way to infinity, but only to a distance $\Delta x = x_{W_{min}} - (+x)$, for it to escape. To the right of the minimum we have $dW/dx > 0$ and therefore a positive force that moves the charge away from the interface. Effectively, the energy barrier is reduced from $W_{+x} \approx \Delta G$ to a smaller value, $\Delta G - W_{min}$. We can calculate W_{min} by taking the derivative of Eq. (15) and set it to zero to find $x_{W_{min}}$,

$$x_{W_{min}} = \left(\frac{q}{16\pi\epsilon_0 E} \right)^{1/2}$$

and then substitute this back into Eq. (15),

$$W_{min} = \left(\frac{q^3 E}{4\pi\epsilon_0} \right)^{1/2} \equiv G(E) \quad (16)$$

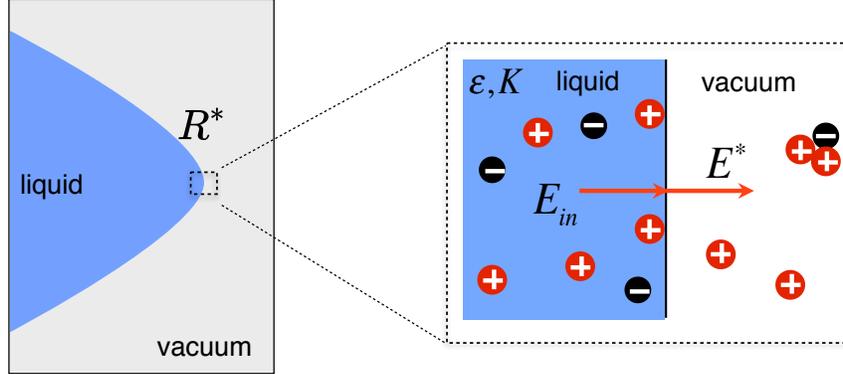
This result, derived by Iribarne and Thompson (1976), gives the field-evaporated current emitted per unit area,

$$j = \sigma \frac{kT}{h} \exp \left[-\frac{\Delta G - G(E)}{kT} \right] \quad (17)$$

$G(E)$ is the reduction of the free energy of solvation due to the normal field E . Even though room temperature, $T \approx 0.025$ eV, is much smaller than ΔG , it should be possible to obtain copious ion emission from electrified menisci when $G(E)$ approaches ΔG .

Scales in Ionic Liquid Ion Sources

In the PIR, there is no jet, and therefore the liquid meniscus forms a closed surface, as shown in the schematic below. Let us assume that the meniscus has a radius of curvature R^* at its apex and that a critical field E^* normal to the liquid surface is required for ion emission. The ionic liquid has a conductivity K and a dielectric constant ε .



From Eq. (17), the rate of ion evaporation is very sensitive to the magnitude of $G(E)$. We could then expect that significant ion emission will be achieved at a critical field E^* such that $G(E^*) \approx \Delta G$,

$$E^* \approx \frac{4\pi\varepsilon_0}{q^3} \Delta G^2 \quad (18)$$

Since the liquid surface is at equilibrium, we have electric stresses balancing surface tension,

$$\frac{1}{2}\varepsilon_0 E^{*2} - \frac{1}{2}\varepsilon_0 E_{in}^2 = \frac{2\gamma}{R^*} \quad (19)$$

where we have neglected hydrostatic pressures. Assuming the charged interface is far from full relaxation, the electric field inside the liquid is approximated by $E_{in} \approx E^*/\varepsilon$. Solving for R^* ,

$$R^* \approx \frac{4\gamma}{\varepsilon_0 E^{*2}} \left(\frac{\varepsilon}{\varepsilon - 1} \right) \quad (20)$$

For ions to evaporate, they need first to arrive to the surface, which they do at a rate,

$$j = K E_{in} \approx K \frac{E^*}{\varepsilon} \quad (21)$$

Given the exponential nature of the ion emission process described by Eq. (17), it is clear that Eq. (21) will regulate the emission process, since j needs to be the same in both.

Assuming that emission occurs from a hemispherical surface of radius R^* at the meniscus apex, the total field evaporated current will be,

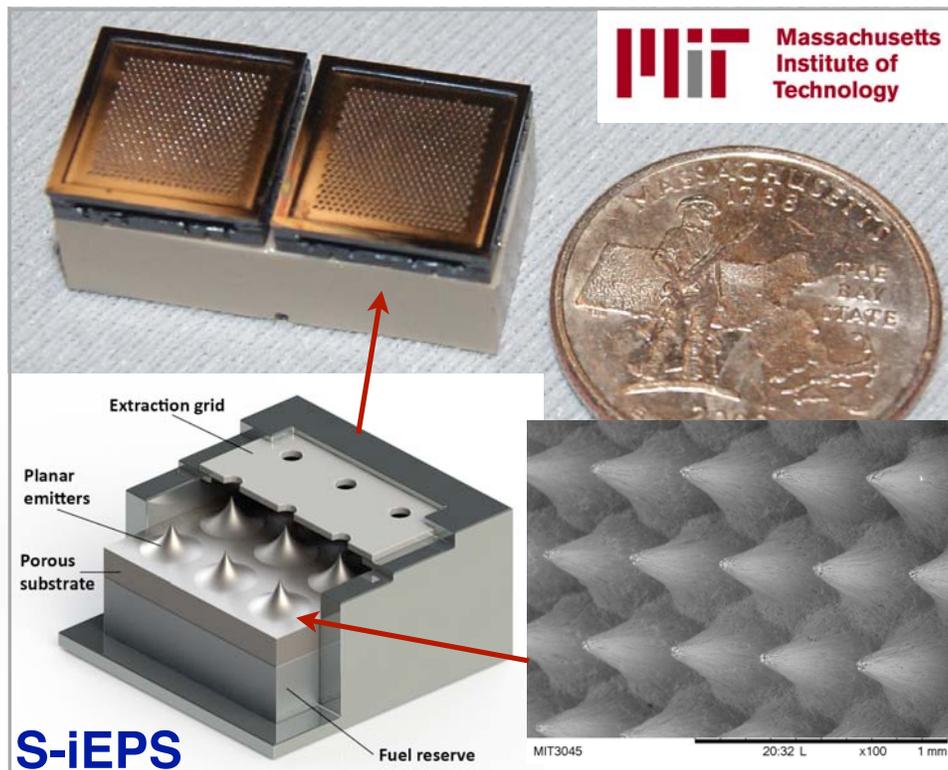
$$I \approx \frac{32\pi K \gamma^2}{\varepsilon_0^2 E^{*3}} \frac{\varepsilon}{(\varepsilon - 1)^2} \quad (22)$$

Take for example an ionic liquid with $K = 1 \text{ Si/m}$, $\gamma = 0.058 \text{ N/m}$, $E^* = 1.5 \times 10^9 \text{ V/m}$ and $\varepsilon = 10$. In this case, we obtain a current of $I \approx 157 \text{ nA}$, evaporated from a surface of dimension $R^* \approx 13 \text{ nm}$. The value for current is very close to what is experimentally observed in IL's with similar properties, while R^* is, not surprisingly, in the same order as the characteristic dimension r^* , deduced for low Q/K electrospays.

The corresponding thrust for such low currents will be on the order of 10 nN. On the other hand, the dimension R^* is so small that the expected thrust density at the apex,

$$\frac{F}{A} = \frac{1}{2} \varepsilon_0 E^{*2} \left(\frac{\varepsilon - 1}{\varepsilon} \right) \quad (23)$$

will be on the order of 10^7 N/m^2 ! This means that there is much to be gained in clustering dense arrays of emitters in a single propulsion device. An example of such implementation is shown in the figure.



This implementation is known as the ion Electro spray Propulsion System (iEPS) and has been developed at MIT's Space Propulsion Laboratory, in particular for applications in nano-satellites. It consists of an array of 480 emitter tips micro machined on a 1 cm^2 porous borosilicate glass substrate using laser ablation. Since the glass is porous, it can absorb propellant directly via capillarity from an upstream propellant reservoir. This means that

no valves or pumps are needed, and actuation is achieved with voltage alone applied between the IL permeating the tips and a downstream extractor electrode with matching apertures for every glass tip. The thrust density of this particular device is about 0.5 N/m^2 , which is similar to ion engines, but at least an order of magnitude smaller than Hall thrusters. Increasing thrust density would require clustering emitters more tightly. If manufacturing was not an issue, then F/A should be able to increase almost arbitrarily. However, several limitations might prevent “infinite” clustering:

- (a) Space charge. PIR thrusters are electrostatic devices, similar to ion engines, and therefore should be prone to space charge effects, including perhaps current limitation (recall the Child-Langmuir argument). As more and more tips are grouped together, the current densities will increase. Interestingly, as long as photographic scaling of the tip to extractor geometry is retained, then each emitter will have its own independent environment and there will not be space-charge *cross talk* between emitters. In ion engines, space charge has the effect of decreasing the field that allows ions to enter the grids. In electrosprays operating in the PIR, however, the field cannot be decreased below E^* , since emission will then cease. In fact, the value of the field will *always* stay near E^* , even in the presence of space charge, as the shape of the liquid-vacuum interface will deform, precisely to compensate for accumulation of emitted charges, to keep the field relatively constant.
- (b) Electrochemistry. As ions of a given polarity are extracted, counter-ions will accumulate over the electrode that provides the high voltage contact. This creates a molecular-sized, double-layer of charge on this interface that grows in potential as more ions are accumulated. The corresponding field could become so strong as to trigger electron discharge, from the liquid or the electrode, depending on the ion polarity. These are in effect electrochemical reactions that degrade the thruster and compromise its life. While the electrochemical window of IL’s is large (thus allowing more ions to accumulate at the interface), clustering of tighter arrangements produce more current density and faster degradation. To compensate for this, the polarity of the power supply is periodically alternated to discharge the double layer. The frequency of alternation depends on the current density. At some point the frequency might become so large that electrified menisci (which have their own characteristic formation times) will not be able to form and emission will stop.
- (c) Hydraulics. As the liquid moves through tighter arrangements, viscous losses will become more and more significant. At some point, the current will no longer be limited by conductivity (from Eq. (22)), but by transport. There will not be an incentive then to continue reducing the spacing between emitters in an array, as the current will stagnate.

In the iEPS device, the separation between emitters is set at $450 \mu\text{m}$. The three arguments described above (and other considerations), will limit the practical spacing to $1\text{-}10 \mu\text{m}$. Implementing such arrangements would increase the thrust density to about 10^3 to 10^5 N/m^2 , as high, or much higher, than MPD’s. This has become a strong research area in recent years as an alternative to enable ultra-compact high power electric propulsion thrusters.

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